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Abstracts

International Symposium
on
Relations between Homogeneous and Heterogeneous Catalysis

July 16-20, 2007

Gabor Somorjai, Ed.
University of California, Berkeley, CA

The International Symposium on Relations between Homogeneous and Heterogeneous Catalysis (ISHHC) has a long and distinguished history. Since 1974, in Brussels, this event has been held in Lyon, France (1977), Gröningen, The Netherlands (1981); Asilomar, California (1983); Novosibirsk, Russia (1986); Pisa, Italy (1989); Tokyo, Japan (1992); Balatonfüred, Hungary (1995); Southampton, United Kingdom (1999); Lyon, France (2001); Evanston, Illinois (2001) and Florence, Italy (2005).

The aim of this international conference in Berkeley is to bring together practitioners in the three fields of catalysis, heterogeneous, homogeneous and enzyme, which utilize mostly nanosize particles. Recent advances in instrumentation, synthesis and reaction studies permit the nanoscale characterization of the catalyst systems, often for the same reaction, under similar experimental conditions. It is hoped that this circumstance will permit the development of correlations of these three different fields of catalysis on the molecular level. To further this goal we aim to uncover and focus on common concepts that emerge from nanoscale studies of structures and dynamics of the three types of catalysts.

Another area of focus that will be addressed is the impact on and correlation of nanosciences with catalysis. There is information on the electronic and atomic structures of nanoparticles and their dynamics that should have importance in catalyst design and catalytic activity and selectivity.

There are over 300 attendees registered for this meeting attesting to the vitality of these fields of science.

We look forward to making your visit in Berkeley enjoyable as well as scientifically rewarding.

Gabor A. Somorjai
Chair, ISHHC XIII

Advisory Board

Lecture Hall A – 105 Stanley Hall **Lecture Hall B – 106 Stanley Hall**

Sunday, July 15	
4:00-6:00 p.m.	Reception and Registration Faculty Club, University of California, Berkeley

Monday, July 16			
7:30-8:30	Registration Stanley Hall Atrium		
Morning	**Lecture Hall A** Chair: Gabor Somorjai		
8:30-9:00	Opening Gabor A. Somorjai		
9:00-9:45	(PL1) – Jan-E. Bäckvall		
9:45-10:30	(PL2) – Hans-Joachim Freund		
	Break		
10:50-11:35	(PL3) – Jens Nørskov		
11:35-12:20	(PL4) – Bruno Chaudret		
	Lunch		
Afternoon	**Lecture Hall A** Chair: Francisco Zaera		**Lecture Hall B** Chair: Bruce Gates
2:00-2:35	(KN1) – Jean-Marie Basset	2:00-2:20	(O1) – Nicola Scott
2:35-3:10	(KN2) – Norbert Kruse	2:20-2:40	(O2) – Eric L. Margelefsky
		2:40-3:00	(O3) – Christopher W. Jones
		3:00-3:20	(O4) – Imre Kirisci
	Break		
3:30-4:05	(KN3) – Walter Kaminsky	3:30-3:50	(O5) – Ive Hermans
4:05-4:40	(KN4) – Georg Held	3:50-4:10	(O6) – Harold H. Kung
4:40-5:00	(O9) – Alex Bell	4:10-4:30	(O7) – Jie Fan
		4:30-4:50	(O8) – Richard Joyner

Tuesday, July 17

	Lecture Hall A		**Lecture Hall B**
Morning	Chair: Ron Mason		
8:30-9:15	(PL5) – Sunney Xie		
9:15-10:00	(PL6) – Per Siegbahn		
	Break		
10:20-11:05	(PL7) – Francisco Zaera		
11:05-11:50	(PL8) – Carolyn Bertozzi		
11:50-12:25	(KN5) – Paul Alivisatos		
	Lunch		
	Lecture Hall A		**Lecture Hall B**
Afternoon	Chair: Tobin Marks		Chair: Richard Joyner
2:00-2:35	(KN6) – István Horváth	2:00-2:20	(O10) – Devis Di Tommaso
2:35-3:10	(KN7) – Anders Holmen	2:20-2:40	(O11) – Xinhe Bao
		2:40-3:00	(O12) – Hans Schulz
		3:00-3:20	(O13) – Heinz Frei
	Break		
3:30-4:05	(KN8) – Malgorzata Witko	3:30-3:50	(O14) – Gerd Buntkowsky
4:05-4:25	(O15) – Peter Maitlis	3:50-4:10	(O16) – Philippe Sautet
4:25-4:45	(O17) – Peter Stair	4:10-4:30	(O18) – Randall Meyer
4:45-5:05	(O19) – Thomas Maschmeyer	4:30-4:50	(O20) – Alex Katz
6:30-9:00	Banquet and Cruise, San Francisco Bay		

Wednesday, July 18

	Lecture Hall A
Morning	Chair: Peter Stair
8:30-9:15	(PL9) – Avelino Corma
9:15-10:00	(PL10) – Tobin Marks
	Break
10:20-11:05	(PL12) – Mostafa El-Sayed
11:05-11:40	(KN9) – Graham Hutchings
11:40-12:15	(KN10) – Neville Richardson
	Lunch
	Stanley Hall Atrium
2:00-5:00	Poster Session Wine and Cheese Reception

Thursday, July 19

Morning	**Lecture Hall A** Chair: Heinz Frei	
8:30-9:15	(PL12) – Yasuhiro Iwasawa	
9:15-10:00	(PL13) – T. Don Tilley	
	Break	
10:20-11:05	(PL14) – Peidong Yang	
11:05-11:50	(PL15) – Thomas Colacot	
11:50-12:25	(KN11) – Riitta Keiski	
	Lunch	
Afternoon	**Lecture Hall A** Chair: Graham Hutchings	**Lecture Hall B** Chair: Steve Overbury
2:00-2:20	(O21) – Wolfgang E. Hoelderich	(O22) – Esther Sulman
2:20-2:40	(O23) – Song Ihl Woo	(O24) – Atsushi Fukuoki
2:40-3:00	(O25) – Giuliano Giambastiani	(O26) – Carlos F. Sanz-Navarro
3:00-3:20	(O26) – I.V. Kozhevnikov	(O28) – Ágnes Mastalir
	Break	
3:40-4:00	(O29) – Thomas F. Jaramillo	(O30) – Mohd Ambar Yarmo
4:00-4:20	(O31) – Bruce Gates	(O32) – Yunjie Ding
4:20-4:40	(O33) – Robert M. Rioux	(O34) – Gabor Laurenczy
4:40-5:00	(O35) – Sven Oscarsson	(O36) – Yousung Jung

Friday, July 20

Morning	**Lecture Hall A** Chair: Georg Held	
8:30-9:15	(PL16) – Chris Hardacre	
9:15-9:50	(KN12) – Michael Bowker	
	Break	
	Lecture Hall A Chair: Georg Held	**Lecture Hall B** Chair: Imre Kiricsi
10:10-10:30	(O37) – Mizuki Tada	(O38) – Matthias Koebel
10:30-10:50	(O39) – Miquel Salmeron	(O40) – Thomas Bligaard
10:50-11:10	(O41) – Steven H. Overbury	(O42) – Hongbo Li
	Lecture Hall A	
11:10-11:25	Poster Awards	
11:30-12:00	Conclusion and Summary Sir Ronald Mason	

PL1. Jan-E. Bäckvall, Stockholm University, Sweden
"Combination of Enzymes and Homogeneous Metal Catalysts. A Powerful Approach in Asymmetric Catalysis"

PL2. Hans-Joachin Freund, Fritz-Haber-Institute, Germany
"Model Systems in Heterogeneous Catalysis: Selectivity Studied at the Atomic Level"

PL3. Jens K. Nørskov, Technical University of Denmark
"Structural Effects in Reactivity of Metal Surface and Nanoparticles"

PL4. Bruno Chaudret, CNRS, Toulouse, France
"Organometallic Nanoparticles: A Link between Molecular Organometallic Complexes and Heterogeneous Catalysts"

PL5. Sunney Xie, Harvard University, USA
"Single Molecule Enzymology"

PL6. Per Siegbahn, University of Stockholm, Sweden
"Reaction Mechanisms of Redox-Active Enzymes"

PL7. Francisco Zaera, Univ. of California, Riverside, USA
"Mechanistic Details of Chiral Modification in Catalysis"

PL8. Carolyn Bertozzi, Univ. of California, Berkeley, USA
"Catalysis at the Interface of Chemistry and Biology"

PL9. Avelino Corma, Univ. Politecnica de Valencia, Spain
"Well Defined Active Sites Help to Relate Homogeneous and Heterogeneous Catalysis"

PL10. Tobin J. Marks, Northwestern University, USA
"Synthesis of New Polymeric Materials Using Highly Electrophilic Homogeneous and Heterogeneous Catalysts"

PL11. Mostafa El-Sayed, Georgia Institute of Technology, USA
"On Colloidal Nano-Catalysis"

PL12. Yasuhiro Iwasawa, The University of Tokyo, Japan
"Conceptual Integration of Homogeneous and Heterogeneous Catalyses for New Sustainable Green Processes on Catalyst Surfaces"

PL13. T. Don Tilley, University of California, Berkeley, USA
"Well-defined, Surface-Bound Catalytic Centers: Relationships between Homogeneous and Heterogeneous Catalysis"

PL14. Peidong Yang, University of California, Berkeley, USA
"Metal Nanocrystals: Shape Control, Assembly, Surface Chemistry and Catalysis"

PL15. Thomas Colacot, Johnson Matthey, USA
"Highly Active Supported and Unsupported Homogeneous Tunable Catalysts for Challenging Coupling Reactions"

PL16. Christopher Hardacre, Queens University, Belfast, UK
"Ionic Liquid Mediated Homogeneously and Heterogeneously Catalysed Reactions"

KN1. Jean-Marie Basset, CNRS, Villeurbanne, France
"Where are We Today in the Overlap between Homogeneous and Heterogeneous Catalysis?"

KN2. Norbert Kruse, Universite Libre de Bruxelles, Belgium
"Catalytic CO Hydrogenation: Mechanisms and Kinetics from Studies on the Nano- and Macroscale"

KN3. Walter Kaminsky, University of Hamburg, Germany
"In-situ Polymerization of Olefins on Nanoparticles or Fibers by Metallocene Catalysis"

KN4. Georg Held, Reading University, UK
"The Chemistry of Intrinsically Chiral Surfaces – Enzymes in Two dimensions"

KN5. Paul Alivisatos, University of California, Berkeley, USA
"Hollow, Nested, Striped and Segmented Colloidal Inorganic Nanocrystals as Potential New Catalysts"

KN6. István Horváth, Eötvös University, Budapest, Hungary
"Integration of Homogeneous and Heterogeneous Catalytic Processes for Sustainable Biomass Conversion"

KN7. Anders Holmen, Norwegian University of Science and Technology, Norway
"The Relation between Structure and Composition of Supported Nanoparticles on Catalyst Performance"

KN8. Malgorzata Witko, Polish Academy of Sciences, Poland
"Molybdenum Active Centers in Hetero- and Homogeneous Catalytic Systems – Description from First Principles"

KN9. Graham Hutchings, Cardiff University, UK
"Gold Catalysis using Heterogeneous and Homogeneous Catalysts"

KN10. Neville V. Richardson, University of St. Andrews, UK
"The Quest for Enantioselectivity in Heterogeneous Catalysis

KN11. Riitta Keiski, University of Oulu, Finland
"Combining the Best Features of Heterogeneous and Homogeneous Catalysis – The Importance of Catalyst Nanoparticles in Microreactors Design"

KN12. Michael Bowker, Cardiff University, UK
"The Role of Mo in Selective Oxidation Catalysis"

O1. Nicola Scott, Cambridge University, UK
"Enantiospecific Interaction at an Intrinsically Chiral Surface: A RAIRS Study of Alanine on CU {531}"

O2. Eric L. Margelefsky, California Institute of Technology, USA
"A Mesoporous Silica Heterogeneous Catalyst Containing Adjacent Sulfonic Acid and Thiol Groups for the Synthesis of Bisphenol A"

O3. Christopher W. Jones, Georgia Institute of Technology, USA
"Design of Highly Active and Enantioselective Recyclable Oligomeric/Polymeric Co-Salen Catalysts for the Hydrolytic Kinetic Resolution of Epoxides"

O4. Imre Kiricsi, University of Szeged, Hungary
"Identification of Reaction Intermediates on Supported Metal Surfaces"

O5. Ive Hermans, K. U. Leuven, Belgium
"Autoxidation Chemistry: Bridging the Gap between Homogeneous Radical Chemistry and (Heterogeneous) Catalysis"

O6. Harold H. Kung, Northwestern University, USA
"Catalysis in a Nanocage Environment"

O7. Jie Fan, University of California, Santa Barbara, USA
"Ordered Mesoporous TiO_2-based Materials as Highly Efficient Catalyst for Solvent-Free Benzyl Alcohol Selective Oxidation"

O8. Richard Joyner, Nottingham Trent University, UK
"Heterogeneous Catalysts and Enzymes Moving Closer Together: Mechanistic Similarities and Differences between Fe-ZEM-5 and Cytochrome P450 Oxidation Catalysts"

O9. Alex Bell, University of California, Berkeley, USA
"Selective Oxidation of Methanol to Formaldehyde on Isolated Vanadate Species Supported on Silica and Titania"

O10. Devis Di Tommaso, University College of London, UK
"New Insights into the Enantioselectivity in the Ruthenium Catalysed Asymmmetric Hydrogenation of Ketones. A Computational Study"

O11. Xinhe Bao, The Chinese Academy of Sciences, China
"Synergetic Confinement Effect of Carbon Nanotube and the Encapsulated Metallic Nano-particles on Catalysis"

O12. Hans Schulz, University of Karlsruhe, Germany
"Fischer-Tropsch Synthesis and Hydroformylation of Olefins on Cobalt Catalysts: Differences and Similarities"

O13. Heinz Frei, Lawrence Berkeley National Laboratory, USA
"Time-Resolved Ft-IR Spectroscopy of Heterogeneous Catalysis in Nanoporous Solids under Reaction Conditions"

O14. Gerd Buntkowsky, FSU Jena, Germany
"Solid State and Gas Phase NMR Studies of Immobilized Catalysts and Catalytic Active Nanoparticles"

O15. Peter Maitlis, The University of Sheffield, UK
"Organometallic Models for Reactions on Metal Surfaces: A New Look at Mechanisms for Chain Growth in the Fischer-Tropsch Reaction"

O16. Philippe Sautet, CNRS Lyon, France
"Modeling Surface Organometallic Chemistry by a Combination of Experiments with First Principle Calculations"

O17. Peter Stair, Northwestern University, USA
"Vanadium Oxide Catalysts in AAO Scaffolds"

O18. Randall Meyer, University of Chicago, USA
"A Combined Theoretical and Experimental Study of CO Hydrogenation Mechanisms with Metal Carbonyl Catalysts"

O19. Thomas Maschmeyer, The Univ. of Sydney, Australia
"Immobilised Acidic Ionic Liquids as New Solid Acid Catalysts for Biodiesel Synthesis"

O20. Alex Katz, University of California, Berkeley, USA
"Towards Understanding the Role of Surface in the Heterogenization of Homogeneous Catalysts"

O21. Wolfgang E. Hoelderich, University of Technology Aachen, Germany
"Enantioselective Hydrogenation of Prochiral Olefins by Use of Rhodium-Diphosphine-Complexes Immobilized on Al-MCM-41 Materials"

O22. Esther Sulman, Tver Technical University, Russia
Polymer-stabilized Metal Nanoparticles: An Effective way for Integration of Homogeneous and Heterogeneous Catalysis"

O23. Song Ihl Woo, KAIST, Korea
"Preparation of Polymer Nanocomposites during Polymerizatin catalyzed over Homogeneous Catalysts Support on Nanomaterials"

O24. Atsushi Fukuoka, Hokkaido University, Japan
Fukuoka, Hokkaido University, Japan

O25. Giuliano Giambastiani, ICCOM CNR, Florence, Italy
"Tetrahedral (Imino)pyridine CoII Complexes as a Versatile Tool for the Conversion of Ethylene and Norbornene: From Oligomers to LDPE-coated Nanocomposites"

O26. Carlos F. Sanz-Navarro, NTNU, Norway
"Molecular Dynamics Simulations of Binding of Metal Catalyst Nanoparticles to Carbon Nanostructures by Using ReaxFF"

O27. Ivan V. Kozhevnikov, University of Liverpool, UK
"Heteropoly Acids as Catalysts for Hydrogenation of Carboxylic Acids: Relation with Homogeneous and Heterogeneous Partial Oxidation"

O28. Ágnes Mastalir, University of Szeged, Hungary
"Liquid-phase Dispersion Measurement of Supported Palladium Catalysts by Liquid Chromatography"

O29. Thomas F. Jaramillo, Technical University of Denmark
"From Alloys to Bio-Mimetic Materials: Searching for New Hydrogen Evolution Electrocatalysts"

O30. Mohd Ambar Yarmo, Univ. Kebangsaan Malaysia
"V_2O_5 *Nanorod and Nanoparticles Preparation Using CTAB Micelle Solution"*

O31. Bruce Gates, University of California, Davis, USA
"Tantalum Clusters Supported on SiO_2*: Synthesis, Structural Characterization, and Catalysis of Alkane Conversion"*

O32. Yunjie Ding, Chinese Academy of Sciences, China
"In Situ Formation of Homogeneous Active Species for Hydroformylation Based on Heterogeneous Rh Catalyst"

O33. Robert M. Rioux, Harvard University, USA
"Effect of Pt Cluster Size on the Oxidation of NO to NO_2 *in Excess Oxygen on Supported and Model Pt Catalysts"*

O34. Gabor Laurenczy, EPFL, Lauanne, Switzerland
"Homogeneous Catalytic Cycles: Carbon Dioxide/Hydrogen Formic Acid Systems: High Pressure H_2 *Production and* CO_2 *Utilization"*

O35. Sven Oscarsson, Mlardalen University, Sweden
"The Performance of a Biomimetic Oxidation Catalyst Immobilized on Gold and Silica Substrates"

O36. Yousung Jung, California Inst. of Technology, USA
"Striking Acceleration of Rate of Organic Reaction on Water: A Theory"

O37. Mizuki Tada, The University of Tokyo, Japan
"Active Structure and ReactionMechanism for Direct Phenol Synthesis from Benzene and O_2 *on a Highly Selective N-Interstitial Re-Cluster/HZSM-5 Catalyst"*

O38. Matthias Koebel, EMPA Dubendorf, Switzerland
"Synchrotron Torr-pressure XPS Studies on 2D Pt Nanoparticle Array Cleaning for Model Catalysts"

O39. Miquel Salmeron, Lawrence Berkeley National Laboratory, USA
"Structure and Spectroscopy under Ambient Conditions of Pressure and Temperature: Novel Techniques for Fundamental Studies in Catalysis"

O40. Thomas Bligaard, Technical University of Denmark
"Combining Computational Screening and Reactivity Trends for Alloy Catalyst Design"

O41. Steven H. Overbury, Oak Ridge Nat. Laboratory, USA
"Synthesis, Size Dependence and Mechanistic Studies of Supported Au Catalysts"

O42. Hongbo Li, Argonne National Laboratory, USA
"Supported Organoiridium Catalysts for Alkane Dehydrogenation"

Plenary Lecture Abstracts

Combination of Enzymes and Homogeneous Metal Catalysts. A Powerful Approach in Asymmetric Catalysis

Jan-E. Bäckvall

Department of Organic Chemistry, Arrhenius Laboratory, Stockholm University, SE-106 91 Stockholm, Sweden

The combination of two types of catalysis in the same reaction can lead to significant advantages. In the present work we have combined an enzyme (lipase) and a homogeneous metal catalyst in an organic solvent. Lipases are insoluble in organic solvents and act as heterogeneous catalysts. In addition, most of the enzymes employed in our studies are immobilized on some carrier. The combination of a metal racemization catalyst with an enzyme for resolution can lead to a dynamic kinetic resolution (DKR) if the enzyme and racemization catalysts are compatible with one another. The advantage with this approach is that all of the racemic substrate can be transformed into enantiomerically pure product in up to 100% yield.

We have recently developed efficient procedures for DKR of alcohols and amines by combining an enzyme with a ruthenium racemization catalyst.[1,2] A highly efficient ruthenium catalyst was reported[1] for the racemization of alcohols and the mechanism of this catalyst has recently been studied.[3]

Extension of the enzyme and metal-catalyzed DKR reactions to new substrates such as primary alcohols that are chiral in the β-position and to allenes with an axial chirality will be discussed.[4] By evolution, a highly enantioselective mutant of a lipase for enzymatic resolution of racemic allenes was obtained.[5] The use of DKR in enantioselective organic synthesis will be demonstrated.

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[1] B. Martín-Matute, M. Edin, K. Bogár, F. B. Kaynak, J. E. Bäckvall, *J. Am. Chem. Soc.* 127 (2005) 8817.

[2] J. Paetzold J. E. Bäckvall, *J. Am. Chem. Soc.* 127 (2005) 17620.

[3] B. Martín-Matute, J. B. Åberg, M. Edin, J. E. Bäckvall, Racemization of Secondary Alcohols Catalyzed by Cyclopentadienylruthenium Complexes. Insight into the Reaction Mechanism. Submitted.

[4] D. Strübing, P. Krumlinde, J. Piera, J. E. Bäckvall, Dynamic Kinetic Resolution of Primary Alcohols with an Unfunctionalized Stereogenic Center Submitted.

[5] J. D. Carballeira, P. Krumlinde, M. Bocola, A. Vogel, M. T. Reetz, J. E. Bäckvall Directed Evolution and Axial Chirality: Optimization of the Enantioselectivity of Pseudomonas aeruginosa Lipase Towards the Kinetic Resolution of a Racemic Allene *Chem. Commun.* in press.

Model Systems in Heterogeneous Catalysis: Selectivity Studied at the Atomic Level

Hans-Joachim Freund

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More than activity, selectivity of catalytic reactions is in the focus of research in the 21st century. We review studies on model systems that address the issue of directing a catalytic reaction on disperse metal catalysts by controlling the specific surface site. Several examples on hydrogenation, dehydrogenation and oxidation reactions are presented. We show how surface science can be used by combining a variety of experimental techniques to study the chemistry of model catalysts at the atomic level.

Structural and Electronic Effects in the Reactivity of Metal Surface and Nanoparticles

Jens K.Nørskov

Center for Atomic-scale Materials Design, Department of Physics, NanoDTU, Technical University of Denmark

Density functional theory calculations are used to develop an understanding the geometrical and electronic factors determining the chemical activity of transition metal surfaces. It will be shown that a number of scaling laws hold for the variation of bond energies and activation energies from one metal to the next. The role of low-coordinated metal atoms for the reactivity of surfaces and nano-particles will be discussed in detail.

Organometallic Nanoparticles: A Link between Molecular Organometallic Complexes and Heterogeneous Catalysts

Bruno Chaudret

Laboratoire de Chimie de Coordination CNRS, 205 route de Narbonne 31077 Toulouse, France

The decomposition in mild conditions of organometallic precursors allows the control of the growth of metal nanoparticles. Addition of various ligands leads to nanoparticles of defined sizes and shapes, for example nanorods, nanocubes, nanowires and extended super-lattices of monodisperse nanospheres. Spectroscopic studies evidence the coordination of the ligands on the surface of the particles as well as, in some cases, their dynamics. Nanoparticles stabilized by thiols, amines, carboxylic acids, phosphines and phosphites have been prepared in this way. In addition, NMR and reactivity studies on ruthenium nanoparticles prepared at room temperature in the presence of dihydrogen evidence the presence of over one hydride per surface ruthenium. These hydrides display a high mobility even in the solid state as monitored by solid state NMR and lead to novel reactivities such as C-C bond activation in very mild conditions. The coordination of asymmetric phosphites to palladium nanoparticles leads to a catalyst for C-C bond formation displaying high enantioselectivity and substrate dependence. This is a good evidence for the implication of nanoparticles as the true catalyst in these reactions. Finally the method can be extended to the preparation of bimetallic nanoparticles whether alloyed or segregated and of catalytic nanoparticles encapsulated into an oxide shell.

Single Molecule Enzymology

Sunney Xie

Harvard University, Department of Chemistry and Chemical Biology

Enzymes are biological catalysts vital to life processes. At the single molecule level, an enzymatic reaction occurs stochastically. We study enzymatic turnovers of single enzyme molecules in real time, which yield detailed information otherwise hidden in ensemble averaged measurements.

The classic Michaelis-Menten mechanism provides a highly satisfactory description of catalytic activities for large ensembles of enzyme molecules. We test the Michaelis-Menten equation at the single molecule level. We monitor long time traces of enzymatic turnovers for individual β-galactosidase molecules by detecting one fluorescent product at a time. A molecular memory phenomenon arises at high substrate concentrations, characterized by clustering of turnovers separated by periods of low activity. Such a memory effect lasts for decades of time scales ranging from milliseconds to seconds due to interconverting conformers with broadly distributed lifetimes. We prove that the Michaelis-Menten equation still holds even for a fluctuating single enzyme, but bears a different microscopic interpretation.

We have developed a method based on excited state electron transfer to directly probe conformational fluctuations on the angstrom scale inside an intact protein. With this method, we observed that spontaneous conformation fluctuations span a broad range of time scales, which gives rise to the fluctuation in enzymatic activity.

In addition, we developed another method to probe small scale conformational changes based on the environmental sensitivity of a dye molecule. We used this method to probe a functionally important conformational change in DNA polymerase and study its role in maintaining high specificity and low error in DNA replication.[1,2,3,4,5,6]

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[1] English et al. *Nat. Chem. Bio.* 2 (2006) 87.

[2] Min et al. *J. Phys. Chem. B* 110 (2006) 20093

[3] Kou et al. *J. Phys. Chem. B* 109 (2005) 19068.

[4] Min et al. *Phys. Rev. Lett.* 94 (2005) 198302.

[5] Yang et al. *Science* 302 (2003) 262.

[6] Lu et al. *Science* 282 (1998) 1877.

Reaction Mechanisms of Redox-active Enzymes

Per Siegbahn

University of Stockholm, Sweden

Hybrid density functional theory (DFT) has been used to study the mechanisms of a large number of transition metal containing enzymes. The main example given here is dioxygen formation in photosystem II. After the first x-ray structures of PSII appeared two years ago, the understanding of this fundamental reaction has made significant progress. A detailed mechanistic proposal will be presented including a complete energy diagram. In most of the other enzymes studied, activation of dioxygen is instead required for their function. As one of these enzymes, the mechanism for cytochrome oxidase , the main enzyme in mitochondrial respiration, will be discussed. A major problem has been to understand how protons are pumped across the membrane with the help of the dioxygen chemistry. Again, a detailed energy diagram for the suggested mechanism will be presented, including both dioxygen reduction and proton pumping. Other examples of enzyme mechanisms studied by hybrid DFT will also be mentioned.

Mechanistic Details of Chiral Modification in Catalysis

Francisco Zaera

Department of Chemistry, University of California, Riverside, CA 92521, USA

It has been shown that heterogeneous hydrogenation catalysts such as platinum and nickel can be made enantioselective by the use of molecular chiral modifiers. Two mechanisms have been proposed for this modification, one based on the formation of one-to-one complexes between the modifier and the reactant and another involving chiral templating of the surface via the formation of ordered adsorbate suprastructures. Both mechanisms have been explored in our laboratory by using surface sensitive techniques.

The adsorption of cinchona alkaloids from solution onto platinum surfaces, the prototypical example of the first, has been detailed by using reflection-absorption infrared spectroscopy (RAIRS) in-situ at the liquid-solid interface and also by NMR experiments in solution. This is a particularly interesting system, because cinchona alkaloids are also used in homogeneous catalysis and other organic synthesis. Here, parameters such as adsorption geometry, reversibility of adsorption, and the effect of gases and solvents were investigated, and correlations were identified between the catalytic performance of the cinchona modifiers and their adsorption properties. Further research on the chemical behavior of the cinchona both on surfaces and in solution have pointed to additional connections between the adsorption properties and the structural parameters of those molecules.

For the second mechanism, the templating of Pt(111) surfaces with chiral 2-butanol, 2-methylbutanoic acid and 1-(1-naphthyl)ethylamine adsorbates has been tested under vacuum using enantiopure propylene oxide as a probe. One issue that comes into play when assessing the relevance of each of the two mechanisms for chiral modification in any given chemical system is the relative importance of energetic vs. entropic elements in defining enantioselectivity. Evidence for the participation of both components, the energetic contribution seen in one-to-one complexation and the entropic term associated with suprastructure ordering, was obtained in the latter two cases in the studies on surface templating. A general discussion of the molecular elements driving each mechanism and the relevance of these to both heterogeneous and homogeneous catalysis will be provided.

Catalysis at the Interface of Chemistry and Biology

Carolyn Bertozzi

Department of Chemistry, University of California, Berkeley, CA 94720-1460, USA

A majority of cell surface and secreted proteins are posttranslationally modified by the addition of glycans. These complex structures can provide information regarding the state of health of cells or organisms. Indeed, changes in the structures of protein- and cell surface-associated glycans are a hallmark of many cancers, chronically inflamed tissues, and microbial infections. The ability to probe glycosylation in living systems may therefore reveal new biomarkers of disease and provide new avenues for diagnostic imaging. Glycosylation occurs through the action of enzymes termed glycosyltransferases that are spatially organized in the Golgi compartment. As glycoproteins progress through this series of organelles, they encounter the enzymes sequentially and their glycans are extended accordingly. We have developed chemical strategies to control encounters between glycosyltransferases and their trafficking substrates, and to modify their substrates with chemical reporter groups that allow cell surface visualization. The application of these technologies for biological investigation of glycans will be discussed.

Well Defined Active Sites Help to Relate Homogeneous and Heterogeneous Catalysis

Avelino Corma

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Avda. de los Naranjos s/n, 46022 Valencia, Spain

Homogeneous catalysts involve well defined-isolated-homogeneous sites, being this a reason for high selectivity. To achieve the same active site definition in solid catalysts is more difficult, because the lack of knowledge in many cases of the active site structure at atomic level, specially under reaction conditions.

Will attempt to establish a parallelism between reactions occurring with homogeneous and heterogeneous catalytic systems by synthesizing well defined solid catalysts with isolated sites, showing that some times the catalytic active site is formed by multiatomic structures. Will show that the introduction of operando spectroscopies and labelled molecules together with theoretical calculations, allows to establish the nature of the working catalytic site, together with the reaction elementary steps. Using this methodology, will present the parallelism between homogeneous and heterogeneous catalysts for chemoselective oxidation and hydrogenation reactions, carbonylation of alcohols, and carbon-carbon bond formation.

It will be presented that by properly choosing the support it is possible to stabilize unusual metal valences on solid catalyst that present the same catalytic behaviour than the corresponding metal-organic complexes. Furthermore, it will be presented how it is possible to convert a non chemoselective catalyst into a chemoselective one by preparing a catalyst that exposes only the adequate atom assembly.

Synthesis of New Polymeric Materials Using Highly Electrophilic Homogeneous and Heterogeneous Catalysts

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Transition metal olefin polymerization catalysts, coupled with the appropriate cocatalysts, offer unprecedented control over polymerization activity and selectivity as well as over the tailoring of macromolecular architecture. Nevertheless, our understanding of catalyst-cocatalyst interactions and our ability to exploit them to produce new polymeric materials is at an early stage. This lecture focuses on three interconnected aspects of single-site polymerization catalysis:

1) better understanding the structures and thermodynamic stabilities of catalytically important organometal cation-cocatalyst anion pairs;

2) better understanding the molecular dynamics and enchainment stereoselectivity of these ion pairs;

3) using this information to enhance cooperativity between single-site catalytic centers using polynuclear catalysts and cocatalysts in solution and on tailored surfaces.

The results of these effects include significantly enhanced polymerization catalytic activity, selectivity, chain branching, chain functionalization, dramatic comonomer incorporation selectivities, and new materials for energy storage.

On Colloidal Nano-Catalysis

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Surface atoms on nanoparticles are valency unsaturated, and, due to the surface cuvature, their bonds to the nanoparticle can be weaker. Thus, they become chemically active and physically dynamic. This could be good or bad. It could make nanoparticles more active as catalysts. However, they might also become too active and become reactants. In addition, due to the frequent collisions with the solvent molecules, they can also dissolve and catalyze the reaction in solution. Thus depends on the shape of the nanoparticle, the reaction conditions (especially temperature) and the type of the reactants involved, colloidal nanocatalysis can be heterogeneous (if it takes place on the nanoparticle surface), homogeneous (if it takes place in solution), or both.

The results of our and other studies on the effect of shape, size, capping material and type of reaction will be presented and discussed.[1,2,3,4,5]

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Conceptual Integration of Homogeneous and Heterogeneous Catalyses for New Sustainable Green Processes on Catalyst Surfaces

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Little is known to date about the creation and control of selective catalysis, the site-specific structure and mechanism for green catalytic processes, and the in situ characterization technique of designed surfaces and nanomaterials. The molecular level understanding and controlling of the catalytic reaction processes will signal a marked advance beyond the traditional strategy of heterogeneous catalysis research and guide the development of highly performed catalysts by conceptual integration of homogeneous and heterogeneous catalyses.[1,2] The use of molecularly-designed catalysts seems to be advantageous and prerequisite to examining the origin and mechanism of catalysis.[2.3,4]

Design and regulation of the structure and electronic property of catalyst surfaces are critical in achieving high catalytic performance with good selectivity. However, these issues have not been adequately addressed and are still a serious challenge in catalysis and materials research. In the talk the important but unaddressed issues in catalysis research are treated, showing several typical examples recently discovered about identification and structural change of most active sites on catalyst surfaces, synthesis/preparation methods for active structures on catalyst surfaces, key issues to create and control of selective catalysis, and in situ characterization techniques of catalysis. We have documented the strategy and way to control catalysis by rational design and in situ characterization of active structures at catalyst surfaces, presented nice examples of creation of selective oxidation, and discovered new catalytic phenomenon and concept[1,2,3,4].

Despite the success of analyses of the molecular kinetics and dynamics of gas phase and adsorbed molecules, little is known about the dynamic properties of catalytic materials and surfaces. Time resolved XAFS such as energy dispersive XAFS and time-gating quick XAFS is a powerful technique for study on structural dynamics of active catalysts and surfaces during catalytic reactions, catalyst preparations, and catalyst deactivation and regeneration.[5,6,7]

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Well-defined, Surface-bound Catalytic Centers: Relationships Between Homogeneous and Heterogeneous Catalysis

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For many heterogeneous catalysts, it is apparent that desirable properties are associated with well-defined active sites containing one or only a few metal centers on the surface of a support. This situation is rather like that found for enzymes, which provide a tertiary polypeptide structure for stabilization of reactive centers, and a secondary coordination sphere for binding/activation of substrates. In principle, these latter roles may also be fulfilled by the surface of a suitably modified support material. Given the increasing interest in the structure and catalytic chemistry of supported metal centers, we have attempted to develop reliable routes to stable, well-defined catalytic centers bound to an oxide support. We have utilized a process for the introduction of isolated metal centers, involving grafting reactions with molecular precursors (the thermolytic molecular precursor method). This method produces sites that can be remarkably stable with respect to thermal degradation to oxide clusters. The resulting catalysts display good activities and selectivities for the oxidation of various hydrocarbons, using a variety of oxidants. Considerable effort has been devoted to the study of isolated titanium centers for the catalytic epoxidation of olefins. More recently, the thermolytic molecular precursor method was used to introduce site-isolated Ta(V) centers onto the surface of mesoporous SBA15 silica. The resulting surface Si-OH and Ta-OH sites of the Ta/SBA15 catalysts were modified with a series of (N,N-dimethylamino)trialkylsilanes. Compared to the unmodified catalysts, the surface-modified catalysts exhibit excellent selectivity for epoxide formation (75-95%) in the oxidation of cyclohexene using aqueous H_2O_2 as the oxidant. The local structure of the Ta(V) site has also been investigated.

Metal Nanocrystals: Shape Control, Assembly, Surface Chemistry and Catalysis

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The ultimate goal of catalysis research is to achieve 100% selectivity for the desired products at maximum turnover rate (activity) without generating undesired byproducts. Ways to optimize activity and selectivity have been investigated on the atomic and molecular level using two-dimensional model catalysts (e.g. metal single crystals, nanoparticle arrays). It was found that key characteristics affecting both activity and selectivity are surface structure and particle size. Other features important to catalysis are site-blocking or bonding modifier additives and the metal-oxide interface. Development of a high surface area model catalyst will enable the study of the molecular ingredients which control activity and more importantly selectivity in the multifunctional (oxide / metal) composite systems. We are developing methods for making metal nanocrystals with very narrow particle size distribution and well-defined shape. These nanoparticles are then assembled into 2-dimensional arrays using Langmuir-Blodgett technique or embedded in mesoporous oxide supports. These composites are considered as a high surface area model catalyst system as the precise control of nanocrystal size, shape, surface and interface should impart desired reaction selectivity and activity.

Highly Active Supported and Unsupported Homogeneous Tunable Catalysts for Challenging Coupling Reactions

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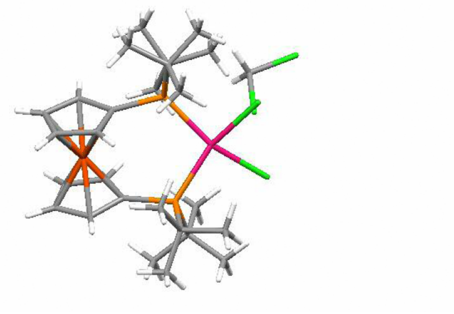
One of the major challenges in the area of homogeneous coupling catalysis is the separation of the catalyst/metal from the product. Although palladium supported on carbon (Pd/C) in the presence or absence of a ligand can be used for coupling of less challenging aryl iodides and bromides, this methodology does not provide any additional advantage over homogeneous systems, as the coupling reaction proceeds *via* a homogeneous mechanism, evidenced by the three-phase test results from various groups. Johnson Matthey addresses this issue with three different approaches: i) develop highly active homogeneous catalysts so as to minimize the catalyst loading in challenging coupling reactions; ii) tune the polyethylene supported FibreCats to be more active and robust; iii) use SMOPEX to scavenge any residual metal from the product.

This work is focused on the strategy that we employed in developing fully formed Pd(0), Pd(I) or Pd(II) complexes of supported and unsupported monodentate and bidentate ligands, with a view to understand the structure-activity relationship in coupling and thereby understanding the selectivity, activity and robustness of the new catalysts. An example each from the supported and unsupported catalysts is given below. These catalysts have been used for coupling various Ar-Cl compounds such as 3- chlorothiophene, chloromesitylene, 3- chloropyridine, etc., with excellent yield. Several examples of FibreCat gave leaching below 1 PPM with good recylability. Details of the work will be presented in the talk.



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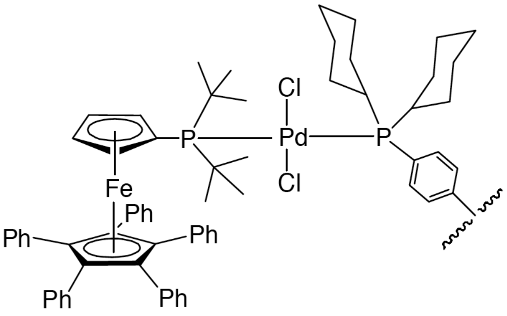

Q-Phos based FibreCat

Ionic Liquid Mediated Homogeneously and Heterogeneously Catalysed Reactions

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Ionic liquids have been studied extensively as clean solvents for a wide range of chemistry. This interest is a direct result of the diverse physical properties which these liquids have and the way in which they may be systematically varied, for example the density, viscosity and water miscibility. Since they also have effectively zero vapour pressure this makes them ideal engineering solvents for reactive chemistry, allowing direct distillation from the solvent and simple solvent recycle without the production of VOCs. Many of the reactions reported in ionic liquids are catalytic, using homogeneous, enzyme and heterogeneous catalysts with the vast majority using homogeneous. This paper describes a range of catalytic processes using homogeneous and heterogeneous catalysts as well as utilising the ionic liquid as a catalyst.

Despite the large number of reactions performed in ionic liquids, few have demonstrated that the ionic medium has a positive effect on the enantioselectivity for asymmetric transformations. The majority of studies concerning catalytic enantioselective reactions have used the ionic liquid in combination with a molecular co-solvent. In many cases no beneficial effect on the enantioselectivity compared with the conventional media is found although the recyclability of the catalyst is improved. In contrast, we have demonstrated that ionic liquids can not only significantly increase the rate of platinum catalysed asymmetric Diels-Alder, carbonyl-ene and aldol reactions and the recyclability of the catalyst but also allow high enantioselectivities to be achieved without the need to recourse to low temperatures. Furthermore, it is possible to combine the ionic liquid supported catalysts with oxide supports to provide a supported ionic liquid phase catalyst for enantioselective reactions.

In gas-liquid-solid reactions ionic liquids have been shown to be highly selective solvents for the C=C double bond hydrogenation of α,β-unsaturated aldehydes to the corresponding saturated aldehyde. By changing the anion of the ionic liquid or the temperature at which the reaction is performed, it is possible to vary the selectivity and selectivities close to 100% are possible when using a Pd/C catalyst although the rate is slower than in conventional organic media. Similarly high selectivity has been demonstrated using Pt/graphite catalysts in an ionic liquid media for the conversion to the unsaturated alcohol. The ionic liquid system also facilitates facile organic solvent extraction or vacuum distillation of the product phase without the removal of the catalyst and the system shows good recyclability.

For the hydrogenation reactions, the catalysis is truly heterogeneous; however, the use of a zeolite in the ionic liquid is likely to be homogeneously catalysed. The Friedel-Crafts benzoylation of anisole has been successfully carried out in $[NTf_2]^-$ based ionic liquids using a range of zeolites. This reaction is thought to proceed via a homogeneous mechanism, catalysed by $HNTf_2$, generated *in-situ* by the exchange of the cation from the ionic liquid with the acid proton on the zeolite. The efficiency of this exchange is shown to be temperature and ionic liquid dependent.

The zeolite catalysed benzolyation of anisole has been compared with a homogeneously catalysed process using metal triflate and bistriflimides as well as a binary ionic liquid based on InCl3 and a chloride ionic liquid. The zeolite catalysed process had the quickest rate; however, it was only recyclable with recalcination of the solid at 500°C. The homogeneously catalysed reactions also showed good rates of reaction and were active for a wide range of substrates. This system was poorly recyclable and the isolated yields low. The chloroindate(III) ionic liquids were also found to be a versatile reaction media for a wide range of Friedel-Crafts acylation reactions. In addition, the system is catalytic and totally recyclable, using an aqueous workup, with no leaching of the indium into the product phase.

A combination of homogeneous and heterogenous catalysts has been used to facilitate the one-pot synthesis of the fungicide Fenpropimorph via a Heck reaction or an aldol condensation and then a reductive amination reaction. Although both Heck and aldol processes proceed efficiently in the ionic liquid only the aldol pathway may be recycled. By using the amine catalyst from the aldol condensation as the reagent in the subsequent reductive amination reaction a highly atom efficient process is possible. A versatile multistep catalytic synthesis using a single ionic liquid is possible with the ionic liquid able to be easily recycled. In contrast using conventional molecular solvents, the separation is more difficult and requires evaporation and recondensation of the solvent.[1]

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Keynote Lecture Abstracts

Where Are We Today in the Overlap Between Homogeneous and Heterogeneous Catalysis?

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Heterogeneous catalysis is a molecular phenomenon by which molecules react with surfaces to give new molecules or macromolecules via "surface organometallic fragments" which are "real intermediates" in any catalytic cycle. But the links between homogeneous catalysis and heterogeneous catalysis goes far beyond this simple unifying concept.

The field has recently benefited by the spectacular progresses made in the concepts of "molecular" and "supramolecular" chemistry applied to "materials science". It is now possible to achieve the rational design and synthesis of new and well defined materials with the expected structure, acidity, porosity in the field of "oxides" or "zerovalent metal particles". The control of the porosity and acidity has been achieved with mesoporous oxides such as MCM family with specific surface area of more than $1000 m^2/g$. The control of the framework with metal compounds "Metal organic framework" (MOF) allows to achieve specific surface areas of up to $5000 m^2/g$ with tremendous properties of hydrogen and methane storage, leading to possible "dreams" in heterogeneous catalysis. The control of the growing of metallic "nanoparticles" allows now to achieve size, composition, surface structure of mono and bimetallic particles with a rather good accuracy. It is now possible to mimic the catalytic activity of oxides via heteropolyanions which exhibit both acidity and redox properties at will. Such new materials exhibit fantastic catalytic properties especially when they are reacting with organometallic compounds.

Once these well defined materials have been prepared, it is possible by surface organometallic chemistry to design "single site" catalysts both on "oxides" and on "metals"

This new approach to heterogeneous catalysis can bring molecular insight on the design of a new generation of catalysts, the discovery of new catalytic reactions, the improvement of existing catalysts. Examples will be given with the following catalytic reactions: "Ziegler-Natta depolymerisation", "Alkane metathesis", "Methane coupling to ethane and hydrogen", "Methane-olysis of alkanes", direct transformation of "ethylene to propylene", metathesis of olefins with a new generation of extremely active catalysts.

Catalytic CO Hydrogenation: Mechanisms and Kinetics from Studies on the Nano- and Macroscale

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In 1902 Sabatier[1] observed methane formation from reaction of carbon monoxide and hydrogen on nickel and cobalt surfaces. Little later the high-pressure Fischer-Tropsch process paved the way to longer-chain alkane, alkene and oxygenate production. After decades of research the same reaction still sparks considerable interest both in academia and industry. The focus of the present paper is mainly on the kinetics and microscopic mechanism on Co- and CoCu-based catalysts. The latter have more recently been demonstrated to produce long-chain alcohols with high selectivity.[2] Comparison will be made with homogeneous hydroformylation where appropriate.

Chemical Transient Kinetics (CTK) at atmospheric pressures and Pulsed Field Desorption Mass Spectrometry (PFDMS) at low pressures ($\geq 10^{-6}$ mbar) have been employed to cover nine orders of pressures in kinetic measurements under truly in-situ reaction conditions ($p_{H2}/p_{CO} \geq 2$, $T \geq 470$ K). Repetitive field pulse forcing in PFDMS has allowed following CO dissociation with ms time resolution on selected planes of Co single-crystal model catalysts. In accordance with CTK, no evidence for the occurrence of the Boudouard reaction is obtained on clean surfaces. Surface carbon can be hydrogenated in low-pressure studies but according to CTK this route of hydrocarbon production is of minor importance at atmospheric pressures (and most likely above). Interestingly, Co carbonyls, $Co(CO)_{2,3}$, are detected in low-pressure studies by PFDMS. These adsorbed species do not follow the 16/18 electron rules encountered in homogeneous CO hydrogenation with substituted Co hydridocarbonyls. Adsorbed Co carbonyls are likely to be mobile and must be considered as candidates for the geometrical/chemical reconstruction of Co surfaces[3] and as CO donors in insertion steps leading to hydrocarbon chain lengthening.

The quantitative assessment of CTK data demonstrates that neither Co nor CoCu catalysts are in a metallic state during CO hydrogenation at atmospheric pressures. This can be concluded on the basis of build-up and cut-off transients (while switching from hydrogen adsorption to CO hydrogenation conditions and vice versa) which allow the amounts of surface carbon and oxygen to be determined by solving the material balance at any time of the measurement. For example, with CoCu-based catalysts, total amounts of 5.5 nm^{-2} are found at steady state (oxygen amounts being larger than carbon ones) while chemisorption measurements with CO yield 4 nm^{-2}. Transient Anderson-Schulz-Flory distributions of the products vary almost linearly with the CO pressure while they exhibit no simple correlation with the carbon coverage. Thus the monomer responsible for chain lengthening is CO and not a CH_x surface species.[4] Taking into account the different delay times of the various species - CH_4 is formed after several seconds followed by concomitant CO and ethane production while water formation only starts after carbon containing species have reached steady state production - we suggest that the key step enabling hydrocarbon chain growth is the insertion of CO into surface hydroxyl (or alkoxy) to produce formate-type species[4]. As mentioned earlier, adsorbed Co carbonyls are possible candidates to provide low-cost CO for insertion. In some CoCu catalyst formulations cut-off transients have allowed determining a surface ratio of O/C=2 which is in accordance with a $[CO_2{}^\star]$ (spectator) complex of considerable lifetime transforming into the active masi (most abundant surface intermediate) under reactive CO hydrogenation conditions. Overall, CTK results allow formulating a reaction mechanism which is common for both, hydrocarbon and oxygenate formation, and which demonstrates that the origin of the selectivity to hydrocarbons and oxygenates is purely kinetic.

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In-situ Polymerization of Olefins on Nanoparticles or Fibers by Metallocene Catalysis

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Within the last years, much research in academic and industrial laboratories has focused on polyolefin nanocomposites because of their high potential as materials with novel properties. Exceptionally strong materials can be synthesized by in-situ polymerization in a two step process. First, the metallocene or another single site catalyst is absorbed on the surface of the nanofiller, then by addition of ethene or propene, a polyolefin film is formed, covering the nanoparticles, layered silicates, or fibers. Polyolefin nanocomposites produced by in-situ generation show better mechanical properties than material produced by mechanical blending.

Metallocen/methylaluminoxane (MAO) catalysts are soluble in hydrocarbons and therefore they can cover perfectly the surface of particles or fibers. They allow the synthesis of polymers with a precisely defined microstructure, tacticity, and stereoregularity as well as new copolymers with superior properties such as film clarity, tensile strength and lower extractables. These polymer properties can be enlarged by the incorporation of nanofillers. The resulting polyethylene and polypropylene nanocomposites cause a tremendous boost of physical and chemical properties such as improved stiffness, high gas barrier properties, significant flame retardancy, and high crystallization rates.

Monospheres (balls of silica, diameter 200-250 nm), carbon fibers (diameter 200 nm, length 0.5-3 mm), and multiwalled carbon nanotubes (diameter 15-25 nm, length 50 μm) were used as fillers. Before polymerization, the fillers were separated by ultra sound and then treated by MAO. MAO reacts partially with the OH-groups of the silica. Catalytically active centres are formed after adding the zirconocenes or other transition metal complexes. The thickness of the polyolefins can be controlled by the pressure of ethene or propene and by the polymerization time.

By this method, highly filled nanocomposite polyethylenes or polypropylenes can be obtained with a silica content of up to 85 wt%. Such combined materials are stiff and hard. Every particle is surrounded by a thin film of polyolefin with a thickness of 30 to 100 nm.[1,2]

Carbon fibers and carbon nanotubes are covered with isotactic or syndiotactic polypropylene. Because of the hydrophobic character of the carbon surface, the polymer is drawing on the fiber. This leads to a reinforced combined polymer with special properties. The crystallization temperature is 10°C higher and therefore the crystallization rate up to 20 times faster than that of pure syndiotactic polypropylene.

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The Chemistry of Intrinsically Chiral Surfaces – Enzymes in Two Dimensions?

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The last decade has seen a dramatic increase in research into chiral surface systems, driven by the growing demand for optically pure chemicals in drug manufacturing and, hence, a desire for enantioselective heterogeneous catalysts. These avoid the problem of phase separation inherent in homogeneous enantioselective processes which are predominantly used today. So far, significant success has been achieved by modifying achiral Pt or Ni catalyst surfaces with chiral molecules thus creating a stereo-selective reaction environment for α and β-ketoesters.[1,2] Alternatively, intrinsically chiral metal and mineral surfaces show enantioselective behaviour without such modifiers,[3,4] although these mechanisms are much less well understood. The talk will focus on the latter type. Examples are artificial high-Miller-index surfaces of metal single crystals with cubic bulk lattice symmetry, which have no mirror planes and are therefore chiral, or surfaces of naturally occurring crystallites of some common minerals, such as α-quartz (chiral bulk symmetry) or calcite (achiral bulk symmetry). The first reports about enantioselective reactions catalysed by α-quartz particles date back to the 1930s.[5] Recent findings with regards to the surface geometry, reactivity and thermal stability of intrinsically chiral surfaces will be discussed. A number of enantioselective effects have been reported in connection with the adsorption of small amino acids (e.g. alanine, cysteine) on intrinsically chiral surfaces under well defined conditions. From a combination of experimental structural surface science techniques (NEXAFS, LEED, STM) and ab-initio model calculations it emerges that these effects are due to a combination of hydrogen bonding between adjacent molecules and attractive and repulsive adsorbate-substrate interactions.[6]

Although these interactions are of the same type as those involved in the formation of enzyme-reactant complexes (or in homogeneous enantioselective catalysis), there are important differences, e.g the much greater flexibility of the protein carbon skeleton as compared to an inorganic solid surface and typical distances of interacting active sites. Implications of these differences for enantioselective catalysis will be discussed.

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Hollow, Nested, Striped and Segmented Colloidal Inorganic Nanocrystals as Potential New Catalysts

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In the previous decade, a great deal of success was achieved in developing new methods for the preparation of colloidal inorganic nanocrystals with controlled size and simple shapes (spheres, rods, disks). It is now possible to use these materials as building blocks to create more complex nanocrsytal assemblies. This talk will describe recent efforts to produce more complex nanoparticles with potential catalytic activity. Of particular interest are nested nanocrystals in which a catalytically active particle such as Pt or Au is wholly surrounded by a porous nanoscale shell. Efforts to understand and control the diffusion of species across the shell will be described. In addition, recent work by which metallic catalysts are photochemically deposited on semiconductor rods will also be described.

Integration of Homogeneous and Heterogeneous Catalytic Processes for Sustainable Biomass Conversion

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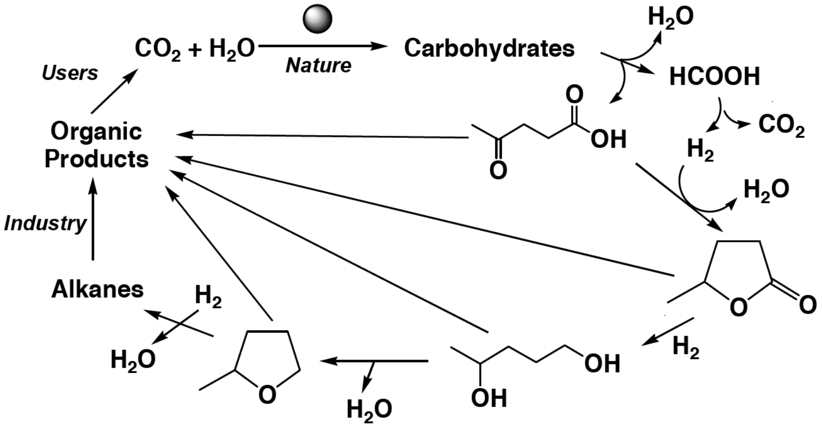
The sustainability of mankind depends whether we can supply the increasing population with enough energy, food, and chemicals, including carbon-based consumer products, simultaneously without compromising the long term health of our planet. While it is difficult to predict the exact date of the depletion of fossil fuels, the transition to renewable resources should be accelerated because of the frequently and unexpectedly changing political/economical environments resulting in limited access to and rising costs of fossil fuels. The development of sustainable liquids for energy and the chemical industry should be considered as a key research area in the next decades.

The conversion of biomass to chemicals represents a major challenge because of the complex nature of the substrates, e.g. the biomass, both chemically and physically. While large scale processes could take the advantages of heterogeneous catalysis, their use could be limited by the solid nature of biomass. The application of homogeneous catalysts, especially water soluble systems, could offer the possibility to deliver the catalytically species into the solid or swelled biomass. Integration of heterogeneous and homogeneous catalysts including enzymes could lead to the development of novel, commercially attractive multi-step processes.

We have proposed that γ-valerolactone (GVL), a frequently used food additive, exhibits the most important characteristics of an ideal sustainable liquid. It is important to recognize that the use of a single chemical entity instead of a mixture of compounds could significantly simplify its worldwide monitoring and regulation. We have been investigating the selective conversion of carbohydrates to various C_5-oxygenates including levulinic acid, GVL, 2-methyl-THF and alkanes using homogeneous and heterogeneous catalysts:



The preliminary evaluation of GVL as a fuel additive, performed by adding 3, 6 and 9% to 95-octane gasoline, shows very attractive properties, comparable to ethanol.

The Relation Between Structure and Composition of Supported Nanoparticles on Catalyst Performance

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For supported catalysts, the performance depends on the structure, size and composition of the catalyst particles. Knowledge of this dependency is important in catalyst design and recent advances in synthetic methodologies used to control nanometer-sized assembly, offer new opportunities for optimizing catalyst performance. Some examples of the relationship between catalyst performance (activity, selectivity, stability) and catalyst particles (structure, size, composition) based on recent studies in our laboratory will be presented.

For CO hydrogenation of supported Co catalysts it has usually been observed that the turnover frequency is constant. It has recently been shown, however, that for Co particles smaller than about 7 nm the turnover frequency depends on the particle size.[1] Transient experiments have indicated that a decrease in particle size is accompanied with an increase in surface residence time of CO and CHx and a decrease in surface coverage of CO.[2] Larger particles (> ca 7 nm) displayed constant surface residence times. The selectivity to higher hydrocarbons (C^{5+}) seems to have a complex dependency on the catalyst particles. The size and the appearance (large crystals, clusters of small particles etc) as studied by high resolution electron microscopy, have an influence on the selectivity.[3] It is also shown that the addition of Re is beneficial for the selectivity, but the addition of Re does not influence the turnover frequency provided that the particles are larger than ca. 7 nm[3]. Model systems using Co supported on carbon nanofibers have also shown that the support may interact with the Co-particle changing the catalytic performance of Co.[4]

For Pt dehydrogenation catalysts and steam reforming Ni catalysts the focus has been on the rate of carbon formation. For steam methane reforming catalysts relatively small particles have higher carbon resistance than larger particles,[5] but for the Pt dehydrogenation catalysts the rate of carbon formation increases with decreasing particle size.[6] The effect of the particle size could also hold the key to understand the role of Sn in bimetallic Pt-catalysts.[6,7]

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Molybdenum Active Centers in Hetero- and Homogeneous Catalytic Systems-Description from First Principles

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Molecular oxygen, which plays a fundamental role in catalytic oxidation processes of many organic substrates, as a stable paramagnetic species, has to be activated in order to make the reaction possible. The activation may be caused by bonding of O_2 to the metal center, either in the coordination compound (homogeneous catalysis) or at the surface of a solid (heterogeneous catalysis). The reactivity of bonded molecular oxygen depends on the type of bond that is defined by the properties of metal (its oxidation state and coordination number) and by the surrounding ligands or surface neighbor atoms. Molybdenum containing systems are particularly good examples to study O_2 activation process because allow comparison of homo- and hetero-type catalysts.

Ab initio quantum chemical DFT method within GGA functional is used to study bonding of oxygen into the MoP complex (where P=porphyrin ligand) and (010) surface of MoO_3 that model homo- and heterogeneous systems, respectively. The obtained results are discussed in terms of geometric (distances and angles), electronic (atomic charges, bond orders, charge transfers) and energetic (bonding energies) parameters.

In heterogeneous selective oxidation, which proceeds according to Mars van Krevelen mechanism, oxygen that is introduces into hydrocarbon comes from the catalysts surface/bulk. Catalyst becomes reduced and in the next step has to be reoxidized by gaseous oxygen. The homogeneous oxidation starts with bonding of dioxygen to the metal center, and its further transformation (in the presence of hydrogen donor), into other reactive hydroperoxo and oxo species that are involved in hydrocarbon oxidation. A common block for both homo and hetero processes includes adsorption of molecular oxygen, formation of differently bonded oxygen species and their transformation into oxo species.

Results of performed calculations allow one to show differences and similarities in oxygen activation in the course of homo and hetero processes. In all studied systems dioxygen is bonded to Mo in side-on geometry. It is found that in any system the direct consequence of O_2 binding to the Mo ions is the O_2 activation that is expressed by the elongation and weakening of the O-O bond. In majority of cases (except the porphyrin complexes with Mo^{2+}) hydrogen adsorption leads to the formation of OOH group bonded to the metal center. Adsorption of second hydrogen results in water species that can be removed both from homogeneous and heterogeneous systems. Activation of oxygen causes of formation of oxo species that are different depending on the system. The differences concern charges on Mo and O, bond orders describing Mo-O bond and energies needed to form this bond, thus influencing the properties of oxo species and determining the type of catalytic reaction.

Gold Catalysis using Heterogeneous and Homogeneous Catalysts

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A key discovery in the last two decades has been the identification that gold, when prepared as supported nanoparticles, is exceptionally effective as an oxidation catalyst. To some extent this observation is counter intuitive since extended gold surfaces do not chemisorb oxygen, nor do they corrode. Gold is known as an immutable material, much prized for its beauty and value, which, for many years, has diverted attention from its intrinsic high reactivity. Following this discovery, there has been an explosion of interest in gold as a catalyst and several hundred papers and tens of patents are being published annually, although much of this concerns the relatively simple oxidation of CO. Gold catalysis is now a major topic for both heterogeneous and homogeneous catalysis worldwide.[1,2,3] This presentation will explore the latest developments using supported gold and bimetallic gold catalysts. In the first part of the talk the hydrochlorination of alkynes will be revisited. This is a reaction that is catalysed by Au^{3+} supported on carbon for the heterogeneous catalysts. New data concerning the reaction mechanism and the use of bimetallic catalysts will be discussed. This will then be contrasted with homogeneous catalysis of alkynes using homogeneous cationic gold, which has become a major research field. In the latter part of the talk the selective oxidation of alkenes and alcohols using carbon supported nanoparticles will be described and discussed.

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The Quest for Enantioselectivity in Heterogeneous Catalysis

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Broadly speaking, of the three types of catalytic process; enzymatic; homogeneous and heterogeneous, it is the last of these, which has had almost imperceptible impact on the commercial production of single enantiomer fine chemicals for the pharmaceutical, agrochemical, scents and flavours industries. This is despite the enormous significance that heterogeneous catalysis has had in the bulk and petrochemical sectors and the potential benefits that might accrue from the development of successful heterogeneous catalysts capable of achieving sustainable high enantioselectivity.

At the heart of this dilemma, is the relatively poor understanding, which there has been until relatively recently, of all aspects of chirality at surfaces in terms of adsorbed species, chiral substrates and, most importantly, the interaction between them. In this presentation, I will describe some of the more recent developments in understanding of chirality at surfaces focusing on the adsorption behaviour of single enantiomers, the 2D separation of racemic mixtures, adsorption induced chirality and aspects of chiral recognition both between like molecules and that between different molecules leading to the formation of diasteroisomers. The description will attempt to show the relevance of this improved understanding to successfully achieving heterogeneous catalysis with high enantioselectivity.

Combining the Best Features of Heterogeneous and Homogeneous Catalysis – The Importance of Catalyst Nanoparticles in Microreactors Design

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The role of green chemistry and environmental catalysis has been growing enormously during the past years. The different classes of catalysis, i.e. homogeneous, heterogeneous and enzymatic, have their attractive features if their functioning in different environments is considered. These remarkable features should be researched simultaneously and brought together at the molecular level to find new innovations in catalysis. The importance of unifying the molecular level know-how and designing new experimental approaches to understand and control surface phenomena, and the idea to more strongly focus on the selectivity of chemical reactions via tailored catalysts are the main goals for the future green chemistry and catalysis approach. This approach opens up completely new innovations in designing new greener processes, e.g. in microreactors and catalyst fabrication, and nanomaterials with improved selectivity.[1,2]

The research in nanotechnology and nanocatalysis has lately been actively funded by the Finnish basic research funding organization, the Academy of Finland (AF), as well as by the Finnish Funding Organization for Technology and Innovations, Tekes. The AF has established two 4-year research programmes on Sustainable Production and Products in 2006 and Sustainable Energy in 2007. These programmes fund nanocatalysis and green chemistry and technology oriented research. The AF and Tekes are jointly financing also the FinNano research programme. This research projects are typically very multidisciplinary and can thus serve as the platform for completely new innovations.

The aim of our research group and collaboration partners has been to develop and study new catalyst materials based on metal nanoparticles (1-10 nm) supported on nanostructured (meso-porous) SiO_2, Al_2O_3 and ZrO_2 templates and on single- and multi-walled carbon nanotubes.[3,4] The advantages of the novel catalyst systems over the conventional zeolite and washcoat supports are the easy tenability of pore/particle size within a wide range and also the thermal durability. These are all important factors when the catalyst requires long life time at high temperatures, e.g. in automotive exhaust gas catalysis. The ultimate goal has been to design cost-effective catalyst systems of high catalytic activity with potential automotive, domestic and industrial applications. These novel catalyst systems enable the management of CO, NOx and VOCs in a microreactor environment with optimal contact time, efficient heat and mass transfer, and mixing. Thus, this project combines relevant green chemistry principles, e.g. nanocatalysis, microreactors, ionic liguids, improved selectivity, into one approach for the benefit of catalyst design.

In the experimental work, Pd nanoparticles have been deposited at ambient temperature into anodic Al_2O_3 templates via a pure chemical route using ammonia-complexed Pd ions and formaldehyde in the precursor solution[4]. 2-propanol added to the precursor during the process enables the deposition of monodisperse Pd particles ($\sim$4.2 nm), which form small agglomerates ($\sim$20 nm) in the pores. The agglomerates of palladium nanocrystallites turn into crystalline PdO particles of $\sim$10 nm in size when the samples are treated in air at 600°C for 20 hours. After repeated oxidation and reduction at 500°C, the reduced catalyst showed complete catalytic oxidation of CO by O_2 over the oxidized catalyst already at 140°C. The reduced catalyst showed only moderate catalytic activity in reduction reactions.

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The Role of Mo in Selective Oxidation Catalysis

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The role of Mo in the selective oxidation reactions will be considered in some detail, focusing on the selective oxidation of methanol to formaldehyde. The reaction mechanism and kinetics will be described. It is notable that Mo tends to segregate to the surface of iron molybdate catalysts, proven by scanning transmission electron microscopy and XPS, and so it dominates the surface, even at very low loadings. This is manifest in reaction data too: for instance, the selectivity to formaldehyde for a catalyst with only 20% Mo present is 50% at 50% conversion, whereas for pure iron oxide it is close to zero at all conversions. However, commercial catalysts comprise of high levels of Mo and so we may ask ourselves, in light of the previous statement, why is this necessary? It appears to be necessary for a number of reasons:

a) the surface must be maintained as pure molybdenum oxide;

b) there is Mo loss from the catalyst during the course of the reaction – extra Mo keeps a complete layer of Mo at the surface always present;

c) when in the form of iron molybdate the surface area of the exposed MoO_3 is significantly higher than for pure molybdena;

d) there is a small effect of the spillover phenomenon described by Delmon as the remote control mechanism.

Some of this behaviour is analogous to the role of Mo in homogeneous and enzymatic processes, such as xanthine oxidation, and the three areas of catalysis by molybdenum will compared and contrasted. The role of different types of oxygen, such as lattice oxygen, surface oxygen, bridging and terminal oxygen species will be defined and clarified, and the modified Mars-van Krevelen description of the heterogeneous reaction will be given.

Oral Presentation Abstracts

Enantiospecific Interaction at an Intrinsically Chiral Surface: A RAIRS Study of Alanine on Cu{531}

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An enantiospecific effect has been observed for the adsorption of the chiral amino acid alanine on the intrinsically chiral Cu{531} surface. Using Reflection-Absorption Infrared Spectroscopy (RAIRS) we have detected a marked difference between the vibrational spectra of L-alanine and D-alanine on Cu{531}-D (Figure 1). RAIRS is inherently sensitive to the orientation of the molecule at the surface and hence our results clearly indicate that the adsorbate geometry of alanine is enantiospecific. The opposite chirality of surface gives the opposite result, providing conclusive evidence of an enantiospecific adsorption interaction. The interaction of chiral molecules with surfaces has attracted considerable interest in recent years due to its underlying importance in fields such as enantioselective heterogeneous catalysis and biosensors[1,2]. Our observation of an enantiospecific effect has important consequences both in understanding adsorption on chiral surfaces and in areas such as catalyst and biosensor design.

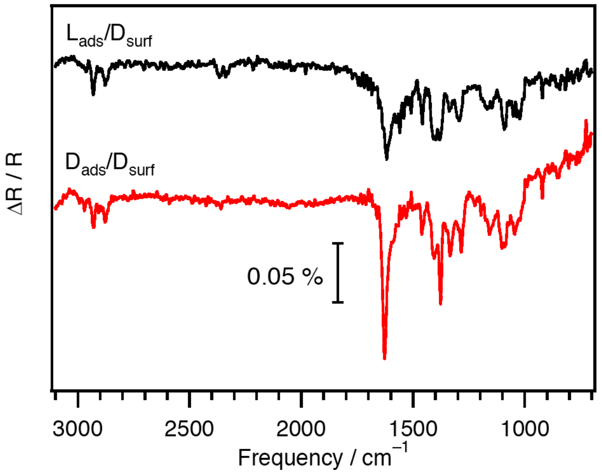

Figure 1. RAIR spectra of L-alanine (top) and D-alanine (bottom) adsorbed on Cu{531}-D at 300 K.

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A Mesoporous Silica Heterogeneous Catalyst Containing Adjacent Sulfonic Acid and Thiol Groups for the Synthesis of Bisphenol A

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Solid acids are widely used as catalysts and in particular for the production of Bisphenol A from acetone and phenol. It has been demonstrated that the addition of thiol groups to the acidic catalysts improves both the conversion and selectivity to Bisphenol A. We have prepared mesoporous silica (SBA-15) materials functionalized with alkylsulfonic acid/thiol pairs at fixed distances via a non-oxidative method. A trialkoxyorganosilane was synthesized containing a 1,3-propanesultone ring. After being grafted onto the surface of SBA-15, these sultone groups can be modified by treatment with a nucleophile. Hydrolysis of the sultone ring yields sulfonic acid groups with nearby hydroxyl groups, whereas treatment with hydrosulfide ion results in adjacent thiol groups. The resulting materials were characterized by IR, ^{13}C CPMAS NMR, acid titration, and thiol titration with Ellmans reagent. The acid/thiol-paired catalyst exhibits very high activity in the synthesis of Bisphenol A (Per site yield = 70, selectivity = 95%). Control materials containing no thiol groups or containing randomly mixed thiol and sulfonic acid groups and homogeneous analogues were found to exhibit lower catalytic activity. Thus, site adjacency is an important factor governing the activity of the bifunctional acid/thiol catalyst. This work represents one of the first examples of the nanoscale organization of two disparate functional groups on the surface of a heterogeneous catalyst.

Design of Highly Active and Enantioselective Recyclable Oligomeric/Polymeric Co-Salen Catalysts for the Hydrolytic Kinetic Resolution of Epoxides

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Chiral epoxides are among the most versatile building blocks for modern asymmetric organic synthesis. Among many available methods for the preparation of enantiomerically enriched epoxides, the kinetic resolution of racemic epoxides has been attracting increasing attention.[1] The pre-eminent catalysts for epoxide kinetic resolutions are Co or Cr-Salens.[2] These were originally discovered and used as soluble homogeneous catalysts. However, the design of supported versions of these molecular catalysts can have tremendous practical benefit. In addition to standard benefits of metal recovery and recyclability, in this case, *properly designed supported catalysts can be even more active and selective than their homogeneous analogues*. This is because the asymmetric ring-opening reaction is second order in salen complex, requiring two complexes in the transition state of the rate-limiting step[2]. Thus, a supporting strategy that allows for a high local concentration of salen complexes can give catalysts with enhanced rates compared to the homogeneous, monometallic analogue. The design of such catalysts presents unique constraints in molecular or materials design, requiring supporting strategies that enhance bimolecular interactions exactly the opposite case of most rigid immobilization strategies that require or impart site isolation. Here we present two unique strategies for the creation of heterogeneous Co-Salen catalysts that allow for cooperative interactions between the metal complexes, (i) creation of cyclic oligomeric flexible catalyst supports[3] and (ii) synthesis of inorganic/organic hybrids based on polymer brushes grown off nanoparticle surfaces.[4] The cyclic oligomeric Co-Salen catalyst is synthesized by a novel ring-expanding olefin metathesis[3], giving a highly flexible, extremely active and selective catalyst. This catalyst is among the most active HKR catalysts known, being the most active catalyst for some substrates and similar to the best catalysts for others.

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Identification of Reaction Intermediates on Supported Metal Surfaces

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It is well known in the heterogeneous catalysis that chemical transformations may occur both on the metal surface and the support, and a dynamic surface traffic of intermediates goes on between the metal and support components. The in situ IR spectroscopy gives indispensable information on the elementary steps of heterogeneous transformations, however rather high concentration of catalytically active metal particles are required to obtain high quality spectra. In this paper we report on a method combining experimental spectroscopy and theoretical computation of the vibration modes of adsorbed intermediate products, which allows us to follow the reactions taking place on the catalysts.

0.1 w% Pt/SBA-15 samples were prepared and treated as described elsewhere. The self supported wafer was loaded to cyclohexene or cyclohexene-hydrogen mixture and the spectra both of the gas phase and the adsorbed phase were taken. Then the temperature was increased stepwise and spectra were taken at each stage.

First it was proven that SBA-15 alone is inactive in the cyclohexene conversion and no spectroscopic change was found for adsorption of cyclohexane and benzene either. Upon introduction of cyclohexene into the cell containing the Pt/SBA-15 wafer at ambient temperature, new bands appeared and simultaneously the OH band of the silicate was shifted to lower wavelength. The new bands were attributed to the adsorbed cyclohexene. Upon heating the sample at 473 K for increasing time the spectral feature of the system changed. At longer reaction times new bands appeared in the spectra of adsorbed species. These bands are due to the adsorbed benzene as dehydrogenation product. When a mixture of cyclohexene and hydrogen was adsorbed on the wafer at 323 K the vanishing of the double bond of the ring at 3023 cm^{-1} occurred.

For theoretical studies, a small model system, $HO\text{-}Si(OSiH_3)_3$, was chosen first to represent the local environment of the OH groups in SBA-15. The interaction of the surface intermediates were studied at Hartree-Fock (HF), density functional B3LYP and second-order Mller-Plessett (MP2) levels of theory using the Gaussian program package. Full geometry optimizations were performed for the model system and adsorption complexes, and the stationary points obtained were checked through the eigenvalues of the computed hessians. It was found that the HF and B3LYP theoretical levels were not appropriate for studying the intermolecular interactions under consideration. The theoretical IR spectra of the small model system and adsorption complexes were calculated at the MP2 level of theory within harmonic approximation via normal coordinate analysis. Good correlation between the experimental and computed results was found.

With the help of the Own N-Layer Integrated Molecular Orbital-Molecular Mechanics (ONIOM) method in GAUSSIAN quantum chemistry code, it is possible to use larger and larger clusters as model systems. It is clear that with increasing cluster size, more of the important local electronic and steric effects are included, while the effect of the terminating region diminishes when it is further separated from the OH group. The gas phase spectra of compounds expected to be the products of hydrogenation and dehydrogenation of cyclohexene are cyclohexane, 1,4-cyclohexadiene, 1,3-cyclohexadiene and benzene. The spectra of these compounds show bands that are used for analysis in the 2700 and 3200 cm^{-1} and in the 500-1900 cm^{-1} spectral ranges.

The advantage of such a combined IR spectroscopic measurement is the parallel investigation of the catalyst surface and the gas phase. From this it follows that one has much greater chance to observe even small differences in the nature of surface species, opening new surface reaction pathways, accumulation one of the surface intermediate or other changes remaining locked for the analysis only the gas phase or investigation of surface transformation separately and not simultaneously.

Autoxidation Chemistry: Bridging the Gap between Homogeneous Radical Chemistry and (Heterogeneous) Catalysis

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Liquid-phase autoxidations are important processes in the chemical industry,[1] upgrading a hydrocarbon feedstock to value-added products by using O_2. Despite their industrial relevance, the chemistry of autoxidations remained however poorly understood for many decades.

It was widely accepted that the hydroperoxide product is formed in a fast propagation reaction of chain carrying peroxyl radicals with the hydrocarbon substrate, while alcohol and ketone would be formed exclusively in the slow termination reaction between two peroxyl radicals[1]. This view is however in disagreement with several experimental observations. Based on a combined theoretical and experimental study on the cyclohexane and ethylbenzene autoxidation, we identified the hitherto overlooked but very fast propagation of the hydroperoxide as the predominant source of ketone and alcohol.[2,3] The major impact of cage reactions on this liquid phase reaction will be discussed for these two model substrates. We also discovered that the homolytic dissociation of the hydroperoxide product is very inefficient as initiation step in the liquid phase as the nascent radicals mainly recombine within their solvent cage rather than to light off new chains. The actual initiation mechanism has been newly identified and fully quantified. For the case of cyclohexane autoxidation, the $^\bullet$OH radical breaking away from CyO-OH abstracts an αH-atom from the cyclohexanone product, producing the resonance stabilized ketonyl radical and a cyclohexoxy radical (CyO$^\bullet$). This reaction features a lower energy barrier and prevents in-cage recombination, thus greatly enhancing the initiation efficiency.[4] This reaction accounts for the observed autocatalytic upswing of the cyclohexane autoxidation. For substrates such as ethylbenzene where the αH-atoms of the products are bound more strongly than those in cyclohexanone, the conversion rate increases less sharply in time compared to cyclohexane autoxidation. In fact, even some slight inhibition can be observed, due to the formation of chainterminating $HO_2^\bullet$ radicals in the alcohol co-oxidation[3]. The hypothesis that overoxidation of cyclohexanone would be the most important route to ring-opened by-products during cyclohexane autoxidation is critically evaluated. Solid evidence is found that such by-products also originate mainly from the propagation of CyOOH.[5]

From this revised mechanism, important conclusions can be drawn with respect to the design of new (heterogeneous) catalytic systems. Two different model approaches will be presented: (i) the use of perfluorinated compounds such as Teflon and perfluorodecalin,[6] and (ii) silicaimmobilized Cr_2O_3 nano-particles.[7] Both systems increase the cyclohexanone yield in the autoxidation of cyclohexane, the first via a catalyzed hydroperoxide propagation[6], and the second via catalytic dehydration of the hydroperoxide[7]. In situ synthesis and precipitation of colloids on an inert support material will thereby be presented as a novel strategy for the synthesis of supported nano-catalysts. Via the aggregation of elementary building block colloids, the size of the nano-catalyst can be tuned by simple process parameters.

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Catalysis in a Nanocage Environment

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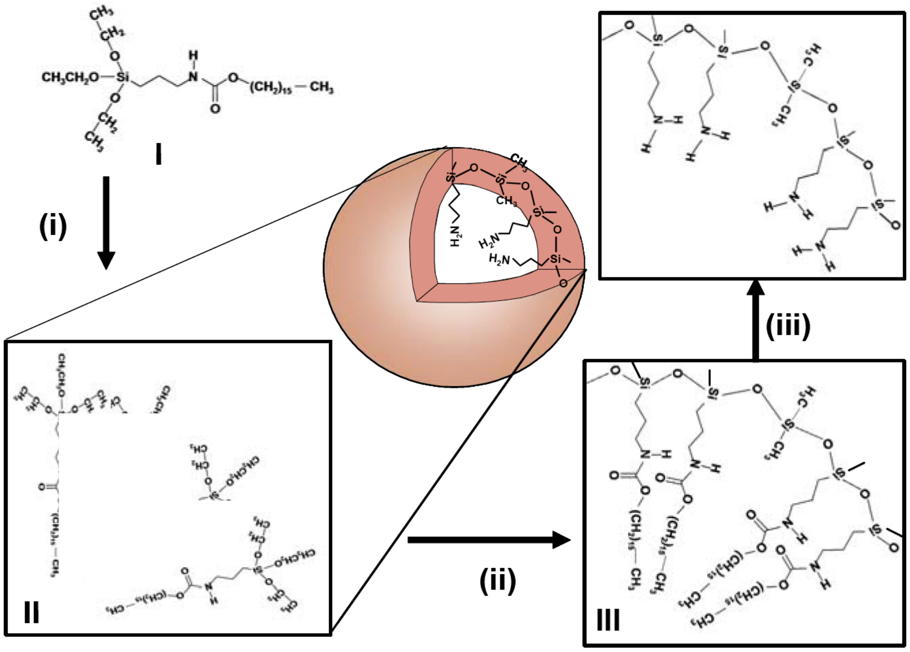
Environment around an active site has long been shown to play crucial roles in biological catalysts and homogeneous catalysts. In enzymes, the hydrophobic environment provided by the protein is known to facilitate binding of substrates that possess nonpolar groups, and the cooperative effects of side groups of amino acids at positions far away from an active center have been known to participate in activation of reactants. For homogeneous metal complex catalysts, the steric effect of the ligands often determines the orientation of the substrate binding in addition to their electronic effects on the metal center.

The effect of the environment on catalytic properties in heterogeneous catalysis is much less understood. However, based on knowledge gained from biological and homogeneous catalytic systems, it is expected that the environment should play an equally significant role in heterogeneous systems. We have been designing systems to explore the environment effect in systems that mimic heterogeneous catalytic systems. In particular, in view of the importance of zeolites, we explore nanocage systems that possess molecular-size cages with interior active sites.

2-nm diameter siloxane nanocages can be prepared using surfactant molecules that possess alkoxysilane head groups and carbamate-containing hydrophobic tails. After hydrolysis and condensation of the alkoxysilane head groups to form a crosslinked shell, the core can be evacuated by cleaving the carbamate bonds (Figure 1). These nanocages exhibit molecular size-selectivity for access to their interior, as well as confinement effect in the activity and selectivity in the decarboxylation of acetylacetone catalyzed by amine groups tethered to the interior surface of the cage wall. These amine groups are five times more active than a corresponding amine group in solution, and produce much more acetals and hemiacetals as the initial products than amines in free solution.



Ordered Mesoporous TiO_2-based Materials as Highly Efficient Catalyst for Solvent-Free Benzyl Alcohol Selective Oxidation

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Recently, we developed a versatile sol-gel (AcHE) system to prepare ordered mesoporous multi-component metal oxides[1]. It provides great opportunity to investigate their structural and component effect on their catalytic properties. In this work, the oxidation of benzyl alcohol to benzaldehyde has been studied in the absence of solvent using ordered mesoporous TiO_2-based two-component systems (K, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, Bi-TiO_2, Ti/M = 20) and three-component system (3K-Cu-TiO_2) as the catalysts. The catalysts have highly uniform one-dimensional meso-channels with size of 3∼6 nm packing in two-dimensional hexagonal symmetry (Figure 1). Their inorganic walls consist of anatase nanocrystals (5∼7 nm). The catalytic performance of various catalysts was evaluated in terms of their activity and selectivity. The best catalysis result was obtained in mesoporous Cu-TiO_2 system. It shows a very high conversion (up to 90%) and selectivity (∼90%) of benzyl alcohol selective oxidation to benzaldehyde, which distinguish it from the other Cu catalyst systems (Cu/P25 and Cu/ZSM-5). However, significant deactivation of the catalysts after 20 h reaction along with a color change to black is presumably a consequence of the carbon deposition. The introduction of third component, alkali cations (K^+), to mesoporous Cu-TiO_2 system was found not only to increase the reaction selectivity to benzaldehyde (from 90% to >98%), but also keep the catalyst resistant to the coke formation. Other factors, like Cu/Ti ratio and size of nanocrystals embedded on inorganic walls, were also investigated.

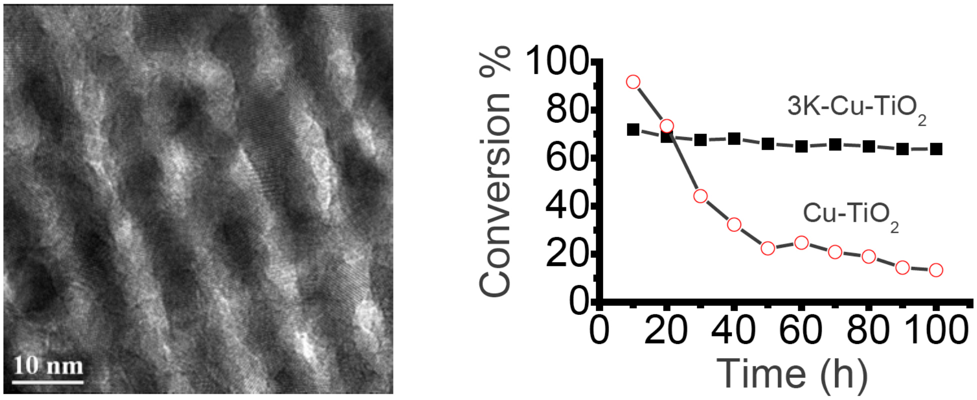

Figure 1. (left) TEM images of mesoporous TiO_2-based material and (right) benzyl alcohol oxidation conversion as the function of the reaction time over mesoporous TiO_2-based materials.

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Heterogeneous Catalysts and Enzymes Moving Closer Together: Mechanistic Similarities and Differences Between Fe-ZEM-5 and Cytochrome P450 Oxidation Catalysts

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The cytochrome P450s are a class of hemeproteins (iron-containing enzymes) that oxidise a very wide range of organic substrates, including alkanes, alkenes and aromatic molecules such as styrene. Their mechanism of oxidation has been the subject of extensive investigation, and the preferred route involves a ferryl species.[1]

Panov and co-workers have shown that, when correctly treated, the transition metal ion containing zeolite Fe-ZSM-5 is able to perform the catalytic oxidation of benzene to phenol with high selectivity, but only when nitrous oxide is used as the oxidant.[2] Based on reactivity patterns and structural characterisation, Panov et al. have suggested that there are mechanistic parallels between Fe-ZSM-5 and P450.[3] His group has also shown that, after activation in nitrous oxide, Fe-ZSM-5 is capable of carrying out stoichiometric oxidation of alkanes at room temperature.

In an effort to gain a better understanding of the mechanism of the Fe-ZSM-5 catalyst we have carried our a range of stoichiometric oxidations of alkenes at room temperature. We were initially interested in the proposal that the first step in benzene oxidation is the formation of benzene epoxide, which then rapidly rearranges to give phenol.[4]

We have found that cyclohexene epoxide is indeed one of the products of the oxidation of cyclohexene by N2O-activated Fe-ZSM-5 at room temperature. However it is the minor product [selectivity $< 15\%$], with the major primary product being 1-cyclohexene-3-hydroperoxide. Over time the hydroperoxide readily converts to a mixture of 1-cyclohexene-3-one and 1-cyclohexene-3-ol.

Oxidation of cyclohexene with cytochrome P450 has as its main products cyclohexene epoxide and 1-cyclohexene-3-ol, and Vaz et al have shown that mutagenesis (modification) of the enzyme can cause variation of the ratio in which these products are produced.[5] Although they have been able to detect it, these authors propose the involvement of an Fe-hydroperoxide species in the P450 oxidation mechanism, as an alternative to the standard view, and our results show clearly that the hydroperoxide can be a precursor of 1-cyclohexene-3-ol. It therefore seems that there are increasingly close parallels between the mechanisms of Fe-ZSM-5 and cytochrome P450 as oxidation catalysts, although why the former must be activated in nitrous oxide rather than molecular oxygen remains unclear.

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Selective Oxidation of Methanol to Formaldehyde on Isolated Vanadate Species Supported on Silica and Titania

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Isolated vandate species supported on silica or titania are active for the selective oxidation of methanol to formaldehyde. However, for identical reaction conditions, VO_x/TiO_2 is more than tenfold more active per vanadium atom than VO_x/SiO_2. The present work was undertaken with the aim of understanding the origins of this of this effect of the support. To this end, highly dispersed mono-vanadate centers were deposited on both silica and titania and then investigated using a combination of experimental and theoretical methods. Catalyst characterization by Raman spectroscopy, XANES, and EXAFS showed that on both supports vanadium is present as isolated $\equiv$V=O species and quantum chemical calculations of the geometry and vibrational spectra of such species fully support the interpretation of the experimental observation. The adsorption of methanol occurs by addition across V-O-Si or V-O-Ti bonds leading to the formation of V-OCH_3/Si-OH or V-OCH_3/Ti-OH pairs or, alternatively, Si-OCH_3/V-OH or Ti-OCH_3/V-OH pairs. Experimental studies suggest that the intramolecular transfer of a hydrogen atom from V-OCH_3 groups to the V=O bond associated with the same vanadate species is the rate limiting step in the formation of formaldehyde, a conclusion that is well supported by first principles calculations of reaction rates for both silica- and titania-supported vanadate species. The theoretical work also shows very good agreement between with experimental observation for the apparent rate coefficient and its dependence on temperature for VO_x/SiO_2. Similar calculations for VO_x/TiO_2 reveal that the support composition influences the intrinsic rate at which V-OCH_3 groups are converted to formaldehyde but does fully capture the experimentally observed increase. Experimental studies suggest that the difference between theory and experiment is attributable to the role of titania in serving as a supply of methoxide groups to the vanadate species via a process of reverse spill over. We have also investigated the processes by which reduced vandate centers, produced upon desorption of formaldehyde are reoxidized by O_2. Evidence from both experimental and theoretical investigations suggests two possible pathways via which reoxidation can occur, both of which involve the formation of a vanadium peroxide species [$\equiv V(O_2)$] in the first step. However, in both cases the rate of reoxidation is much more rapid than the rate of formaldehyde formation and, hence, the rate of reoxidation is not kinetically relevant.

New Insights into the Enantioselectivity in the Ruthenium Catalysed Asymmetric Hydrogenation of Ketones. A Computational study.

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One of the most significant developments in synthesis of enantiomerically pure alcohols was the discovery by Noyori and co-workers of highly efficient ruthenium complexes for hydrogenation of prochiral ketones.[1] Among the best catalysts discovered are Ru(II) octahedral complexes combined with a chiral diphosphine and a chiral diamine.

The rationalisation of enantioselectivity for Ru-diphosphine/diamine catalysed ketone hydrogenation is still an open question. In fact, the experimental evidence shows that subtle modifications of the substituents at phosphorus produce very significant changes of the enantioselectivity.[2]

We present a density functional theory study on the hydrogenation of prochiral ketones catalysed by *trans*-Ru$(H)_2$(diphosphine)(diamine) catalysts.[3,4] Our results show that the effect of the substituents on the enantioselectivity may reside not only in changes at the transition state level but also in the docking of the substrate into the reactive pocket well before the bond breaking/forming interactions are established.

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Synergetic Confinement Effect of Carbon Nanotube and the Encapsulated Metallic Nano-particles on Catalysis

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Carbon nanotubes (CNTs) have well defined hollow interiors and exhibit unusual mechanical and thermal stability as well as electron conductivity. This opens intriguing possibilities to introduce other matter into the cavities, which may lead to nanocomposite materials with interesting properties or behaviour different from the bulk. In the present talk, two unique properties concerning the redox and catalysis of the CNT-encapsulated metals and metal oxides will be addressed. The autoreduction of the encapsulated Fe_2O_3 is significantly facilitated inside CNTs with respect to the outside nanoparticles, and it becomes more facile with decreasing CNT channel diameter as evidenced by temperature programmed reaction, in situ XRD and Raman spectroscopy. The oxidation of encapsulated metallic Fe nanoparticles on the other hand is retarded in comparison to that of the outside Fe particles as shown by in situ XRD and gravimetrical measurements with an online microbalance. A striking enhancement of the catalytic activity of Rh particles confined inside nanotubes for the conversion of CO and H_2 to ethanol has been found. The overall formation rate of ethanol (84 mol per mol Rh and per hour) inside nanotubes exceeds that on the outside of the nanotubes by more than an order of magnitude, although the latter is much better accessible. We attribute these unique behaviours of transition metal nanoparticles inside CNTs to a particular electronic interaction of the encapsulates with the interior CNT surface.[1,2,3,4,5]

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Fischer-Tropsch Synthesis and Hydroformylation of Olefins on Cobalt Catalysts: Differences and Similarities

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Recycling gaseous olefins in Fischer-Tropsch synthesis on a (heterogeneous) cobalt catalyst in order to increase the yield of gasoline, *Otto Roelen (in 1938)* discovered the "Oxo synthesis", the formation of aldehydes by adding CO and H_2 to the olefin. Today, (homogenous) hydroformylation is well understood, however, the mechanism of (heterogeneous) FT-synthesis is still being debated. There should be strong relations between the systems and principle differences, due to the homogeneous or heterogeneous nature of the reactions.

At increasing pressure (partial pressure of CO), FT-synthesis approaches a (thermodynamic) border where the cobalt metal reacts with CO to cobalt carbonyls (*Hemut Pichler*[1]), and the regime of FT-synthesis turns into the regime of hydroformylation.

It is an interesting feature of the FT-synthesis regime that it establishes under reaction conditions. Recent investigations of this selforganisation have disclosed distinct FT principles (*H. Schulz*[2]). The activity increases (e.g. 5-fold), methane selectivity decreases, chain growth probability increases, branching probability decreases and olefin secondary hydrogenation decreases. Simultaneously, the cobalt surface is restructured, being orderly roughened (*Wilson, de Groot*[3]). This surface restructuring is explained as a thermodynamically controlled process (*H. Schulz*[2]): Strong CO chemisorption causes breakup of crystal planes for more CO molecules to be adsorbed, the cobalt surface area increases and simultaneously the Co-on-plane sites disproportionate for such of higher and of lower coordination (in-pit and on-top sites). In thermodynamic equilibrium then the energy for enlarging the cobalt surface equals the energy of additional CO adsorption. Now there are three kinds of Co-sites on the surface to co-operate in FT-synthesis: (1) On-top sites, comparable to the central atom of cobalt carbonyl complexes, capable for alkyl chain growth, (2) In-pit sites, active for CO dissociation (see *Ponec*[4] for CO adsorption on Ni) and thus CH_2 monomer formation and (3) Common on-plane sites, these widely deactivated through strongly adsorbed CO and CH_3-species, however, still available for olefin secondary reactions and some methanation (see *Albers*[5] for deactivating CH_3-species).

The changes of selectivity of CO-hydrogenation on cobalt during the initial time of synthesis and the changes with variation of the parameters temperature and partial pressures and additionally the reactions of co-fed olefins substantiate the mechanistic view about a continuous shift from heterogeneous FT-synthesis to homogeneous hydroformylation and the involved elemental reactions and catalytic principles.

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Time-Resolved FT-IR Spectroscopy of Heterogeneous Catalysis in Nanoporous Solids Under Reaction Conditions

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The high surface area and nanostructured features of silica supports such as SBA-15 and MCM-41 offer unique opportunities for exploiting catalyst supports for steering reactions to desired products. A mechanistic understanding of reactions inside the nanopores will be instrumental for optimizing the support structure for target reactions. For the elucidation of the mechanism of heterogeneous (thermal) catalysis or photocatalysis on nanoporous supports under reaction conditions, time-resolved FT-IR spectroscopy on the time scale of nanoseconds to milliseconds has emerged as a unique tool. The method allows the detection of short-lived transient surface intermediates and determination of the kinetically relevant species by monitoring their interconversion to final products. Furthermore, the behavior of emerging products and escape from the nanoscale channels can be followed in real time. Our most recent studies include propylene hydrogenation over Pt nanoparticles on SBA-15 support, the dynamics of carbon monoxide molecules inside MCM-41 silica mesopores, and time-resolved photocatalytic oxidation of liquid cyclohexene by O_2 at single vanadium sites in mesoporous silica TUD-1 with visible light.

Propylene hydrogenation over Pt nanoparticles supported on SBA-15 was monitored at 20 ms resolution using ms propylene gas pulses joining a continuous flow of H_2 (in N_2, 1 atm, temperature range 323–413 K). Surface propyl (1457 cm^{-1}) to propane hydrogenation was found to be rate limiting (56 ms at 383 K). The CH stretching region revealed distinct bands for propane molecules emerging inside the nanoscale channels. Spectral and kinetic analysis showed that the escape of propane molecules from the channels into the gas phase occurred within hundreds of ms. This is the first direct spectroscopic observation of emerging products of heterogeneous catalysis on a nanoporous support. The dynamics of carbon monoxide molecules inside the channels of MCM-41 silica support were investigated on the nano to ms time scale using laserinduced dissociation of a photolabile precursor. Spectra of the infrared CO band revealed that the molecules interact O or C end-on with surface silanol (SiOH) groups as well as siloxane oxygens (SiOSi) as they diffuse through the channels. The escape time from 3 nm channels (1μ long) is 500 μs at room temperature. In the case of the time-resolved photocatalytic oxidation study of liquid cyclohexene over isolated tetrahedral V=O sites in mesoporous V-TUD-1 silica support (ATR mode), a transient intermediate of alkene reaction with the vanidyl group was observed (room temperature). The result expands our previous time-resolved FT-IR spectroscopy of heterogeneous photocatalytic reactions in the gas phase to systems involving liquids. Highlights of these studies will be presented.

Solid State and Gas Phase NMR Studies of Immobilized Catalysts and Catalytic Active Nanoparticles

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In recent years, interest has grown in the field of immobilized catalyst, due to their high catalytic efficiency and their application potential in environmentally benign (green) chemistry. This interest has triggered active research in the synthesis of new materials which are organized on the meso- and nanoscale and several spectroscopic and computational techniques for the characterization of these materials and the kinetic processes on their active surfaces have been developed.

In the current study two new classes of stabile, catalytic active Nanomaterials are investigated. The first class of nanoparticles consists of an inner metal core. To stabilize their structure the metal core is surrounded by organic ligands or embedded in a polymer. The second class consists of catalysts immobilized on mesoporous silica supports. Employing a combination of ^{1}H, ^{2}H, ^{13}C and ^{29}Si-solid state NMR spectroscopy the structure of the catalysts is analyzed.

As a simple model for the catalytic properties of the particles, the activation of $^2H_2$ gas on the surface of the particles is studied. Employing ^{1}H and ^{2}H gas phase NMR the kinetics of simple catalytic model reactions are studied. Employing ^{2}H-NMR solid state NMR spectroscopy, the interaction of the metal surface with the substrate is characterized and kinetic data, which characterize the mobility of the deuterium on the surface, are extracted.

For the interpretation of these data, parallel NMR studies of model η^2-bound transition metal complexes are employed, which allow, owing to their simpler geometry and higher sensitivity, a quantitative modeling of the spin dynamics in the NMR experiment.

Organometallic Models for Reactions on Metal Surfaces: A New Look at Mechanisms for Chain Growth in the Fischer-Tropsch Reaction

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The hydrogenation of CO over Fe, Ru, Co, or Rh metal catalysts (150-250°C, 1 atm) typically gives α-olefins as *primary* products.[1] There is considerable spectroscopic and other evidence for the following reaction steps: CO adsorption on the surface (i.e., metal-coordination); H_2-aided deoxygenation giving water plus a surface carbide ($C_{(ads)}$), which then undergoes further stepwise hydrogenation giving, $CH_{x(ads)}$ ($x = 1 - 3$), and finally methane (CH_4.)[2] The $CH_{x(ads)}$ surface species are formally equivalent to the organometallic C_1 ligands: CH (methylidyne or carbyne), CH_2 (methylene or carbene), and CH_3 (methyl), and may be expected to show related behavior.

Chain growth then occurs involving the $CH_{x(ads)}$ ($x = 0 - 3$) species. A previously favored path for this involved the coupling of surface $-CH_{3(ads)}$ (or alkyl$_{(ads)}$) and $>CH_{2(ads)}$ units, followed by β-elimination to yield the free α-olefins.[3] However recent theoretical studies show that the couplings $-CH_3 + >CH_2$ have very high activation energies and are thus unlikely.

Both DFT calculations and spectroscopy indicate that the most common and stable surface species is methylidyne, $\equiv$CH (or $\equiv$C-alkyl), in a three-fold hollow ("3-coordinate") surface site, and a number of theoretical approaches have been devised in which the chain growth involves C_1 units coupling as, for example: $\equiv CH + >RCH$; $\equiv CH + RCH_2-$; $>CH_2 + >CH_2$; or $-CH_3 + >C<$.[4,5] However, allowance still needs to be made to accommodate evidence inferring the intermediacy of C_2 units in initiating chain growth[1], and the effects of surface restructuring occurring during the reactions[2].

A further factor that plays a highly significant role in organometallic coupling processes is charge (oxidation state). An example discovered by the Sheffield group is the stoichiometric decomposition of $[Rh_2(Cp^\star)_2(Me)_2(\mu\text{-}CH_2)_2]$ to give propene; in the presence of 1-electron oxidizers coupling of the three C_1 ligands occurs easily to give propene in high yield; in the absence of the oxidizer high temperatures are needed to decompose the di-rhodium complex and produce propene[6].

We suggest that the effect reported by Watson and Somorjai is related: they found that in Rh-catalyzed CO hydrogenation the charge on Rh determines whether methanation or chain growth, accompanied by CO insertion, occurs.[7] It is likely that charge and organizational effects (eg packing, ligand) play key roles in both metal complex (homogeneous) and metal surface (heterogeneous) reactions and the talk will concentrate on this aspect of chain growth in Fischer-Tropsch reactions.

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Modeling Surface Organometallic Chemistry by a Combination of Experiments with First Principle Calculations

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By grafting well defined metallic complexes on a solid support, surface organometallic chemistry provides a bridge between homogeneous and heterogeneous catalysis. This innovative approach has already proven its efficiency for several reactions: polymerization, olefin and alkane metathesis, However several fundamental questions remain open on the chemical role of the oxide surface, on the grafting mechanism and on the reactivity of the grafted complex. Are the active species created well defined (single site)? What are their structures? What are the factors governing their catalytic reactivity and selectivity?

In this communication we combine on the one hand reactivity and spectroscopic experiments with on the other hand total energy calculations and spectra simulations (NMR, IR) in order to propose insights for these open questions, in the case of metallic complexes (Zr, W) grafted on gammaalumina. The simulations of spectra create a strong interplay between experiment and theory, and allow the validation of the total energy calculations results.

The first aspect is the chemical role of the alumina support, and its potential difference with other frequently used systems, as silica. Hydroxyl groups are the key anchoring features for alkyl complexes $[\mathrm{Zr}(\mathrm{CH}_2t\mathrm{Bu})_4]$ or $[\mathrm{W}(\mathrm{C}t\mathrm{Bu})(\mathrm{CH}_2t\mathrm{Bu})_3]$, and we use here a recently developed model of alumina in realistic hydration conditions (1). The complete grafting reaction pathways are described: for the Zr complex, a cationic bis-aluminoxy complex is preferentially formed $[(\mathrm{AlsO})_2\mathrm{Zr}(\mathrm{CH}_2t\mathrm{Bu})^+(\mathrm{Als}\text{-}t\mathrm{BuCH}_2)^-]$, while the W complex gives a neutral mono-aluminoxy surface species $[(\mathrm{AlsO})\mathrm{W}(\mathrm{C}t\mathrm{Bu})(\mathrm{CH}_2t\mathrm{Bu})_2]$.[1] The reactivity of the alumina support is not limited to that of the OH groups. It presents strong Lewis sites from hydration defects allowing the formation of the cationic Zr complex. These sites are reactive toward H_2 and methane.[2] CH_4 reacts selectively at 100-150°C on the most reactive Al sites to form the corresponding Al-CH_3 species. The Lewis sites hence give a specific behavior of alumina versus silica, both for grafting and reactive properties.

The second point concerns the reactivity of the grafted complexes. The perhydrocarbyl W complex on alumina is active in alkane metathesis. Calculations of the reaction pathways show that hydration defects on the alumina surface are responsible for the activity of the alumina support in alkane dehydrogenation leading to alkenes, while the tungsten complex catalyses the olefin metathesis step. This opens the way to a direct participation of the support in alkane activation reactions.

Finally, when treated under H_2, the grafted Zr and W complexes form alumina supported metal hydride species. The structure of these hydrides has been determined, and their reactivity has been explored. The grafted Zr complex is active for alkane hydrogenolysis: reaction selectivity and calculation of the reaction pathways show that β-alkyl transfer is the key carbon-carbon cleavage step on the Zr grafted complex.

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Vanadium Oxide Catalysts in AAO Scaffolds

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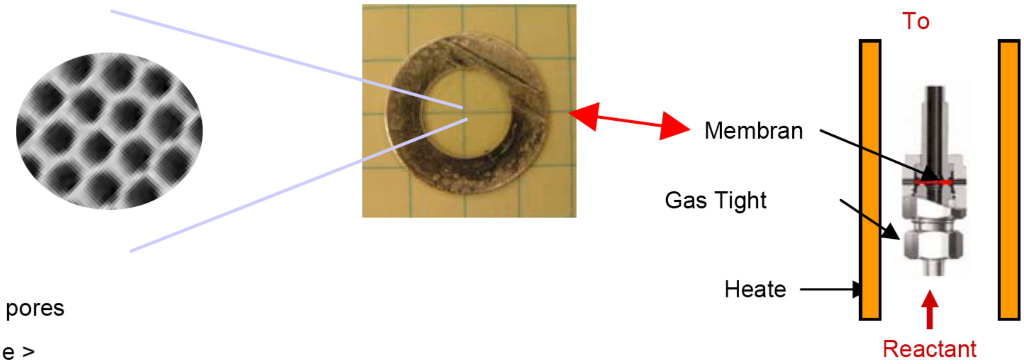
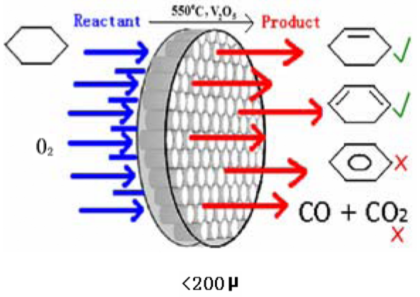
Chemistry Division, Argonne National Laboratory

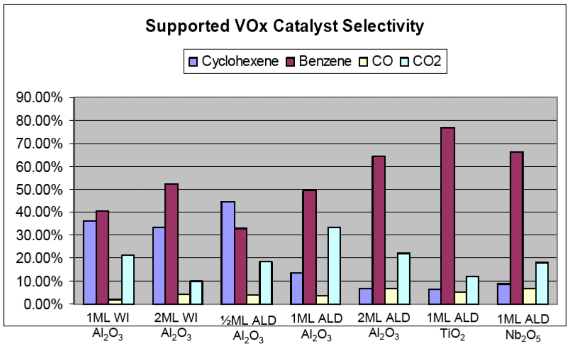
Nanostructured membranes based on anodic aluminum oxide (AAO) modified by atomic layer deposition (ALD) offer a platform for catalysts with highly uniform, controllable pore dimensions and highly flexible wall compositions. The ALD process provides chemical control of catalytically active surfaces that is analogous to the chemical control obtained in homogeneous catalysts. A series of vanadium oxide catalysts has been synthesized using ALD to produce both the support (e.g. Al_2O_3, TiO_2, Nb_2O_5) and the catalytically active vanadium oxide surface. The catalyst material has been characterized by electron microscopy, elemental analysis, surface area, UV-Vis absorption, Raman spectroscopy, and catalytic performance. The catalytic performance of these materials was investigated for the oxidative dehydrogenation of cyclohexane to cyclohexene, benzene, and carbon oxides. Characteristic differences in the specific activity and selectivity were observed for this reaction depending on the method of catalyst preparation. The results are consistent with vanadiium oxide being highly active and selective for the catalytic dissociation of single C-H bonds in methylene units. The activity and selectivity of membrane catalysts were observed to be superior to powder catalysts with the same active species.

Membrane Catalysis



- 10^{10} pores
- Stable > 550°C
- ΔP > 10 psi





A Combined Theoretical and Experimental Study of CO Hydrogenation Mechanisms with Metal Carbonyl Catalysts

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In a combined approach, density functional theory calculations have been paired to with NMR data to study the mechanism of CO hydrogenation using a cobalt carbonyl catalyst, $HCo(CO)_4$, as a model system. All stable intermediates in the reaction cycle have been examined allowing for the creation of a potential energy surface. Two different product pathways are possible based upon the insertion of CO leading to either ethylene glycol and methanol or methyl formate and methanol. Previous calculations in the literature have indicated much higher energy paths for these reactions than have been observed experimentally. However, our own examination of this system has revealed significantly better agreement with experiment. The calculations also confirm experimental observations with regard to the nature of the transition state: $(CO)_3H_2CoCOH$. The results also indicate that $(CO)_4CoCOH$ should be an observable intermediate although experiments have not observed this species to date. Vibrational frequency calculations can be used to evaluate partition functions which can then be used to predict product distributions. New results will more thoroughly examine the influence of ligands such as triethylphosphine (replacing carbonyl groups) upon the product selectivity as well as comparing the performance of $HCo(CO)_4$ with $HMn(CO)_5$.

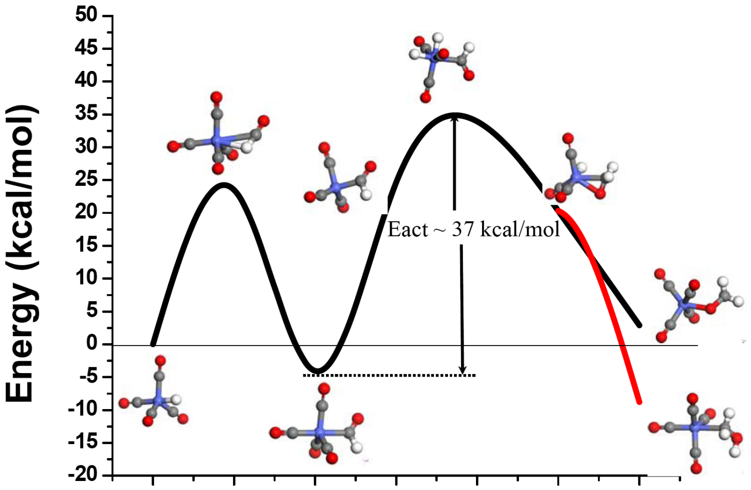

Figure 1. A view of the potential energy surface for CO hydrogenation. The black line indicates the energy of intermediates leading to methyl formate and methanol production. The red line indicates an alternative path leading to the formation of methanol and ethylene glycol.

Immobilised Acidic Ionic Liquids As New Solid Acid Catalysts for Biodiesel Synthesis

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Ionic liquids are becoming increasingly prominent in a range of different areas, such as organic synthesis[1] and catalysis.[1,2,3,4,5,6] Here, we show how acidic ionic liquids (i.e. 1-(4-sulfonic acid)butylpyridinium hydrogen sulfate, cf. Wu, et al.[7]) can be used to functionalise the surface of silica to yield new acid catalysts with unusual properties in the transesterification of oils and fats with methanol to produce fatty acid methyl esters (FAMEs), otherwise referred to as biodiesel.

Due to differences in the reaction mechanism the conventional base-catalysed reaction (S_N2 attack by the methoxide ion) has a lower energy of activation as compared to the acid-catalysed one (protonation of carbonyl group, followed by the formation of the tetrahedral intermediate with methanol). This results in an inherently lower rate of reaction for acid catalysts. However, we observed this to be much less pronounced in our system.

The transesterifaction reactions were performed in a Parr reactor at temperatures ranging from 120°C to 175°C at a pressure of 750 psi. The reactions used the approximate molar ratios of MeOH: tallow of 1:0.04 with 760 mg of catalyst. In the case of the reaction being performed at 175°C, a FAME yield of 94.5% was obtained with a turnover frequency of more than 150 h^{-1}. In comparison, H_2SO_4 (760 mg) achieved a turnover frequency of 24 h^{-1}. The activity of the heterogeneous catalyst exceeds that reported for the free ionic liquid (~ 9 h^{-1}).[7] Furthermore, we did not observe any partial transesterification products, such as monoand di-glycerides.

To explain these observables we propose a mechanism that proceeds via the acidcatalysed route, but in which the reactant interacts with the catalytically active surface in a pre-oriented way, such that the reaction rates and selectivity are enhanced.

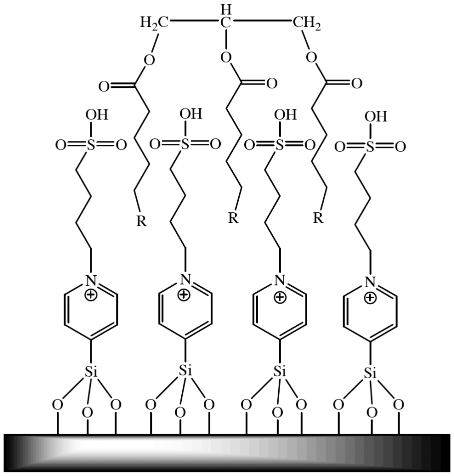

Figure 1. Schematic representation of proposed pre-orientation of the triglyceride.

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Towards Understanding the Role of Surface in the Heterogenization of Homogeneous Catalysts

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The goal of this research is to elucidate rules by which support environment surrounding immobilized active sites affects heterogeneous catalysis, in two model systems consisting of i) organic base catalysis using isolated, tethered primary amines as active sites, and ii) isolated Ti within an oxo environment as a Lewis acid active site. The former class of catalysts is central to lysine base catalysis in enzymes, whereas the latter provides a relevant model for Ti on silica catalysts used for selective oxidation, including olefin epoxidation. Understanding the role of the surface in these systems provides a method for catalyst optimization, beyond the notion of surface for ease of catalyst separation via filtration, and towards being able to design the surface, including defect sites, as an active participant in the catalysis mechanism. In addition, the nature of the bonds that are made and broken in kinetically relevant steps is determined.

Catalysis using synthetically tailored heterogeneous and homogeneous model catalysts, having similar atomic connectivity, are combined with characterization using XANES, diffuse reflectance UV-Vis spectroscopy, ^{13}C and ^{29}Si CP/MAS NMR spectroscopy, and thermogravimetric analysis to understand critical structure-property correlations. In the first system consisting of amines on silica, we have elucidated how acidic silanols surrounding the amine active site shuttle heterogeneous catalysis via a covalent iminium ion intermediate, which could be observed upon binding salicylaldehyde as a probe molecule and leads to olefin product in the nitroaldol condensation of 4-nitrobenzaldehyde and nitromethane. Amines on silica with silanols partially replaced with cyano functionality do not exhibit formation of iminium ion upon salicylaldehyde binding; and while equally active relative to amines in a silanol-rich environment in the nitroaldol reaction, they produce alcohol rather than olefin product due to the different reaction mechanism.

Grafted calixarenes are used as persistent surface organometallic ligands to study the effect of environment on Ti(IV) Lewis acid-catalyzed heterogeneous epoxidation catalysis. This is accomplished by systematically varying the metal coordination environment and characterizing d-electron occupancy at the metal center using Ti K-edge XANES. Use of *tert*-butyl-calix[4]arene as ligand leads to a more Lewis acidic heterogeneous catalyst compared to *tert*-butyl-homooxacalix[3]arene as ligand, due to a dative carbonyl ligand, which donates electron density to the metal in the latter.

Altogether, our results lead to a unified model in which there is an active role for support defect sites within the epoxidation mechanism for activating bound hydroperoxide, as well as an active role for these defect sites in heterogeneous aminocatalysis.

Enantioselective Hydrogenation of Prochiral Olefins by Use of Rhodium-Diphosphine-Complexes Immobilized on Al-MCM-41 Materials

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Hydrogenation, among all catalytic asymmetric reactions, has a particular industrial relevance because of its high efficiency and reduced enviromental impact.[1,2] The goal of heterogenization of homogeneous catalysts is to combine the superior activity and selectivity offered by homogeneous catalysts with the ease of separation and recycling of heterogeneous systems. For the heterogenisation of chiral catalysts, a novel method has been developed and applied to the enantioselective hydrogenation of dimethyl itaconate (**I**), α-acetamidoacrylic methyl ester (**II**) and α-acetamidocinnamic methyl ester (**III**). Our studies focused on mesoporous MCM-41 as a solid support with a tailorable and well-defined pore structure as well as high surface area . These MCM-41 type molecular sieves offer new opportunities for the immobilization of large catalyst species.[3]

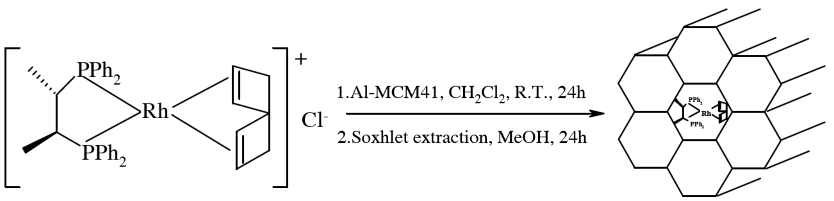

Figure 1. Immobilization of CODRhChiraphos on Al-MCM41.

Chiral Rh diphosphane complexes (Duphos, Chiraphos, Diop, Norphos) were immobilized on Al-MCM41 (Si/Al=40) through 24h stirring, using CH_2Cl_2 as solvent. The solid obtained by filtration was then Soxhlet extracted with MeOH and dried under reduced pressure. Different characterization techniques such as ICP-AES, FTIR, MAS-NMR, N_2 sorption experiments) were applied. In the case of our materials the Rh diphosphane complex is deposited on the inner surface of Al-MCM41. The high field shift of the ^{31}P signal in the case of heterogenized complex is a prove of the electron density modification from an interaction of the cationic Rh and the negative charge of MCM-41 framework. Also, an interaction between Lewis base P and Lewis acid Al is observed.

The hydrogenation of prochiral olefins was carried out in glass autoclaves, under 3bar H_2 for 24h (see Table)

Table 1. The Catalytic Activity and Selectivity of Immobilized Rh Diphosphane Complexes.

Substrate label	*Immobilized complex, used ligand*					
	S,S-Me-Duphos			S,S-Chiraphos		
	Conversion (%)	Regio selectivity (%)	e.e. (%)	Conversion (%)	Regio selectivity (%)	e.e. (%)
I	>99	>99	92	8	>99	48
II	>99	>99	97	>99	>99	74
III	37	>99	>99	>99	>99	>99

The immobilized catalysts showed high activity and excellent regio and enantioselectivity. Up to 99% e.e., >99% conversion and 99% regioselectivity were observed in the case of checked prochiral olefins. The obtained results indicate that the stereochemistry of the product is mainly dictated by the chirality of the diphosphine ligands. The recyclability was demonstrated using standard procedures. The catalysts could be reused at least five times without any activity loss. The TON exceeds 20000. More new examples of our research will be presented demonstrating the efficiency of our catalytic system.

Our work, clearly shows that chiral Rh catalysts can be simply and efficiently immobilized onto the surface of the MCM-41. These novel heterogeneous chiral catalysts are recyclable and stable towards leaching. Enantioselectivity and activity achieved in the hydrogenation of prochiral olefins are as good as in the case of homogeneous systems.and sometimes even better.

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Polymer-stabilized Metal Nanoparticles: An Effective Way for Integration of Homogeneous and Heterogeneous Catalysis

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Achieving the combination of high selectivity, activity and technological performance of catalytic systems is one of the most complex problems of modern catalysis. Traditional heterogeneous catalysts are easy regenerated and separated from the reaction mixture and provide relatively high selectivity (when properly modified), but the low surface area makes them insufficiently efficient while the high content of the noble metals results in their high cost. Nanocatalysts have large metal surface area-to-volume ratio, which allows utilizing effectively the expensive metals and providing the higher activity and selectivity compared to the traditional onescatalysts. However, without a suitable support the metal nanoparticles (NPs) aggregate reducing the surface area and restricting the control over the particle size.

Polymers which contain complexes or metal NPs may be used as the catalysts in a variety of organic reactions as they combine the advantages both of homogeneous (high activity and selectivity) and heterogeneous (easy recovery from the reaction mixture and a possibility of regeneration) catalysts. Catalytic properties of such systems can be changed by varying the type of polymeric matrix and characteristics of complexes or metal NPs.

Here we discuss development, structure and properties of novel metal-polymeric systems which are catalytically active and selective in oxidation and hydrogenation reactions used in synthesis of vitamin intermediates and medications.

The methods of NP formation in nanostructured polymers were combined into the three groups depending on the polymer type:

(i) NP formation in amphiphilic block copolymer micelles such as poly(ethylene oxide)-block-poly(2-vinylpyridine) (PEO-b-P2VP) and polystyrene-blockpoly(4-vinylpyridine) (PS-b-P4VP); it is worth noting that the heterogeneous nanocatalysts based PEO-b-P2VP and PS-P4VP deposited on alumina were also studied;

(ii) formation of metal NPs in polyelectrolyte layers (for example, in polydiallyldimethyl ammonium chloride, PDADMAC);

(iii) metal NP formation in the pores of hypercrosslinked polystyrene (HPS).

Catalytic properties of the nanostructured composites were studied in selective hydrogenation of long-chain acetylene alcohols, enantioselective hydrogenation of ethylpyruvate to (R)-ethyllactate and in direct partial oxidation of D-glucose and L-sorbose and full oxidation of phenol. Kinetic studies and physicochemical characterization of catalytic systems and substrates were conducted and the hypothesis of the reaction mechanisms was proposed. It was shown that the interaction of the metal active sites with the solvent, support, modifier and substrate occurs. Moreover, selective hydrogenation and oxidation were found to proceed via multiligand reaction complex. Substrate activation occurs by a transfer of electron density from the metal active component of the catalystsite. In all the catalysts, the metal NP diameter was found to be in the range 2-3 nm. The above methods for preparation of the polymer-containing nanocomposites allowed us to develop highly active, selective (selectivity reached 99% at 100% conversion) and stable catalytic systems of selective and enantioselective hydrogenation and selective and full oxidation.[1]

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[1] We sincerely thank NATO Science for Peace programme (SfP 974173 and SfP 981438) and Sixth framework programme no.: 506621-1 for financial support.

Preparation of Polymer Nanocomposites During Polymerization Catalyzed over Homogeneous Catalysts Supported on Nanomaterials

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Polymer-layered silicate and carbon nanotube (CNT) nanocomposites are a new class of organic polymer materials, which serve as novel composite materials.[1,2,3] Clay and CNT/polymer nanocomposites strongly influence polymer properties of only a few weight percent of total material. In our study, polyethylene (PE)/clay, polymethyl methacrylate (PMMA)/clay, PE/CNT and PMMA/CNT were prepared by *in situ* solution polymerization. PE/clay nanocomposites were synthesized by intercalation Zigler-Natta catalyst in layers of clay and PE/CNT nanocomposites were synthesized by supported metallocene on hydroxyl functionalized CNT (CNT-OH) with MAO. The thermal, physical and mechanical properties of the PE/clay nanocomposites were significantly improved by the presence of nanometric silicate layers compared to that of virgin PE. The maximum value in tensile strength (33.4 MPa) was achieved when clay contents was 7.7 wt%. The maximum thermal decomposition temperature was increased to 110°C. And also PMMA/clay, PMMA/CNT nanocomposites were successfully prepared by *in situ* polymerization initiated with a nickel(II) acetylacetonate [$\mathrm{Ni(acac)_2}$]/MAO catalyst system in presence of modified clay or MAO treated CNT-OH. PMMA/clay nanocomposites having low clay contents (< 5 wt%) were found to retain over 90% of transparency, which is important for optical applications. For the PMMA/clay nanocomposites, a 5∼10°C increase in T_g and up to a 50°C increase in decomposition temperatures were observed. The unique properties of the nanocomposites resulted from strong interactions between the silicate layers and the polymer chains.

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Preferential Oxidation of CO catalyzed by Pt Nanoparticles in Mesoporous Silica

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Mesoporous silicas have been extensively explored for practical applications in catalysis. However, so far the characteristic of high surface area has been simply used to give higher dispersion of active sites than over the conventional silica. Unique promotional effects of the mesoporous silica were described in several literatures, but the effect remains unclear at the molecular level. In our study of the synthesis and catalysis of Pt nanoclusters in mesoporous silica,[1,2,3,4] we targeted the preferential oxidation (PROX) of CO for the purification of H2 for polymer electrolyte fuel cells (PEFCs).[5]

PROX reactions were carried out using a plug flow reactor. Pt particle/FSM-16 provided high CO conversions below 373 K, while SiO_{2-}, Al_2O_{3-} and HMM-1-supported catalysts showed low activity. The selectivity for CO oxidation was 95-100% over Pt/FSM-16, indicating the suppression of H_2 oxidation. Pt/MCM-41 showed similar high catalytic performances. Reaction mechanism of PROX over Pt/FSM-16 was studied by IR using the isotopic labeling method. In admission of CO or ^{13}CO to Pt/FSM-16, the corresponding CO_2 or $1^{3C}O_2$ was formed in the gas phase in the absence of O_2. Even in further addition of $^{18}O_2$ and D_2, no ^{18}O was involved in CO_2. These results suggest that oxygen of FSM-16 is used in the CO oxidation. We propose the PROX mechanism as shown in Figure 1, where active OH groups attacks CO to give CO_2. Hence, the unique promotional effect of mesoporous silica is due to the high reactivity of OH and the facile regeneration of OH from activated H_2 on Pt and O_2 on support. Water is not formed from H_2 and O_2, which is a key to the high selectivity for CO oxidation.

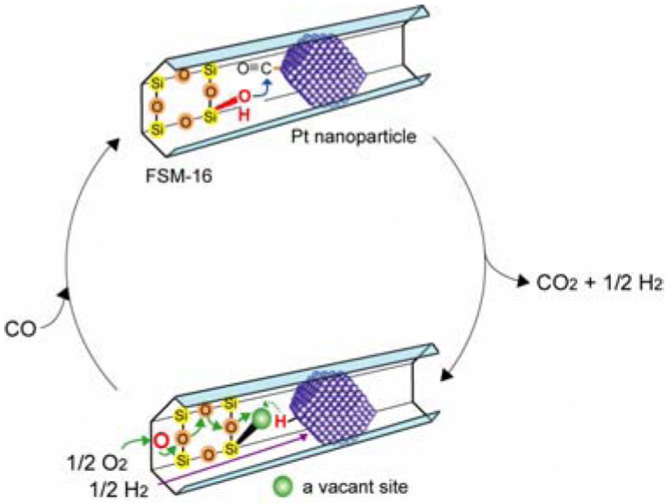

Figure 1. Proposed mechanism for PROX over Pt/FSM-16.

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Tetrahedral (Imino)pyridine Co^{II} Complexes as a Versatile Tool for the Conversion of Ethylene and Norbornene: From Oligomers to LDPE-coated Nanocomposites

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Tetrahedral bis-halide Co^{II} complexes of (imino)pyridines substituted in the 6-position of the pyridine ring form, upon activation with methylalumoxane (MAO), very active and selective catalysts for the oligomerization of ethylene to α-olefins with a Schulz-Flory distribution.[1] We have recently demonstrated that no catalytic polymerization/oligomerization reaction occurs with cyclic olefins such as norbornene (NB), whereas the ethyl-vinylation of the latter substrate takes place with high activity and complete diastereoselectivity on feeding the reactor with a mixture of ethylene (E) and NB.[2]

Branched polyethylenes (PEs) have been also obtained from E alone by using a tandem co-polymerization system comprising an (imino)pyridine Co^{II} oligomerization catalyst and a metallocene as co-polymerization system. The type and degree of branching has been found to depend on either catalyst as well as the appropriate choice of the experimental conditions.

This original tandem co-polymerization approach to LDPEs has been successfully applied to the preparation of polyolefin-CNTs nanocomposite. Despite the outstanding properties of CNTs, such as high mechanical strength, high electrical, and thermal conductivity, they are of difficult use to make nanocomposites due to their tendency to aggregate in long bundles.[3] The first tandem co-polymerization protocol for the surface modification of CNTs with LDPE, leading to different CNTs/LDPE morphologies, will also be discussed.

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Molecular Dynamics Simulations of Binding of Metal Catalyst Nanoparticles to Carbon Nanostructures by Using ReaxFF

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Carbon nanofibers have attractive properties as support materials for catalyst nanoparticles. Nonetheless, there is still a need for more insights into the actual atomic structure of a metal particle interacting with carbon nanostructures such as nanofibers or nanocones. Detailed information on bond length distribution and local coordination of adhered nanoclusters is still inaccessible to direct imaging by modern electron microscopes. In contrast, molecular dynamics (MD) simulations provide atomistic structural information of a metal cluster placed in different environments. However, MD results are known to depend straight on the force field chosen for the description of the interatomic interactions. Thus there is an increasing need for reliable force fields that take into account the effects stemming from the electronic structure at the same time as force fields must be computationally efficient. In this sense, the Reax force field (ReaxFF)[1] aims to provide a good compromise between accuracy and computational efficiency. We present novel results of MD simulations of platinum and nickel clusters adsorbed on several different carbon supports by using the ReaxFF. This work seeks to provide insights into recent experiments[2] that found a high correlation between carbon nanofiber-induced strain and catalytic activity of Ni clusters. We show how some metal atoms are detached from the surface of the nanoclusters over time scales unreachable by electronic-structure methods. The adatom migration is compensated by a rearrangement of the atomic structure of the cluster, leading to an enlargement of the mean Pt-Pt bond length in agreement with experimental results[2]. We also show differences in the bond length distribution of the cluster when adsorbed to carbon nanocones with different radii as well as differences found between Pt and Ni clusters.

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Heteropoly Acids as Catalysts for Hydrogenation of Carboxylic Acids: Relation with Homogeneous and Heterogeneous Partial Oxidation

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Heteropoly acids (HPAs) possess controllable acid and redox properties and are widely used as acid and oxidation catalyst.[1,2] The Keggin HPAs $H_{3+n}[PMo_{12-n}V_nO_{40}]$ (n = 0, 1, 2) are well known as catalysts of partial oxidation in homogeneous and heterogeneous systems[1,2]. Here we report that these HPAs and their Cs^+ salts are active catalysts for the vapour-phase hydrogenation of propanoic and hexanoic acids to the corresponding aldehydes. Hydrogenation of carboxylic acids to aldehydes over oxide catalysts has attracted significant interest.[3]

It is demonstrated that the hydrogenation activity and selectivity of HPA catalysts strongly depend on their acid and redox properties in a manner that is well established for homogeneous and heterogeneous partial oxidation catalyzed by HPA[1,2]. The acid and redox properties of HPAs can be controlled by varying their composition. Partial substitution of Mo(VI) by V(V) in the $PMo_{12}O_40^{3-}$ anion, enhancing the redox properties of the polyanion[1,2], was found to improve catalyst activity and selectivity to aldehydes (fixed-bed flow reactor, 300-400°C, 1 bar H_2 pressure, 2 vol.% acid concentration in the gas flow). Heteropoly acids $H_{3+n}[PMo_{12-n}V_nO_{40}]$ exhibited high catalytic activities but low selectivities to aldehydes, yielding C_3-C_8 hydrocarbons (predominantly C_6) as the main products. The hydrocarbons probably resulted from reduction of carboxylic acids followed by acid-catalyzed cracking and alkylation. Partially substituted Cs^+ heteropoly salts showed high selectivities (up to 80%) to aldehydes, which indicates that this reaction requires only a moderate acidity of the catalyst. Neutral Cs^+ heteropoly salts, $Cs_3PMo_{12}O_{40}$, $Cs_4PMo_{11}VO_{40}$ and $Cs_5PMo_{10}V_2O_{40}$, gave mainly ketones, 3-pentanone and 6-undecanone from propanoic and hexanoic acid respectively. The ketonisation of carboxylic acids over metal oxide catalysts has been observed previously[3].

The HPA catalysts were characterized before and after reaction by XRD, FTIR, TG/DSC and surface area/porosity analysis. Catalyst surface area was found significantly decreased after reaction. From FTIR, the Keggin (primary) structure of catalysts remained intact during the reaction. In contrast, the secondary structure of HPA catalysts changed, as XRD showed that initially crystalline catalysts became amorphous after reaction.

The hydrogenation of propanoic acid was found to be zero order in propanoic acid and had an activation energy of 85 kJ/mol (320-380°C). The reaction rate did not depend on the flow rate at constant GHSV. It is suggested that the reaction occurs in chemical regime via a Mars-van Krevelen mechanism.[3]

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Liquid-phase Dispersion Measurement of Supported Palladium Catalysts by Liquid Chromatography

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The activity of supported metal catalysts is preferably characterized in terms of the turn-over frequency (TOF) on a per-active-metal-atom basis. The calculation of TOF is critically dependent on the correct value of the dispersion D of the metal particles under reaction conditions. To date, there are no generally accepted solution-based standard methods for the determination of D for liquid phase reactions. Hereby we report on a novel liquid chromatographic (LC) method designed for the liquid-phase dispersion measurement of supported metal catalysts. 5% $Pd/\gamma\text{-}Al_2O_3$ was placed in a liquid chromatographic column and the CS_2 uptake of the catalyst was determined by applying CS_2 pulses in methanol solution until surface saturation was attained. The reliability of the LC method was confirmed by quantitative CS_2 poisoning of the catalyst in the liquid-phase hydrogenation of styrene to ethylbenzene in methanol solution until the reaction ceased. The liquid-phase dispersion of the metal, D_L=11% proved to be significantly smaller than D_G=35% determined by conventional methods applied under non-wet conditions, including CO and H_2 gas-phase adsorption microcalorimetry, and TEM particle size analysis. Whereas the LC method measured the true number of active sites in the liquid-phase reaction, traditional methods measured the total number of the surface sites of the Pd particles and thus substantially overestimated the dispersion of the metal, at least on a peractive-metal atom basis. The difference between D_G and D_L may thus be regarded as an indication that the number of exposed metal atoms at the solid/gas interface determined in chemisorption experiments is less than the number of active surface sites at the solid/solution interface. The relation $D_L < D_G$ can be explained by taking into consideration that, while single-component gas adsorption is not competitive, adsorption from solution is a displacement process where the solute and the solvent molecules compete for the surface sites. It may well occur, therefore, that only a fraction of the surface sites are accessible for the reactant molecules. The remainder of the Pd surface atoms remains covered by solvent molecules and hence these sites are not involved in the catalytic reaction.[1]

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From Alloys to Bio-mimetic Materials: Searching for New Hydrogen Evolution Electrocatalysts

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Clean, alternative energy carriers will be needed if we are to achieve a sustainable energy economy. One candidate fuel under consideration is H_2, which can be produced cleanly and renewably if solar or wind energy is coupled to water electrolysis. Unfortunately, the hydrogen evolution reaction (HER) is catalyzed most effectively by Pt group metals materials that are expensive and scarce. New materials are needed if this scheme is to ever become viable.

Having studied different metal surfaces and enzymes that catalyze hydrogen evolution, we have found a necessary criterion for high catalytic activity – the binding energy (Gibbs free energy) of atomic hydrogen adsorption must be close to zero.[1] Our search strategy to identify new electrocatalytically active materials combines DFT calculations with experimental synthesis and evaluation. This paper begins with results on metal alloy surfaces, where computational screening on 736 different surfaces identified a Pt-Bi surface alloy to be more active than Pt; experimental work on this particular surface structure validates computational predictions.[2]

Moving away from Pt-based systems, we have examined different forms of molybdenum sulfide which resemble, in many ways, the enzymatic active centers found in nitrogenase and hydrogenase.[3,4] In order to identify relationships between structure and catalytic activity within MoS_2 nanoparticles, we have combined ultra high vacuum techniques with electrochemical measurements under ambient conditions. MoS_2 nanoparticles were first synthesized on Au(111) in ultra-high vacuum, where scanning tunnelling microscopy (STM) was used to investigate their structure, morphology, and surface coverage. Surface spectroscopy was also employed for chemical characterization. The same samples were then transferred to an electrochemical cell where catalytic activity for hydrogen evolution was measured. By varying particle size and coverage within the sample set, our measurements have established – for the first time – a clear relationship between the structure and catalytic activity of MoS_2 nanoparticles. A similar approach has also been used in the investigation of supported $[Mo_3S_4]^{4+}$ molecular complexes.

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V_2O_5 Nanorod and Nanoparticles Preparation Using CTAB Micelle Solution

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Using the surfactant-mediated method (surfactant based on cetyltrimethyl ammonium bromide, CTAB) V_2O_5 nanorod and nanoparticles have been successfully prepared. By applying the different precursors and by varying reaction conditions in the same CTAB soft template morphologies of V_2O_5 nanostructures can be controlled. Analysis using VPSEM and TEM shows that ammonium metavanadate and sulfuric acid as precursors yield nano particles with sizes of 45-160 nm. Vanadyl sulfate hydrate and sodium hydroxide as precursors yield vanadium pentoxide nanorods with diameter of 30-90 nm and the length of 260-600 nm. X-ray powder diffraction (XRD) analysis shows that V_2O_5 is form as crystalline with orthorhombic structure. Although V_2O_5 are formed at different shapes and sizes but all of them form as V_2O_5 as shown by XPS techniques. For catalytic performance the temperature programmed reduction (TPR) has been used. The results of analysis showed the better performance for nanoparticles and nanorods of V_2O_5 compare to bulk V_2O_5 with showing lower onset temperature, workability at lower temperature and higher H_2 consumption (μmol/g).

Tantalum Clusters Supported on SiO_2: Synthesis, Structural Characterization, and Catalysis of Alkane Conversion

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The synthesis of clusters of catalytically important group-8 metals on oxide surfaces is now a well-established field, having been guided by the known chemistry of these syntheses in solution. In contrast, clusters of early transition metals have only recently been synthesized on surfaces; the examples involve the group-5 metal tantalum on porous SiO_2, and the chemistry of the synthesis and reactions of the clusters has been inferred to be similar to that occurring in solution.

Tantalum clusters were synthesized from $Ta(CH_2Ph)_5$ on the surface of porous fumed SiO_2. When these clusters are small, incorporating, on average, only several Ta atoms, their chemistry is similar to that of molecular tantalum clusters (and other early transition metal) clusters. For example, these small supported clusters have been characterized by TEM (Fig. 1) and EXAFS, IR, and UV-vis spectroscopies; the clusters incorporate TaTa bonds similar to those in molecular analogues. The redox reactions of the supported clusters, characterized by XANES, are analogous to those of early transition metal clusters in solution. In contrast to the largest of these clusters in solution and in the solid state, those supported on SiO_2 are raft-like, facilitating the substantial metalsupport-oxygen bonding that is evident in the EXAFS spectra. Samples consisting of tantalum clusters on SiO_2 catalyze alkane disproportionation and the conversion of methane with *n*-butane to give other alkanes.

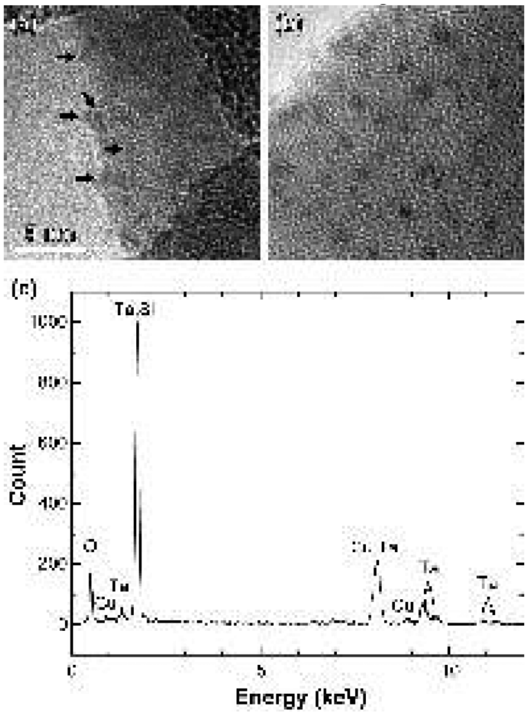

Figure 1. TEM bright-field images of Ta clusters formed by treating adsorbed $Ta(CH_2Ph)_5$ in flowing H_2 at (a) 523 K and (b) 723 K. Tritantalum clusters are indicated by arrows in (a); the scale bar in (a) applies to (b). (c) EDX spectrum characterizing clusters in (b), clearly identifying them as tantalum clusters.

In Situ Formation of Homogeneous Active Species for Hydroformylation Based on Heterogeneous Rh Catalyst

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The CO insertion reaction such as hydroformylation is an excellent model for studying the relation between heterogeneous and homogeneous catalysis. So far, intensive work has been focused on developing efficient catalytic system for heterogenization of homogeneous catalysts,[1] only minor attention has been given to heterogeneous catalysts, because they provide lower activity and selectivity when compared to homogeneous catalysts. In many cases, various metal promoters, such as Na, Zn, Ag, etc.,[2] are employed to improve the activity of heterogeneous catalysts.

Phosphine ligands are probably the most widely used ligands in homogeneous catalysis. Our previous study shows that PPh_3 modified heterogeneous Rh/SiO_2 is a new important class of catalyst (PPh_3-Rh/SiO_2), which combines the high activity and selectivity of homogeneous catalyst with the processing advantages of a heterogeneous catalyst.[3,4] To further investigate how the Rh-phosphine carbonyl complexes form on the surface of heterogeneous Rh catalyst, we employed SBA-15 as a support in the PPh_3-Rh/SBA-15 system. We have applied PPh_3-Rh/SBA-15 catalysts to the hydroformylation of propylene to investigate its performance, and we also find that the pore size of support has a great influence on the catalytic performance of PPh_3-Rh/SBA-15 catalysts.

The activity of the PPh_3-Rh/SBA-15 catalyst is far higher than that of the heterogeneous Rh/SBA-15 catalyst, but a little lower than $HRh(CO)(PPh_3)_3$/SBA-15 catalyst due to bareness of 80% of Rh particles, while the selectivity to aldehyde of PPh_3-Rh/SBA-15 catalyst is comparable to that of $HRh(CO)(PPh_3)_3$/SBA-15 catalyst. And PPh_3-Rh/SBA-15 catalyst even displays higher n/i ratio for butyraldehyde than $HRh(CO)(PPh_3)_3$/SBA-15 catalyst, that is because the active species for hydroformylation in situ form on the Rh nano-particles and lead to a larger steric hindrance on PPh_3-Rh/SBA-15 than on heterogenizing homogeneous catalysts ($HRh(CO)(PPh_3)_3$/SBA-15). The catalysts and reaction were characterized by TG, solid-state ^{31}P NMR, XPS, in situ FT-IR, ICP-AES, GC-MS to elucidate the structure, bonding, and interaction between Rh and triphenyl phosphine, and to verify the formation of homogeneous intermediates.

Catalyst	^{a}TOF	n/i ratio	Selec. (%)
Rh/SBA-15	2.74	2.6	19.2
PPh_3-Rh/SBA-15	245	12.7	100
$HRh(CO)(PPh_3)_3$/SBA-15	301	10.7	100

Reaction conditions: T=393 K; time on stream= 4 h; P=1.0 MPa; SV=2000 h^{-1}
^{a}TOF: mol butyraldehyde /mol Rh · hour.

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Effect of Pt Cluster Size on the Oxidation of NO to NO_2 in Excess Oxygen on Supported and Model Pt Catalysts

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The three-way catalyst (TWC) system used today operates effectively within a very narrow lean-burn zone leading to exhaust gas that contains properly balanced CO, H_2 and hydrocarbon levels to reduce nitrogen oxides (NO_x).[1] The operation of gasoline engines at leaner conditions leads to increased fuel efficiency and a reduction in CO_2 emissions. However, under oxygen rich conditions, TWCs are unable to reduce NO_x. Two separate solutions - selective catalytic reduction (SCR) and NO_x storage/removal (NSR) - have been proposed for NO_x abatement in lean-burn engines.[2] The activity and selectivity of SCR catalysts is increased in the presence of NO_2, and the NSR catalyst prefers to store NO_2. Therefore it is important to understand the kinetics and mechanism of NO oxidation to NO_2 on Pt.

The kinetics and reaction mechanism of NO oxidation on supported Pt catalysts have been measured in the presence of NO_2 and corrected for approach to thermodynamic equilibrium.[3] The oxidation reaction kinetics are nearly first order with respect to NO and O_2 and negative first order with respect to NO_2. The reaction mechanism consists of equilibrated adsorption of NO, equilibrated dissociation of NO_2, and the non-dissociative adsorption of O_2 as the rate-determining step. The Pt particle size affects the rate of NO oxidation significantly; larger particles (>5 nm) are more active on a surface atom basis than smaller particles (1-4 nm), regardless of the support material. Detailed analysis of the particle size distribution by TEM and rate measurements on a Pt(111) suggests that the large particles on the catalyst are responsible for most of the observed activity. X-ray absorption experiments demonstrate small particles (1-3 nm) are more oxidized upon exposure to $NO/O_2/NO_2$ or NO_2 only, than large particles (8-9 nm) under steady state conditions. The oxidation was time-dependent, with small particles continuously oxidizing during the reaction, while larger particles were immediately oxidized on the surface. Particles of ∼4 nm in diameter displayed intermediate behavior with regards to oxidation by NO_2. The extent of surface oxidation controls the catalyst activity; larger particles are active and small particles over-oxidize and deactivate.

The coverage of oxygen on Pt(111) in 0.7±0.1 ML after exposure to 0.2 Torr NO_2 was measured by in-situ high pressure photoelectron spectroscopy[4]. The Pt binding energy increases suggesting the formation of PtO, and the average oxygen uptake determined by CO titration is about 1.5 times the number of Pt surface atoms for a Pt catalyst operating at steady state[2]. In these high O coverage domains, adsorbed O_2 dissociation becomes thermodynamically inhibited, and NO oxidation involves direct reaction of surface activated O_2 with NO to form NO_2.[4]

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Homogeneous Catalytic Cycles: Carbon Dioxide/Hydrogen – Formic Acid Systems: High Pressure H_2 Production and CO_2 Utilization

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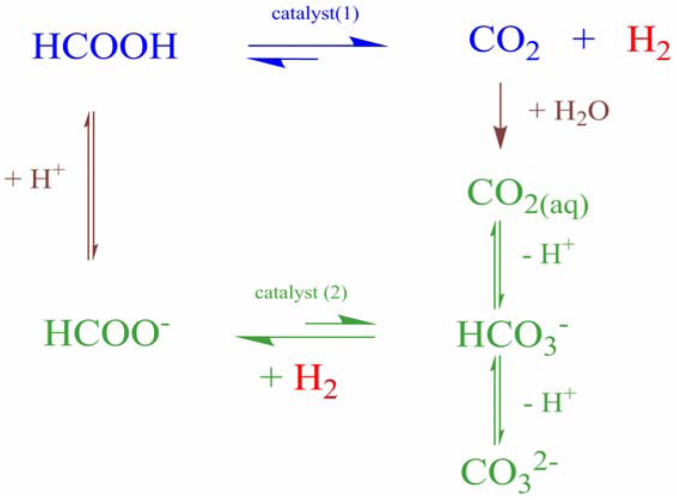
Hydrogen gas is a versatile source of energy and an important starting material for many chemical reactions. H_2 has a low molecular weight and it is extremely volatile. As a consequence, H_2 gas is stored at high pressure or low temperature in gas containers made of steel, the weight of which is exceeding by far the weight of the hydrogen gas stored in it.[1] Given the difficulty in storing the hydrogen gas, it is a particular objective to provide a process of preparing H_2 in situ, instantly upon demand of a hydrogen consuming device or process.

In the other hand, the utilization of the widely available greenhouse gas, CO_2 (or the carbonates), as C1 building blocks is a major challenge for chemistry. Several attempts have been made to reduce CO_2: in the presence of amines, platinum group metal complexes have been found active to produce formic acid (or derivatives) in different media.

In this contribution we present some results on the reduction of carbon dioxide/carbonate systems using Ru-phosphine catalysts, in relation with the new homogeneous catalytic method, which we have developed, to generate high pressure H_2 in a continuous way from formic acid.[2]



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The Performance of a Biomimetic Oxidation Catalyst Immobilized on Gold and Silica Substrates

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Thiol-functionalized cobalt porphyrins[1] were used as a model system for investigating catalytic activity in homogeneous and heterogeneous oxidation catalysis. Self-assembled monolayers of thiol-functionalized cobalt porphyrins were prepared on a gold surface and served as heterogeneous catalysts. The immobilization of the molecules prevented the strong inactivation observed for their homogeneous congener. As a result, the turnover number per molecule in heterogeneous catalysis was at least 100 times higher than that of the corresponding homogeneous catalyst.[2] It is atypical for a heterogenized catalyst to outperform its homogeneous congener. The properties of the molecular layers were characterized on the molecular level by means of X-ray photoelectron spectroscopy (XPS) and scanning probe microscopy (SPM). The results demonstrate that the performance of these biomimetic catalysts can be dramatically improved if the catalyst arrangement can be controlled on the molecular level. In order to further investigate the influence of the substrate on the catalytic performance, monolayers of the cobalt porphyrins were grafted onto silica surfaces. The observed catalytic activity together with the surface analytical results are interpreted in relation to the supporting substrate. Preliminary results from this investigation (silicon wafer) show that the catalytic activity is similar to that of gold substrates.

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Striking Acceleration of Rate of Organic Reaction on water: A Theory

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Water can be used as a catalyst for organic reactions. In this talk, we present a striking difference in catalytic effects of water, a factor of 1000 in rate constant, between a molecular surface (in water) and a bulk surface (on water). For a cycloaddition reaction of quadricyclane with DMAD, for example, a reaction time of 48 hours in a neat (solvent-free) reaction is reduced to 4 hours in an aqueous homogeneous reaction (in water), which is then substantially further reduced to 10 minutes in an aqueous emulsion reaction (on water). Both catalyses in water and on water make use of the formation of hydrogen (H) bonds between the OH groups of water and the H-bond accepting groups of reactants, where stronger H-bonds of water in the transition state as compared to those in the reactants lowers the activation barrier and enhances the rate. A key difference between the homogeneous and heterogeneous water catalysis, however, is interpreted to be due to the different structural arrangement of water, a catalyst, in each environment. In aqueous homogeneous solution, water molecules are tangentially oriented around a small hydrophobic solute, which implies that a breaking of the existing H-bond network of water is needed in order to permit a catalytic effect of water. In contrast, at a bulk oil-water interface, approximately 25% of surface water molecules have a free OH group that protrudes into the organic phase, ready to catalyze reactions without rupturing existing H-bonds, as in the ice surface. The on-water surface reaction is then calculated and found to be more than 5 orders of magnitude more efficient in terms of rate constant than the neat reaction, and three orders of magnitude more efficient than the aqueous homogeneous reaction. Experiments that can test the above interpretation are also suggested.

Active Structure and ReactionMechanism for Direct Phenol Synthesis from Benzene and O_2 on a Highly Selective N-Interstitial Re-Cluster/HZSM-5 Catalyst

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Phenol is produced by the three-steps cumene process all over the world but there are serious problems such as low phenol yield, low energy consumption, stoichiometric byproducts, use of sulphuric acid, and explosive intermediate, etc. Direct phenol synthesis from benzene and O_2 is the most desirable reaction, but there are no catalysts with high phenol yield discovered to date. Recently, we have succeeded in preparing a novel N-interstitial Re_{10}-cluster catalyst supported on HZSM-5 zeolite, which exhibited the highest phenol selectivity of 94% at 9.9% benzene conversion for the direct phenol synthesis from benzene and O_2. NH_3 promoted the formation of the N-interstitial Re cluster, which was the active species for the selective oxidation. Dynamic structural transformations of the Re clusters were investigated by time-resolved DXAFS and correlated with the catalytic performances.[1,2]

A Re/HZSM-5 catalyst (SiO_2/Al_2O_3=19) was the best catalyst for the direct phenol synthesis with 87.7% selectivity under the steady-state reaction conditions in the presence of NH_3. No other liquid products were detected and only a by-product was gaseous CO_2. The rate of phenol formation decreased in the order: ZSM-5 (19) > ZSM-5 (24) > ZSM-5 (39) > Mordenite > beta > USY, indicating that the amount of Al acid sites and their strengths influence the catalytic performances. Re L_3-edge EXAFS indicated that NH_3 produced Re cluster with Re-Re bonds at 0.276 nm, which released N_2 in TPD. DFT calculations revealed that two octahedral Re_6 frameworks with interstitial nitrogen atoms edge-shared to each other as illustrated in Fig. 1. It is to be noted that the interstitial N atoms supplied from NH_3 are the key element to stabilize the Re_{10} cluster.

The Re_{10} cluster reacted with benzene and O_2 in the absence of NH_3, where a tremendous phenol selectivity of 94% was achieved and the Re clusters converted to inactive Re^{7+} monomers with Re=O and Re-O bonds at 0.173 nm and 0.213 nm, respectively. During the catalytic cycle, the supported Re species dynamically transform their structures as shown in Fig. 1. Insitu time-resolved DXAFS revealed that the structural change from the Re cluster to the monomers was of the first-order to the amount of the Re cluster, suggesting that the Re cluster was directly transformed to the Re monomers without any stable intermediates with low phenol selectivity. The inactive Re monomers were transformed to the active Re_{10} clusters with NH_3. A concerted mechanism was demonstrated for the oxygen insertion of a benzene C-H bond in the phenol synthesis.

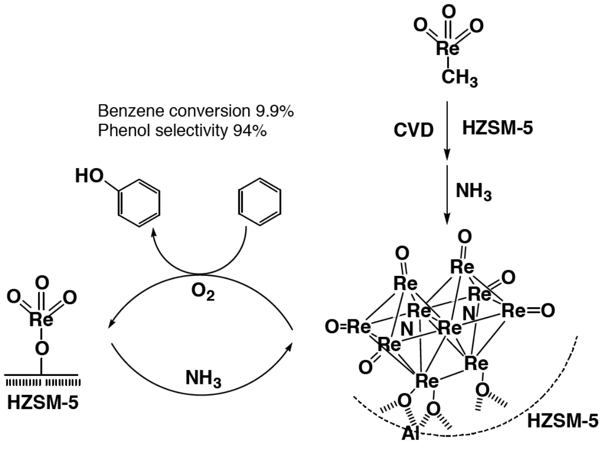

Figure 1. The structures of HZSM-5-supported Re catalysts for direct phenol synthesis from benzene and O_2.

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Synchrotron Torr-pressure XPS Studies on 2D Pt Nanoparticle Array Cleaning for Model Catalysts

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Two-dimensional (2D) Pt-nanoparticle of high spatial density were manufactured through Langmuir-Schaeffer deposition onto silicon/silicon oxide wafers. Cleaning of 2D model catalysts manufactured in this way was investigated with a novel Torr-pressure synchrotron XPS system. Exposure to 0.5 Torr of oxygen showed removal of carbon from the nanoparticle surface. Hydrogen exposure resulted in conversion of surface carbon to graphite, particularly at temperatures above 300°C. Alternating O_2 and H_2 exposure (cycling) at lower temperatures (25, 75, 125°C) proved the most effective cleaning method. Different intensities of chemical species in the C1s peak (graphitic carbon, CO adsorbed on Pt)were observed at the three temperatures. Consistent with SEM and ethylene hydrogenation reaction results, XPS data illustrated the nanoparticle cleaning process and enabled us to identify key parameters for future cleaning experiments.

Structure and Spectroscopy Under Ambient Conditions of Pressure and Temperature: Novel Techniques for Fundamental Studies in Catalysis

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The nature of the sites where catalytic reactions take place on surfaces is a matter of fundamental and continuous inquiry in the scientific and engineering community. Of particular relevance are studies that approach the conditions of pressure, temperature and catalyst structure operating in industrial reactions. Common characteristics of surfaces under these conditions are: a) the surfaces are crowded with adsorbates, which means that the chemistry is strongly influenced by the dynamics of vacancies; b) they are complex surfaces, often small particles, whose structure is not well known during the reaction. We have developed techniques that allow us to approach some of these conditions. These include Scanning Probe Microscopies and several X-ray Photoelectron Spectroscopies. With them we have unraveled the structure and composition of model catalyst surfaces that are in equilibrium with reactants at or near atmospheric pressures and ambient temperatures. These include Pd, Pt, Ru and Rh single crystals and Co nanoparticles. I will show results that provide new insights into the nature of H_2 dissociation sites on Pd, Ru and Pt. I will also show how Co nanoparticles can be characterized in situ and the influence of particle size in their electronic and chemical properties.

Combining Computational Screening and Reactivity Trends for Alloy Catalyst Design

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Electronic structure calculations based on density functional theory have reached a level of maturity where they can accurately describe complete catalytic reactions on transition metal surfaces. This gives unprecedented insights into heterogeneous catalytic reactions, and it allows pinpointing the origin of catalytic activity of metals in terms of their electronic structure. The use of electronic structure theory as a tool for designing or searching for new heterogeneous catalysts has, however, so-far been extremely limited. The complexity of the design problem arises to a smaller extent from the high computational cost of the electronic structure calculations and to a larger extent from the enormous number of surfaces and geometries that needs to be considered. In some fortunate cases, reactivity trends determined from density functional calculations can be applied to reduce the complexity of the catalyst design procedure.

Results will be presented on the computational design of a new alloy catalyst for the methanation reaction. The method utilizes the underlying reactivity trends for the reaction intermediates, and the applicability of the design procedure for other reactions is suggested through the identification and analysis of a range of new reactivity trends for intermediates. By correlating the reactivity of a range of simple atomic and molecular adsorbates over different transition metal surfaces, we find a simple set of empiric rules that can be used as guide lines in a rough computational screening of new catalysts for various reactions. A surprising observation from the trends is that a range of seemingly very different hydrogenation and dehydrogenation reactions can all be described on a simple common footing through simple scaling relations.

Finally, it will be discussed why the concepts presented here for heterogeneous reactions might be just as applicable in homogeneous catalysis.

Synthesis, Size Dependence and Mechanistic Studies of Supported Au Catalysts

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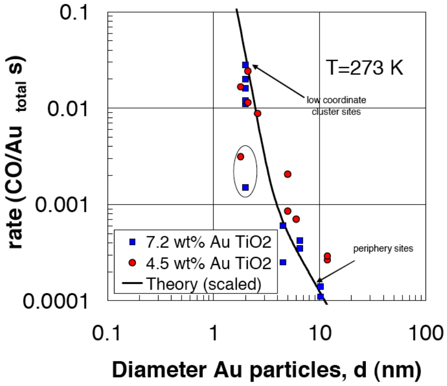
We have explored synthesis methodologies for the preparation and stabilization of Au catalysts on tailored non-porous and mesoporous supports. The control and stabilization of both size and shape of metal particles is exceedingly important for Au catalysts. Although the deposition-precipitation (DP) method using $HAuCl_4$ can be used to prepare gold nanoparticles on titanium oxide substrates, this methodology fails for silica supports because of the low isoelectric point (IEP) of SiO_2. We have explored strategies to overcome this problem by introduction of a high-IEP oxide monolayer component *via* surface sol-gel process (SSP) modification and by using a gold cationic complex precursor $[Au(en)_2]^{3+}$ *via* a wet chemical process. The pH of the gold precursor solution during synthesis plays a key role in the latter method. Applying this method to Au deposition on SBA-15 leads to highly active catalysts with uniform Au particles of 2.9 nm dispersed in the 7 nm pores of the SiO_2 which are resistant to sintering although deactivation by other mechanisms occur. This new DP methodology for gold catalysts opens up a new avenue to deposit gold precursors on low-IEP supports.



The size dependence of activity in gold catalysts was examined experimentally using EXAFS as an *operando* probe of mean particle size. Variable temperature calcination was used to systematically increase the mean Au particle on each catalyst. For Au particles with mean particles size, d, in the range of 2 to 10 nm, the measured TOF at 298 K varies as $d^{-1.9\pm0.2}$ and $d^{-1.1\pm0.2}$ for a 7.2 wt% and 4.5 wt% Au / TiO_2 (P25) catalysts, respectively. DFT computations of relaxed Au clusters on a TiO_2 slab were used to probe the transition states of CO oxidation. Low coordinate sites are the most active sites due to higher O_2 adsorption energy and freer molecular motion that lowers reaction barrier. Statistical analysis of many cluster configurations leads to a size dependence which matches the experimental result (see Figure). It is concluded that the observed decrease in activity as particle sizes grow larger than 2 nm is controlled by the population of low coordinate sites, rather than size dependent changes in electronic structure of the nanoparticle.

Transient studies of CO oxidation over Au/TiO_2 and Au/SiO_2 have been performed to explore reaction pathways and causes of deactivation. Two different FTIR compatible reactor cells are used, a zero dead volume reactor for transmission mode and a higher temperature DRIFTS cell. Gas switching/pulsing permit transient changes in gas composition to correlate surface species and catalytic activity as a function of temperature. Using this operando approach we have probed the elementary steps in the CO oxidation and have explored the causes of reversible deactivation which occur in the absence of changes in the Au particle size distribution. Gas switching experiments show that pre-adsorption of O_2 does not interfere with subsequent CO uptake nor does CO pre-adsorption interfere with O_2 uptake. The effect of water and the build-up of carbonate-like species upon activity and deactivation have been explored. Two types of carbonates (bidentate, monodentate) and carboxylates were observed on TiO_2 (but not on SiO_2) which are formed from product gas phase CO_2. Build-up of carbonates and the presence of water do not correlate directly with slow deactivation of the catalysts.[1]

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Supported Organoiridium Catalysts for Alkane Dehydrogenation

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Reaction of tris(allyl)iridium with alumina or sulfated zirconia (MOx) affords propene and supported organoiridium(III) catalysts, (allyl)$_2$Ir-O-MOx. These catalysts were characterized by vibrational spectroscopy, solid state ^{13}C MASNMR, XPS, and X-ray scattering, including *in situ* studies. They have been employed for the efficient dehydrogenation of cycloalkanes and acyclic alkanes to aromatics above 200°C. Related supported iridium catalysts ligated with various Lewis bases have also been prepared and characterized; details of their enhanced catalytic activity and thermal stability will be presented.

Poster Abstracts

Novel Pyrazolyl-Pyridine Vanadium(III) Complexes as Ethene Polymerization Catalysts

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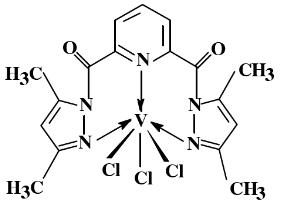
Ziegler-Natta olefin polymerization certainly is amongst the most common catalytic processes for the large-scale production of olefin polymers, which is efficient and selective.[1]

Classical Ziegler-Natta vanadium catalyst systems display a number of interesting characteristics such as: (a) synthesis of high molecular weight polymers with narrow polydispersity. (b) synthesis of ethylene/α-olefin copolymers with high α-olefin incorporation. (c) synthesis of syndiotactic polypropylene.

These systems however have relatively short catalyst lifetime.[2] These aspects of vanadium catalysis prompted us to prepare novel vanadium complexes with N,N,N-tridentate (pyrazolylpyridine) ligands which remain strongly bonded to the metal centre during the cycle which increase the catalytic activity during the reaction time (2h).

Herein we report the synthesis, characterization and catalytic activity in ethylene polymerization of vanadium(III) mononuclear complexes **1** and **2** with the ligands 2,6-bis(3,5-dimethylpyrazol-1-ylcarbonyl)pyridine and 2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine, respectively. With AlEtCl$_2$ cocatalyst the precatalysts **1** and **2** showed good catalytic activity for ethylene polymerization in toluene.

The influence of polymerization conditions such as (Al/V) molar ratio, polymerization time, pressure and temperature were investigated in detail. Both catalysts produce linear polyethylene with narrow polydispersities (2.4-3.2), which is characteristic for single site catalysts. High molecular weight Mw of (0.6-1.8 x 10^6) polymers were isolated under the reaction conditions used. Catalyst **1** generates polyethylenes with molecular weight higher than those from catalyst **2**.



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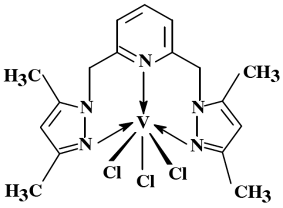

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Influence of Precipitating and Solvent on the Formation of Antimony Tetraoxide Catalyst

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Antimony oxide has found application in various area including clarification, pigment, material synthesis and catalyst. This study investigated the influence of synthesis parameters (precipitating agent and solvent) on the formation of antimony oxide powder. Characterizations of the samples were carried out by Thermogravimetry Analysis (TGA), X-Ray Diffraction (XRD), Fourier Transform Infrared (FTIR) spectroscopy, BET surface area measurement and Scanning Electron Microscopy (SEM). Investigations on the influence of the type of precipitating agents (NaOH and NH_4OH), on the formation of antimony oxide revealed that α-Sb_2O_4 was produced after the precursors were calcined. The precursors were a mixture of $Sb_4O_5Cl_2$ and Sb_2O_3 phase when precipitated with NaOH but only Sb_2O_3 phase when precipitated with NH_4OH. By varying the concentration two precipitation agent, NH_4OH solution gave higher surface area and fine morphologies for the samples compared to NaOH solution. On the influence of solvent, ethanol gave full reflection of Sb_2O_3 and different structure phase before calcination process. No phase of the antimony oxy chloride was obtained for these samples. After calcined process, all samples gave full reflection of the α-Sb_2O_4. Usage of the NaOH as a precipitating agent gave higher surface area compared to NH_4OH samples.

Comparison of Cerium Oxide- and Lanthanum Oxide-Supported Gold Catalysts for CO Oxidation: Effect of the Support on Catalytic Activity

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Introduction. Gold that is highly dispersed on metal oxide supports is catalytically active for CO oxidation under mild conditions.[1] The activity of supported gold is strongly affected by the choice of the support[1]. Supports that facilitate the formation of reactive oxygen species, including superoxide and peroxide species, have been suggested to improve the catalytic activity.[2,3] Most of these supports have a reducible character, including TiO_2, CeO_2, and Fe_2O_3.[4] However, in some irreducible metal oxides, such as La_2O_3, the formation of these active oxygen species has been shown, as evidenced by EPR and Raman investigations.[5]

In this work, we compared reducible CeO_{2-} with irreducible La_2O_3-supported gold catalysts. By using an organometallic precursor, $Au(CH_3)_2$(acac) [acac is the bidentate ligand $CH_3COCHCOCH_3$], we were able to prepare well-defined, site-isolated supported gold complexes on both supports. Treatment of these supported gold complexes led to the formation of gold clusters with similar sizes on the two supports but different activities for CO oxidation.

Materials and Methods. Samples were synthesized and handled in the absence of moisture and air. The catalyst, containing 1 wt% Au, was synthesized from $Au(CH_3)_2$(acac) (Strem 99.9%) and high- surface-area CeO_2 (173 m^2/g) and La_2O_3 (75 m^2/g). The sample was prepared by forming a slurry of $Au(CH_3)_2$(acac) in *n*-pentane with the support that had been partially dehydroxylated under vacuum at 673 K. The slurry was stirred for 24 h, and the solvent was removed by evacuation for 24 h. After various treatments, the catalysts were tested in a once-through flow reactor for CO oxidation, with on-line product analysis by gas chromatography. Reactions were carried out at atmospheric pressure and at 298 K. Catalyst samples, both before and after use for CO oxidation catalysis, were characterized by EXAFS and XANES spectroscopies.

Results and Discussion. EXAFS characterization of the as-prepared samples, on both CeO_2 and La_2O_3, showed that within the resolution of the EXAFS data the gold species were site-isolated and mononuclear, as indicated by the absence of any detectable Au–Au contributions. The XANES signature indicates cationic gold.

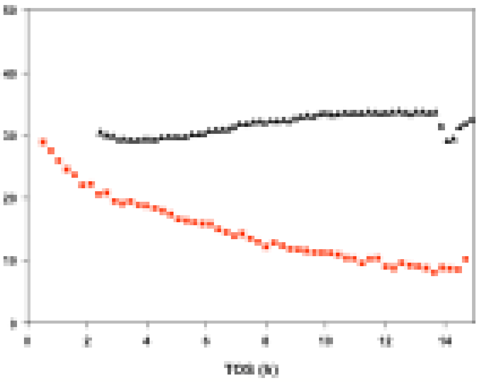

Figure 1. Catalytic activity of gold clusters supported on CeO_2 (black triangles) and La_2O_3 (red squares) for CO oxidation at 298 K

CeO_2-supported gold was treated during CO oxidation catalysis at 353 K for 50 h. When this–now activated–catalyst was cooled to room temperature with reactants flowing, it was found to have become active, characterized by a conversion of about 30%; the conversion kept increasing during time on stream. These conversions are too high to be considered differential and determine only a lower limit of the turnover frequency, namely, 3.2×10^{-2} molecules of CO (Au atom)$^{-1}$ s^{-1}.

La_2O_3-supported gold was treated by heating up the sample in helium to 773 K. When this–now activated–catalyst was cooled to room temperature in helium, it was found to be active with an initial conversion of about 30%. The conversion decreased during time on stream to about 10% after 15 h. The lower limit of the turnover frequency, which was calculated at 10% conversion, was approximately 1.0×10^{-2} molecules of CO (Au atom)$^{-1}$ s^{-1}.

Both catalyst samples were characterized by EXAFS spectroscopy before catalysis. The data representing both samples demonstrate that gold clusters had formed in the catalyst; the Au–Au coordination number of 5.9 for Au on CeO_2 and 6.4 for Au on La_2O_3. These coordination numbers indicate the presence of clusters of approximately 14 and 23 Au atoms respectively, on average.

In summary, the gold clusters supported on CeO_2 and La_2O_3 investigated in this work are among the smallest gold clusters prepared on metal oxide supports. The results point the supported clusters as the catalytically active species in both samples and demonstrate that, although the gold cluster sizes are similar on the two supports, their catalytic properties are different.

This research was supported by DOE (FG002-87ER13790, YH) and by CONACyT (registration nr. 175763 VAG). We thank the NSLS, beamlines X-18B, and X-10C and SSRL, beamline 2-3, for beam time.

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Catalytic Oxidation of Tetralin Over Transition Metal Containing Mesoporous Materials

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Tetralin oxidation produces -tetralone, which can be used as an additive in diesel fuel to enhance the cetane number. The reaction is also used for the commercial production of -naphthol, a pharmaceutical intermediate, and Carbaryl, an insecticide. In general, chromium metal or complexes have been used as catalysts in homogeneous phase, which is undesirable for commercial practice. In our earlier work, the reaction was carried out over a homogeneous catalyst in biphasic mode[1]. We report here heterogeneous tetralin oxidation over transition metal-containing mesoporous materials.

Fe, Co, or Cr-containing hexagonal mesoporous aluminophosphate (HMA) and MCM-41 materials were synthesized either at room temperature or under hydrothermal condition. Well-ordered XRD patterns of the calcined catalysts were obtained. Minute amount of polychromates species were detected, but chromium species were found well dispersed in the CrHMA matrix. The catalytic performance of these materials was tested in the liquid phase reaction using tert-butyl hydrogen peroxide as the oxidant and chlorobenzene as the solvent.

Among the catalysts tested, HMA metal series shows higher performance towards tetralin oxidation as shown in Table 1. The activity of these catalysts follows the order: CrHMA > CoHMA ≈ FeHMA. Cr-HMA developed, however, a serious leaching problem, and efforts were made to remedy the problem by ammonium acetate pre-washing and by conducting the reaction at milder conditions. Microporous Cr-ALPO$_4$-5, despite lower initial catalytic activity, proved more stable than the mesoporous counterpart.

Table 1. Oxidation of tetralin over transition metal incorporated mesoporous materials

Catalysts	Tetralin Conversion (wt%)	Product Selectivity (wt%)			
		1,2 Dihydro naphathlene	α-Tetralone	Tetralol	α-naphthol
FeHMA	30.0	6.2	67.6	24.8	1.4
CoHMA	30.7	2.4	67.5	30.1	-
CrHMA	61.0	0.8	93.5	2.4	3.3
FeMCM-41	10.7	63.8	26.2	5.5	4.4
CoMCM-41	13.7	16.3	71.7	8.5	3.5
CrMCM-41	40.7	3.8	82.1	11.7	2.3

Temperature 120 C; time 12 h; tetralin : TBHP = 1 : 2 (molar ratio); solvent = chlorobenzene; catalyst weight = 50 mg, metal content in the catalyst = 2 mole%.

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The Effect of Pore Size on the Rate of Adsoprtion of Protein on Mesoporous Silicate-SBA-15

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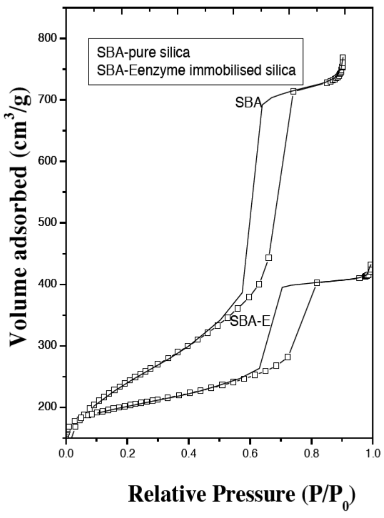
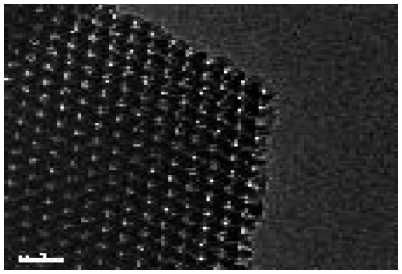
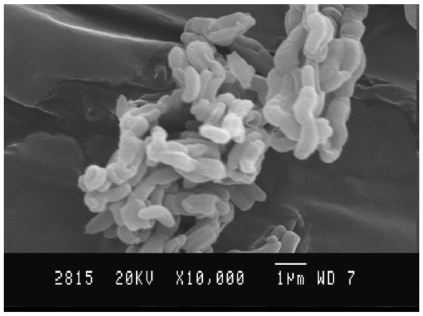
The inventions of mesoporous and nano materials and the interface of biology and chemistry will reduce the boundaries between the three branches of catalysis, namely, homogeneous, heterogeneous and biocatalysis. Stabilized enzymes are of primary importance in a wide variety of scientific and indus-trial sectors, ranging from pharmaceutical formulations, to bioreactors, bionanoelectronics and biosensors. This paper describes the synthesis of rod like SBA-15 of various pore sizes by post synthesis hydrothermal treatment. Increasing the pore size, maintaining the ordered structure of mesoporous silicates for the comfortable entrapment of enzymes is a challenge to chemists. Fixing biomolecules within well-defined and confined matrices has become more and more important. In the present work the pore size of SBA-15 was tailored to suit the kinetic diameter of α amylase ((35Å×40Å×70Å) from Bacillus Subtilis., SAXD, SEM, TEM, N_2 adsorption desorption isotherms, FTIR, ^{29}Si CP MAS NMR, were used to characterize the developed materials. We have also followed the kinetics of adsorption of three enzymes of different dimensions on the same support of pore dimension suitable for the enzyme chosen for the detailed study (pore size 74Å). Here we could find a striking correlation of pore size and size of enzyme. The rate of adsorption of size matching enzyme was much greater than the other enzymes. The linear nature of Line weaver-Burk plot suggests that heterogenised α-amylase obeys MichaelisMenten kinetics.







Time-Resolved Ultraviolet Raman Spectroscopy of Coke Formation on H-MFI

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H-MFI suffers from deactivation due to carbonaceous buildup (coke) during the methanol-to-gasoline reaction. UV-Raman spectroscopy allows in-situ analysis of reaction products during coke formation.[1] Previously heating and cooling was slow (minutes), and coke formation was too fast for real-time UV-Raman measurements. With an infrared laser, heating and cooling are much faster, 10^{-6} to 10^{-3} s. After heating, products and intermediates are trapped inside the zeolite pores and unable to react or desorb. Using this pulse-quench sequence intermediates can be detected by UV-Raman spectroscopy.

The fluidized bed reactor for UV-Raman was modified for IR heating through a BaF_2 side window.[2] A 9.3 micron CO_2 laser was directed onto the sample via computer-controlled beam steering mirrors. The IR laser power was in the range 0.25-2.5 w. Zeolite powder was calcined and cooled to 25°C in helium. Then zeolite was dosed with 100μL of methanol through a bubbler. After 10 minutes the zeolite was heated by systematically increasing laser power (increasing reaction temperatures). Raman spectra were measured with 244 nm excitation after calcination, after dosing, and during heating. The UV laser was aimed at a different position than the IR laser. Helium gas flow and mechanical vibration were used to stir the bed, avoid laser damage, and carry the sample from the IR laser beam to the UV laser beam for detection.

Infrared laser heating is a successful approach to forming coke within zeolite pores. With increasing laser power, reactants disappear and products appear. Approximately 90% of the methanol dosed into the pores undergoes some reaction via laser heating. No product desorption is detectable by mass spectrometry. The reaction temperature can be estimated from the beam power and zeolite thermal properties. From this estimation, a 1% increase in laser power is equivalent to a 100°C increase in temperature. These temperatures are consistent with reaction products seen in conventional heating experiments. Methanol and zeolite peaks decrease due to reaction and optical self-absorption, respectively. A peak at 1551 cm^{-1} signals the presence of polyolefins with 6-8 repeat units. Peaks at 1380 and 1624 cm^{-1} show that naphthalene forms initially, but changes in their relative intensity indicate formation of higher aromatics. Spectral changes can be seen by varying the silicon/aluminum ratio. When the aluminum content is decreased relative to the previous discussion, no detectable 1380 cm^{-1} peak is present. This shows that the reaction path is different, and that naphthalene is not formed. Further, under the same reaction conditions much less coke is formed in the low aluminum content zeolite. The absence of product desorption implies polyaromatic formation takes place inside the pores and not on the external surface of the zeolite.

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Comparison Between Homogeneous and Heterogeneous Catalytic Esterification Reaction for Biodiesel Production from Palm Fatty Acids

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Biodiesel is a fuel alternative to petroleum diesel for reducing emissions of gaseous pollutants such as CO_2, NO_x and SO_x and has an important social impact in countries with agricultural vocation like Brazil. It can be obtained by ethylic or methylic esterification of vegetable oil or animal fat. Homogeneous basic catalysis is the most used process to produce biodiesel nowadays, but acid catalysis has the advantage to be independent of oil free acid content and avoid saponification reaction. This work deals with esterification of palm fatty acids, by-products of edible palm oil production, to produce biodiesel, using homogeneous and heterogeneous acid catalysts. Reactions were carried on anhydrous or hydrated media. Effects of the alcohol used (ethanol or methanol), reactants molar ratio (alcohol/fatty acids), type and concentration of catalysts were also evaluated. Reactions were performed in a Parr stainless steel reactor, equipped with a tube for sample withdrawal, stirring and heating system. Conversion was estimated from the free acid content of the medium by NaOH titration. Kinetic models were proposed for homogeneous and heterogeneous reactions and kinetic parameters were estimated, including activation energy. An experimental design with three variables (temperature, catalyst concentration and alcohol/fatty acid ratio) and two levels was used in heterogeneous reaction. A quantum chemistry study with a conformational analysis was also performed to check the reactivity of two different fatty acids (palmitic and oleic acids). The presence of catalyst has increased conversion significantly, especially in homogeneous medium, where the effect of catalyst concentration was more pronounced. Methanesulfonic acid and sulfuric acid were the best homogeneous catalysts, while Hβ and niobic oxide were the best heterogeneous one. In both homogeneous and heterogeneous media, reactions with methanol showed greater yields than those with ethanol, even in anhydrous or hydrated media, which was assigned to the higher polarity of methanol. Water presence in the reactional medium showed a negative effect in the reaction yield, which was assigned to an equilibrium shift of acidic species presented. The effect is more pronounced in heterogeneous reaction. A good correlation was observed between experimental data and the proposed kinetic models, both in homogeneous and heterogeneous reactions. The homogeneous reaction shows to be pseudo-first order in relation to fat acid, which can be explained by the excess of alcohol used. Activation energy obtained was about 12 kcal/mol. A model based on the Yang-Hougen proposal was proposed for heterogeneous reaction. Chemical reaction was found to be the most determinant step. Experimental design has resulted in an empiric model showing the yield reaction dependence of the three variables analyzed. Catalyst concentration was the most influential one. Second and third order interactions had increasing statistic significance with time. Quantum chemistry study does not reveal significant differences between atomic charges and protonation energies of palmitic and oleic acids in homogeneous and heterogeneous media, indicating no intrinsic reactivity difference and no diffusional limitations.

Cyclohexane Oxidation Catalyzed by 2,2'-bipyridil Cu(II) Complexes

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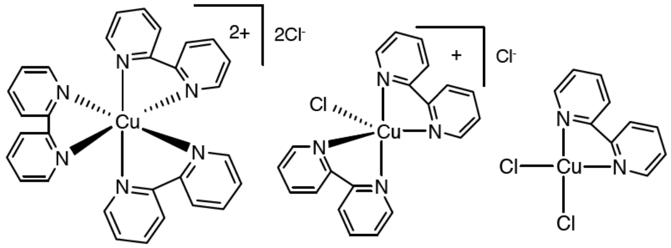
Metalloenzymes are responsible for the catalysis of several organic substrates. Copper is present in the active site of enzymes as pMMO, dopamine-β-monooxygenase, hemocyanins, laccase, and plays fundamental roles in living systems. Mononuclear copper complexes have been synthesized as models for the active site of such enzymes. Many of them are able to functionalize organic substrates, among others, phenolic compounds, cathecol and cyclohexane. In special, the cyclohexane oxidation is of great interest for the industry. Its oxidation products cyclohexanol and cyclohexanone are used to produce adipic acid and ε-caprolactone, precursors for Nylon manufacture. In the present work, we report the cyclohexane oxidation catalyzed by mononuclear Cu(II) complexes. The complexes $[Cu(bipy)_3]Cl_2$ **1**, $[Cu(bipy)_2Cl]Cl$ **2** and$[Cu(bipy)Cl_2]$ **3** were synthesized through $CuCl_2{\cdot}2H_2O$ and 3, 2 or 1 equivalents of bipy (2,2-bipyridine), respectively. The oxidation reactions were carried out using H_2O_2 and t-BuOOH as oxidant and acetonitrile-H_2O as solvent, in mild conditions (temperature of 25°C or 50°C and atmospheric pressure). The products cyclohexanol, cyclohexanone and cyclohexyl hydroperoxide were formed. The reactions exhibited much better results with H_2O_2. The yields with t-BuOOH ranged from 2.5 to 1.4% and the results with H_2O_2 stay around 21.2-43.4%. It is possible to relate the catalytic activity of the complexes with the number of bipy ligands coordinated to the copper ion. Analyzing the table, we can observe that the complex $[Cu(bipy)Cl_2]$ is the most active, reaching a yield around 43% with H_2O_2. The complex $[Cu(bipy)_2Cl]Cl$ showed 36% of yield and the complex $[Cu(bipy)_3]Cl_2$ reached around 24% with H_2O_2. So we can conclude that the complex with only one bipy is more active than the complex with two bipy, and this for its time is better than the complex with three bipy. It other words, fewer is the bipy ligand coordinated to the copper greater is the catalytic activity showed by the complex. This relation is proportionally linear. The temperature appears not to affect the oxidation in the range studied, the yields at 50°C are very close to that obtained at 25°C. In general, the Cy-OH selectivity stayed around 35%, the Cy=O around 20% and the Cy-OOH around 45% with H_2O_2. The results presented here are an interesting example of the activity of biomimetic systems toward cyclohexane under mild conditions.



$[Cu(bipy)_3]Cl_2$ **1** $[Cu(bipy)_2Cl]Cl$ **2** $[Cu(bipy)Cl_2]$ **3**

Cat	Oxidant	Yield(%)	Selectivity(%)		
			Cy-OH	Cy=0	Cy-OOH
1	t-BuOOH	2.5	0	33.2	66.8
1	H_2O_2	21.2	3.6	12.9	83.5
2	t-BuOOH	4.5	0	100.0	0
2	H_2O_2	36.6	35.1	22.7	42.2
3	t-BuOOH	1.4	58.0	32.9	9.1
3	H_2O_2	43.4	32.2	24.0	43.8

Coordination Chemistry onto the Surface of Ruthenium Nanoparticles. Detection of Active Species Through NMR and GC Investigations

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Metal nanoparticles are of considerable interest for their application in the areas of nanoelectronics, magnetic devices, semi-conduction and optics, gas sensing, biodiagnostics or catalysis.[1] Concerning catalysis, metal nanoparticles have been used in heterogeneous catalysis for a long time but more recently, well-defined metal nanoparticles have proven to be efficient and selective catalysts for reactions also catalyzed by molecular complexes, such as olefins hydrogenation or C-C coupling reactions,[2] and moreover for reactions which are not or poorly catalyzed by molecular species such as aromatic hydrocarbons hydrogenation.[3] Although unambiguous distinction between colloidal and true homogeneous catalysis is often very difficult to make,[4] development of new nanocatalysts appears as a very motivating objective to obtain new catalytic properties. This raises the problem of the surface chemistry of these species.

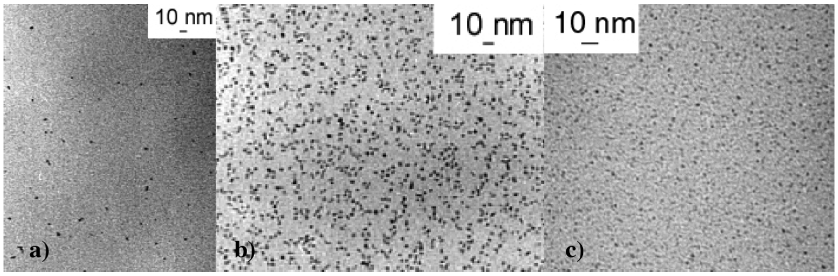

Figure 1. Transmission electron micrographs of rutheium nanoparticles in a) PP10, b) HDA and c) PVP.

This work focuses on the surface chemistry study of ruthenium nanoparticles. Well-defined ruthenium nanoparticles were prepared through the organometallic approach,[5] by hydrogenation of [Ru(COD)(COT)] using different stabilizers: diphosphines dppb (bis(diphenylphosphino)butane) and PP10 (bis(diphenyl-phosphino)decane), PVP (polyvinylpyrrolidone)6 and HDA (hexadecylamine).[6] The amount of hydrides present at the surface of these particles was quantified by setting out a titration with olefins and following alkanes formation by GC analysis. The reactivity of ethylidene has also been investigated in the solid state evidencing an interseting reactivity leading to cleavage of C-C bond in mild conditions.

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A Dioxo(μ-oxo)molybdenum(VI) Dimer with an Unusual All-*cis* Configuration and High Efficiency in Catalytic Olefin Epoxidation

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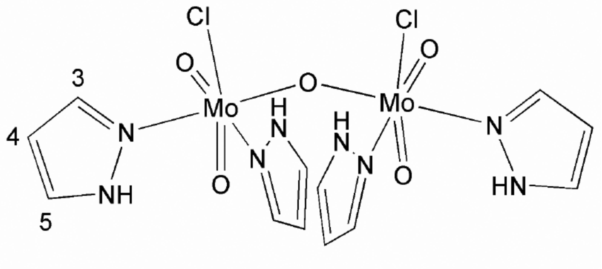
Molybdenum complexes played an important role in homogeneous industrial catalysis through the ARCO and Halcon processes in the late 1960s, which involve the production of propylene oxide using alkyl hydroperoxides as oxidants.[1] In recent years, complexes of the type (η^5-C_5R_5)MoO_2X, $MoO_2X_2L_n$ and $MoO(O_2)_2L_n$ (X = F, Cl, Br, alkyl or *ansa*-alkyl; L = neutral mono- or bidentate N,O,S-ligand) have been extensively investigated as catalysts for liquid-phase olefin epoxidation, usually employing tert-butylhydroperoxide (TBHP) as the mono-oxygen source.[2] The motivation for these studies stems from the fact that epoxides are important building blocks for the fine chemical and pharmaceutical industries. Research has focused on the variation of the co-ligands L which seem to have an important influence on the steric and redox properties of the precursor catalyst. Pyrazole, as a secondary amine, was used for the first time in styrene epoxidation as an additive of MTO.[3] Simple addition of pyrazole and pyridine to the MoO_3/TBHP system afforded very good conversions and selectivities for a range of olefin substrates such as cyclohexene and β-methylstyrene.[4] While oxo-bridged molybdenum complexes have not been frequently used in oxidation processes or oxo-transfer reactions, some Ru oxo-bridged complexes have exhibited activity in catalytic oxidation of water, and Cu and Fe bimetallic oxo complexes have been used as C-H bond activation agents.[5] In the present work we prepared the first dimeric $[Mo_2O_5]^{2+}$ complex with four pyrazole units (**1**). This compound was characterized by IR, ^1H NMR spectroscopy, thermogravimetric analysis and single-crystal Xray diffraction. The dioxo(μ-oxo)molybdenum(VI) dimer is one of the most active catalysts reported to date for the liquid phase epoxidation of cyclic olefins, showing surprisingly high activity and high stability for the epoxidation of *cis*-cyclooctene, (R)-(+)-limonene, α-pinene and styrene.[6]



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Metal Adsorption on Well-defined Oxide Support: Studies by Single-Crystal Microcalorimetry and Electron Spectroscopy

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The energetics of two illustrative cases were investigated: Li on MgO(100) and Ag on CeO_2(111). The former involved the adsorption of a reactive alkali metal on a stable, well-characterized metal-oxide support while the latter represented the deposition of a noble metal onto a reducible metal-oxide support. Thin-film metal oxides were grown by thermal evaporation under a reactive atmosphere of oxygen; the metals were evaporated from an effusive vapor source. The resultant surfaces at various admetal coverages were probed using a combination of low-energy electron diffraction (LEED), Auger electron spectroscopy (AES) and electron-energy loss spectroscopy (EELS). The coverage dependence of the measured heats of adsorption at submonolayer coverages revealed the influence of surface defects on the growth mode of the subject metals. The observed growth behavior of Li and Ag on the chosen oxide support was discussed in terms of relative ease of charge transfer upon adsorption, as indicated by work function measurements.

Entropic and Molecular Assembly Effects on Reaction in Confined Spaces

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Microporous solids such as zeolites are widely used in catalytic and separation processes. Such materials are very strong and selective adsorbents, so that molecules of different nature are adsorbed to a different extent. Chain length, functional groups, molecular shape and so on are all factors which contribute to a different adsorption behavior. According to the classical view on adsorption and zeolite catalysis, mainly energetic interactions govern the adsorption selectivity. For example, it is well accepted that in gas phase conditions at low degree of pore occupancy, longer hydrocarbon chains are adsorbed more selectively than their shorter homologues on most zeolites because of the larger interaction energy. This results in the selective catalytic conversion of the longer chains from mixtures of short and long chains, which already demonstrates the link between adsorption and catalysis on microporous solids.

More recently, it has been found that entropic effects are often at least as important as energetic effects in the adsorption of molecules in confined environments. This is certainly true for adsorption in liquid phase or at high pressure such as encountered in industrial practice, where the organization and packing of molecules in the fully saturated zeolite pores becomes dominant.

In this presentation, several examples of unexpected (entropy driven) adsorption effects are discussed. Rotational entropy driven separation of n-/iso-alkane mixtures in cage forming zeolites, chain length induced selectivity reversal in intersecting pore systems and stacking effects in the liquid phase separation of alkane/alkene/aromatic mixtures on Faujasites will be presented. Attention is devoted to the relation between entropy induced selectivity reversal in the adsorption of alkane mixtures and the selectivity and isomer yield in hydro-isomerisation processes in vapor and liquid phase conditions.

The data presented in these examples were largely obtained with specially developed high throughput techniques and will be briefly presented and discussed.

DFT Study of Propene Adsorption on Gold Nanoclusters

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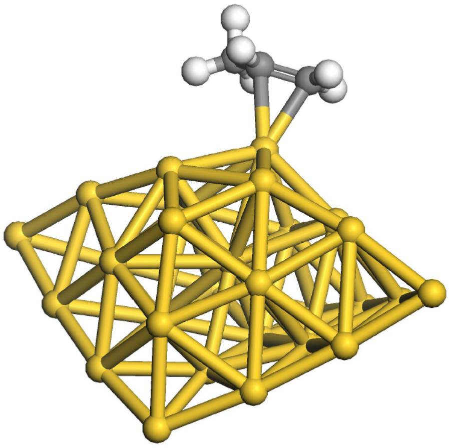
Nano-sized particles of gold have been reported as very active catalyst in selective oxidation of propylene. Several hypotheses have been postulated to explain the reaction mechanism, which probably occurs via a hydroperoxy intermediate. However, the interaction of Au with propene had not been so widely analyzed and few theoretical studies have been carried out to deal with such problem.[1,2] As a preliminary step to solve the reaction pathway, this work will focus on the adsorption alkene of gold surfaces and nanoclusters from a theoretical point of view.

All the calculations have been performed with the DMol^3 program employing the PW91 functional and a numerical DND basis. ECPs were employed to represent gold atoms. The cluster considered in this work includes 29 gold atoms disposed in a three-layer pyramidal structure, which emulates the TEM observed shape for TiO_2 supported gold particles. This configuration is also in agreement with a Wulff-Kaichew construction.[3]

On gold surfaces Au (111) and Au (100) no interaction between the alkene and metal surfaces has been obtained. On the Au_{29} cluster, propylene is adsorbed on a corner position of the cluster in an exothermic process releasing 15.93 kcal/mol. The interaction with one single Au atom is enough to stabilize the adsorption, however a low coordination number of gold is needed to accomplish adsorption. The C=C double bond of propene is elongated upon adsorption, which means that the double bond is activated when adsorbed on the surface of gold clusters.



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Morphology Control of Pd Nanoparticles by a Seed-Mediated Synthesis

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Introduction. In surface-structure sensitive catalytic reactions, selectivity and activity can be closely related to the nature of crystallographic planes exposed to the particle surface. Finding experimental correlations between the catalytic properties and surface structure is subjected to the availability of nanoparticles (NPs) with a well-defined morphology. The synthesis of metallic NPs can be attained, at least partially, by the selective adsorption of ions, surfactants or polymers on specific planes. They act by inhibiting crystal growth along certain crystallographic directions. It is also known that fine-tuning the operational variables involved in the synthesis process modifies to a large extent the size and proportion of the different types of particles. In this way, the seed-mediated growth (SMG), which consists of decoupling the nucleation and growth processes, is a quite versatile method in the sense that the involved operational parameters can be easily tuned. This work is addressed to ascertain the influence of the relevant operational variables of an aqueous SMG on the final shape of Pd NPs.

Experimental. In a first step, Pd NPs (3-4 nm in diameter) were synthesized using Na_2PdCl_4, cetyltrimethylammonium bromide (CTAB), and $NaBH_4$ as a strong reducing agent. The as-formed Pd NPs were used as seeds to control nucleation. The seeds were injected in the growth solution prepared using Na_2PdCl_4, CTAB, and a weak reducing agent, L-ascorbic acid. The seed aging, namely the age of the as-synthesized seeds (just when they are injected to the second solution) has been tested in the range 1.0 120 min. The stirring time and the stirring rate of both solutions have been also investigated.

Results and Discussion. The SMG has been found as a good method to synthesize Pd NPs with a well-defined shape, specifically nanorods, cubes, MTPs and bipyramids (see Fig. 1). In terms of morphology distribution and particle size, our results seem to indicate that seed aging is one of the key parameter in the synthesis process (see Fig. 2). These results constitute a remarkable progress with respect to the traditional approach in which seed aging of 2 h have been generally considered. Highly anisotropic particles, that are nanorods with ~4.5 of aspect ratio and ~87 nm of average length, can be preferentially obtained by reducing the seed aging to 2.5 min. In addition, these data show that an increase of seed aging involves a reduction of the ratio between the amount of twinned-particles (i.e. nanorods, MTPs and bypiramids) and of single crystalline cubes. This could provide evidence of a higher instability of twinned-features in very small particles, in such a way that they can be restructured to grow as single-particles during the synthesis process.

Fig. 1: NPs obtained by SMG

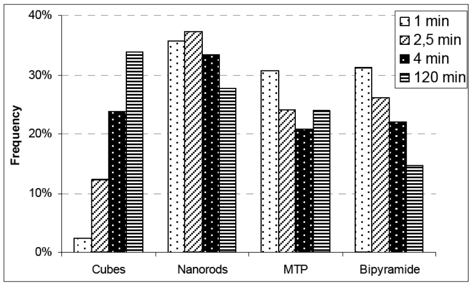

Fig. 2: Influence of seed aging on particle distribution

The growth rate of the crystals also seems to be decisive on the final particle distribution. A very slow growth enhances the synthesis of isotropic objects thermodynamically more stable, while higher rates boost the synthesis of more anisotropic objects. Keeping with this idea, the fraction between thermodynamic and kinetically-controlled particles can be controlled to a certain extent by varying the physical operational variables that might play a role on the flux of monomers toward the growing particles (such as the addition rate of reducing agent, stirring rate and stirring time). In this context, the determination of growth rates by means of a convenient technique (e.g., light scattering, ultra-violet or TEM imaging) could provide new insights into this matter.

Our results also reflect that the addition of some inorganic ions appears to be an efficient strategy to modify the final particle morphology, whose effect might be attributed to a selective adsorption of the ions on certain crystallographic faces.

Conclusion. With the final aim to establish correlations between catalytic properties and surface structure, the SMG appears as a suitable method to synthesize Pd NPs with a well-defined morphology. A fine-tuning of seed aging and the addition of ions seems to be crucial in the synthesis performance.

Size-dependent Catalytic Behavior of Alumina-supported Platinum Nanoparticles in Complete Oxidation of Methane

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Catalytic combustion of methane has many applications, for example, as an alternative to the conventional thermal combustion or for the abatement of methane emissions from the natural gas or methane-combustion devices including lean-burn natural gas vehicles. Supported Pt/Al_2O_3 catalysts serve as a faithfull model suitable for physicochemical studies of the size effects for the afterburning catalyst washcoat. In spite of the significant interest, the size sensitivity of methane oxidation remains under discussion, since a number of contradictory data is available.[1,2,3]

In this work, a direct correlation between the catalytic activity in methane oxidation and platinum particle size is visualized due to the elaboration of a convenient and reproducible method of monodisperse 1%Pt/γ-Al_2O_3 catalysts preparation ensuring a narrow size distribution of platinum nanoparticles (HR TEM data) on gamma-alumina surface. Aqueous impregnating solutions of oligomeric μ-hydroxo Pt(IV) complexes with different acidity used as active component precursors provide the size- controlled formation of supported platinum nanoparticles . Calcination at 400 or 600°C accomplishes the preparation procedure. The mean size of supported platinum particles thus obtained are varied from 0.6 to 20 nm for different samples.

The reaction under study is shown to be strongly size sensitive. The size dependence of the specific catalytic activity per accessible Pt atom was narrow and bell-shaped, with the maximum reaction rate being observed for the mean particle sizes of 1-2 nm (fig. 1). Carrier pretreatment enables one to shift the dependence maximum (fig. 1).

The oxidation state of platinum atoms is another important factor affecting the specific activity (X-Ray absorbtion and XPS data). EXAFS reveals a direct correlation of the catalytic activity with the formation of unusual phases of small oxygenated platinum particles (< 5 nm) differing on preactivated and on untreated alumina. The local environment of supported platinum atoms was similar to the precursor solutions. The less active larger nanoparticles of the active component (> 6 nm), formed due to high-temperature (600°C) calcination of catalysts on untreated alumina, are metallic. Thus, the stronger metal-support interaction with the pre-activated carrier results not only in the higher catalytic activity but also in an increased thermal stability of oxygenated platinum particles.

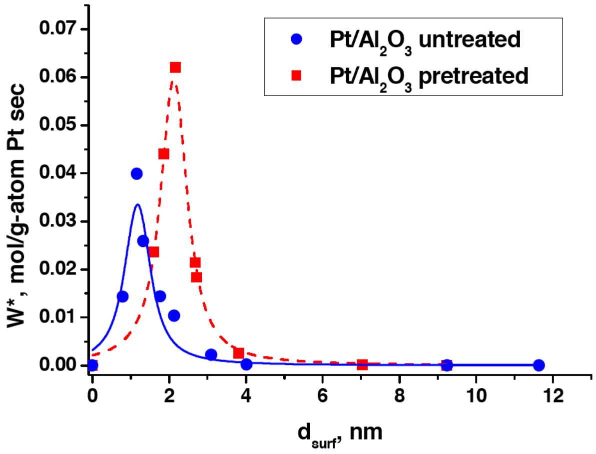

Figure 1. The effect of particle size on the specific activity of the 1%Pt/Al_2O_3 catalysts in complete methane oxidation at constant temperature 450°C under oxidizing conditions. Flow circulation was applied with the space velocity of the initial gas mixture (1 vol.% CH_4, 20.8 vol.% O_2, N_2 as balance gas) varying from 50 to 1100 ml/min per 1 ml catalyst loaded.

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Scaffolds of Di- and Tetraphosphine Linkers that Diminish Interactions of Immobilized Catalysts with Oxide Supports

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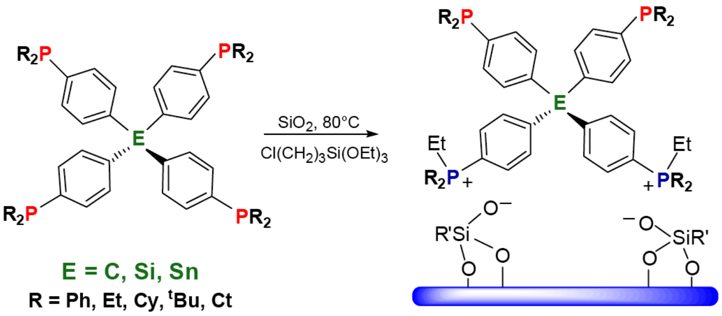
Phosphines bound to oxide surfaces are important as linkers for immobilizing catalysts, or as scavengers for metal complexes after catalysis. The success is always crucially dependent on the nature of the phosphine. For prolonging the lifetime of immobilized catalysts, the primary goal is to prevent any contact of the metal center with the aggressive oxide surface.



Phosphines with a rigid backbone, such as the tetraphenylelement scaffold shown here, prevent any metal/surface contact mechanically in an ideal way. Unfortunately, we could not attach two or three $(EtO)_3Si$ groups to the molecule selectively.

However, based on our previous finding[1] that phosphines can also be attached to silica as ethylphosphonium salts by treating them with ethoxysilanes at higher temperatures, we could cleanly and irreversibly immobilize the phosphines in the shown way. With the help of ^{29}Si,^{31}P, and ^{119}Sn CP/MAS NMR we could also prove that in the presence of an excess of ethoxysilane all the tetraphosphines are bound with two "ionic feet" to the support, and not by one or three. This way, two monodentate phosphine groups per linker molecule remain for binding two metal complexes.[2]

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Modeling Heterogeneous Catalytic Reactions with Gas Phase Neutral Clusters: V_mO_n/SO_2, Nb_m/H_2, CO, Ti_mO_n/H_2O

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Metal and metal oxide clusters are generated in the gas phase by laser ablation of the appropriate metal, reaction with oxygen (for M_xO_y formation) in a He flow, and supersonic expansion into a vacuum systems. The cooled clusters are reacted with various gases (SO_2, H_2, CO, H_2O, etc.) and the reactants and products are analyzed by single photon laser ionization and mass spectroscopy. Calculations of the thermodynamics and reaction pathways for these reactions are accomplished with various levels of density functional theory and basis sets. Overall catalytic cycles can be proposed for condensed phase heterogeneous catalysis based on these studies, and general themes can be suggested for oxidation/reduction catalytic behavior. Other systems will be discussed as appropriate theory and experiments progress.

Theoretical and Far-infrared Studies of Cu,Zn-superoxide Dismutase

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Metalloenzymes are a subclass of metalloproteines which ensure specific catalytic functions. The active site of Cu,Zn-superoxide dismutase metalloenzyme catalyzes the disproportionation of superoxide both in the oxidized (Cu^{2+}) and reduced (Cu^{+}) states. To better understand structural and electronic factors at the origin of this property, Cu,Zn-SOD has been analysed by means of FTIR difference spectroscopy.[1] To specifically monitor changes at the metal-binding site, a new experiment based on FTIR difference spectroscopy coupled to electrochemistry in the far infrared range (1000-50 cm^{-1}, i.e. 10-200 μm) has been developped.[2] Since metal-ligands vibrations contribute in this range new structural information of the metal site center is expected.

Recent experimental results obtained in the far infrared range will be discussed in combination with normal mode predictions performed using density functional calculations and a cluster model approach. Experimental studies and Computational studies of the Cu^{I} and Cu^{II} superoxide dismutase active center including ^{15}N-isotope labelling will be also presented.

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Preparation and Characterisation of Naked Silica-supported Mono-nuclear Ru Species Stable Under H_2 at High Temperatures

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Surface organometallic chemistry[1] aims at designing and understanding heterogeneous catalysts through a molecular approach. Typically, this approach provides single-site species, whose reactivities and stabilities increase through site-isolation compared to their homogeneous counterpart. In fact, highly unsaturated surface complexes on silica have been prepared. For instance, the silica supported zirconium[2] and tantalum hydrides[3] are obtained by hydrogenolysis of their perhydrocarbyl analogues. These highly reactive species can be used in olefin polymerisation[2a] and polyolefin depolymerisation,[4] alkane metathesis[5] or methane-olysis.[6] The formation of these highly unsaturated and reactive species is mainly due to the high oxophilicity of early transition metals, which avoids sintering and allows site isolation. Therefore, obtaining similar species for late transition-metals has been problematic yielding instead particles of various sizes.[7,8]

Here, we will show the preparation of the first naked silica-supported mono-nuclear Ru species (free of ligands such like phosphines, CO,), stable under H_2 at high temperatures (573 K). While Ru(COD)(COT) dispersed on standard silica provides Ru particles upon treatment under H_2, mono-nuclear isolated sites are obtained under the same reaction conditions by tuning the silica support. Both systems have been compared through TEM (Fig. 1), H_2 and O_2 adsorption, EXAFS and reactivity toward hydrogenation of olefins and aromatics, and show dramatic differences in term of structure and reactivity.

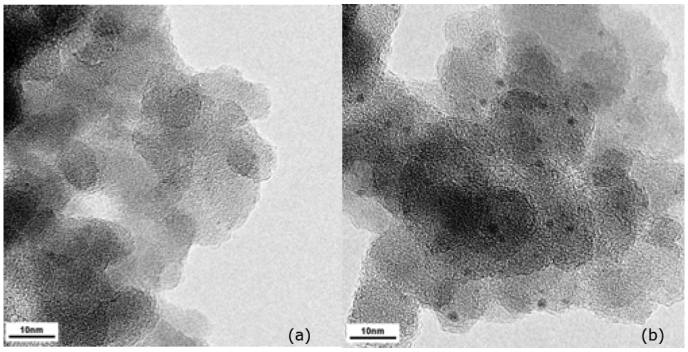

Figure 1. TEM pictures of Ru samples after treatment under H_2 at 573K
(a) Sample prepared on tuned silica. (b) Sample prepared on standard silica.

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Nanoporous Gold – A Novel Catalyst Material

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Despite of being inert as a bulk material, Au in the form of finely dispersed nanoparticles can be a surprisingly active catalyst for oxidation reactions such as the environmentally important CO oxidation. Compared to other metals, gold-based catalysts offer the advantage of maintaining their catalytic activity at lower temperatures. So far, the majority of gold-based catalysts described in the literature are oxide-supported nanoparticles. Here, we report on nanoporous gold (np-Au) as an example of an unsupported Au catalyst. Monolithic pieces of this material can be readily obtained by dealloying Ag-Au alloys, and exhibit an open sponge-like morphology of interconnecting Au ligaments on a nanometer length scale. Our study reveals that nanoporous Au is a very efficient catalyst for CO oxidation at temperatures as low as 0°C. To gain a better understanding of the nature of the catalytic activity of np-Au, we use ion-bombarded gold single crystal surfaces as a model system which allows us to study the interaction of oxygen and CO with undercoordinated Au atoms by means of STM, XPS and TPS.[1]

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Synthesis, Characterization and Modification of Aluminosilicate Nanotubes

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Imogolite is an aluminosilicate with formula $(OH)_3Al_2O_3SiOH$, naturally occurring as nanotubes with inner and outer diameters of 1.0 and 2.0 nm, respectively,[1] which can be obtained by means of laboratory synthesis, too. Notwithstanding its intriguing nanotubes structure, with $\equiv$SiOH groups at the inner surface and Al(OH)Al groups at the outer surface of nanotubes, respectively, its surface properties have not been studied in detail. In this work, an insight into acidic strength, stability and accessibility of hydroxyls groups, as studied by means of FT-IR spectroscopy of adsorbed probe molecules is reported. Imogolite was synthesized via a sol-gel route based on the co-hydrolysis of aluminum sec-butoxide and TEOS (molar ratio = 2:1) at 20°C in $HClO_4$ solution, followed by heating in autoclave, according to Farmer et al.[2] Low angles XRD patterns showed nanotubes self-organized in an ordered structure, stable up to 573 K; fibrous bundles forming a porous network were seen in FESEM images. The total BET surface area is 240 $m^2\ g^{-1}$, of which 170 $m^2\ g^{-1}$ correspond to microporous area; the average micropores diameter, as measured with the NL-DFT method, is 1.1 nm. FT-IR spectra show H-bonded hydroxyls on imogolite outgassed at r.t., 373 and 573 K. Molecular water is removed at 573 K. Adsorption of CO at nominal 77 K shows carbon monoxide adsorbed on internal SiOH species (band at 2156 cm^{-1}), along with CO on traces of Al^{3+} Lewis sites (2191 cm^{-1}). After outgassing at 773 K, Al^{3+} ions are formed, due to surface de-hydroxylation (band in the 2200 2187 cm^{-1} range) and several OH species are seen, with bands at 3747, 3717 and 3660 cm^{-1}. The latter suffer a downward shift of ca. 210 cm^{-1} upon CO adsorption, showing remarkable acidity. NH_3 adsorption gives rise to the formation of ammonium species, reversible only after outgassing at 573 K. SiOH inside nanotubes are accessible to probes like CO and NH_3 and phenol, but also AlOH species at the outer surface play a role, since the actual external surface area cannot be neglected. When heated at 773 K, nanotubes lose their structure and new acidic species, both Lewis and Brønsted sites, are formed.

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Shape and Capping Agent Effects on Platinum Nanoparticle Catalysis

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Our goal is to understand the behavior of real catalyst systems on a molecular level. To accomplish this task, a model system of capped platinum nanoparticles on a silica substrate is used. The nanoparticles exhibit a narrow size distribution and well defined shape. We were able to monitor two different shapes: cubes, comprised of {100} facets, and cuboctahedra, made of {111} and {100} facets. We were also able to investigate the influence of the capping agent on the catalytic activity of the particles. Kinetic studies of benzene hydrogenation on platinum nanoparticles over a range of temperatures (310 – 400 K) were used to relate nanoparticles to single crystals. In this manner, we uncovered implications for reaction mechanisms nanoparticle surfaces

Para-hydrogen Spin Order in Heterogenized Homogeneous Catalytic Systems

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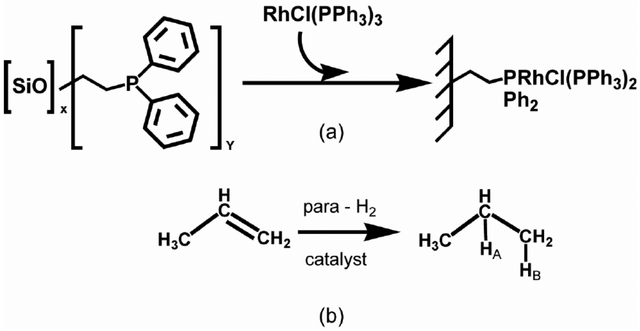
Catalyst separation is an important technique in many chemical reactions of industrial importance, such as hydrogenation, and arises out of a necessity to reuse the catalyst after repeated reactions in a batch continuous process. In this respect, heterogeneous catalysts remain the catalysts of choice, because of the ease by which they can be recovered from the reactant and product mixtures, simply by virtue of being in a different phase (solid). As a result, they do not contaminate the reactant and product mixtures, bypassing the need for elaborate high temperature distillation or ionic exchange-based separations. On the downside, these catalysts do not normally enjoy the many attractive features of homogeneous catalysts such as regio, chemo and stereoselectivities. Furthermore, for heterogeneous catalysts, the number of accessible catalytic sites, generally metal centres, may also be highly limited. Therefore, there is a well-known initiative in the catalysis community centering around the push for getting the best of both the homogeneous and heterogeneous worlds.



In the present work, we focus on the heterogenization of homogeneous Wilkinsons catalyst, by tethering it to a solid functionalized silica support, and the subsequent hydrogenation of olefinic substrates using hydrogen gas enriched in the para isomer. The RhCl(PPh$_3$)$_3$ catalyst is known to undergo rapid ligand exchange and therefore the addition of an approximately stoichiometric amount of 2-diphenylphosphinoethyl-functionalized silica gel to a toluene solution of Wilkinsons catalyst leads to formation of the supported catalyst, RhCl(PPh$_3$)$_2$PPh$_2$(CH$_2$)$_2$-SiO$_2$. For the first time, para-hydrogen induced polarization was observed in the heterogeneous hydrogenation processes.[1,2] Hydrogenation with the para spin isomer allows one to study the catalytic reaction using NMR, and has now become an increasingly important tool to monitor reaction kinetics, mechanisms and the formation of short-lived, low concentration reaction intermediates, thanks to the several orders of magnitude enhancement of the spin polarization afforded by the para isomer.

However, for the polarization to survive all the way through to the product molecule, there are, at the very least, three essential requirements: (a) the addition of the hydrogen molecule to the substrate must be pairwise, (b) the lifetime of the intermediate Rh-alkane-dihydrogen complex must be shorter than the longitudinal relaxation time of the nuclei, and (c) that the dephasing induced by the dipolar couplings in the intermediate complex must be weak so that the spin order in the protons derived from the para-hydrogen can survive to its ultimate destination the (alkane) product. Our present study confirms that all three conditions are satisfied and provides additional insight into the mechanism of hydrogenations using heterogenized catalysts, notably, that the catalytic mechanism of Wilkinsons catalyst involving the oxidative addition of H$_2$, π-complexation of the alkene, intramolecular hydride transfer and reductive elimination of the product molecule IS indeed preserved. This contribution will focus on our recent experimental results.

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Plasma Catalysis with Lanthanum Perovskites in CH_4 Oxidation Treatments

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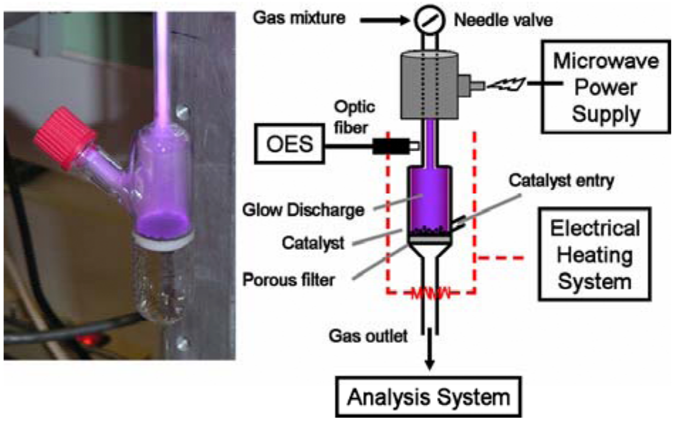
The combination of catalysts and plasmas to induce specific reactions under mild thermal conditions is an emerging approach for the removal of noxious components like NO, soot or volatile organic compounds (VOCs).[1,2,3,4] Most of designs using these mixed plasma+catalyst systems consist of the mere integration of the plasma and the catalysis as two independent processes. Less frequently, plasma and catalysts are combined together such that this latter is embedded in a plasma phase rich in radicals and other activated species.[3,4] In this case, it is still unclear whether the role of the catalyst is just to provide surface sites where the active species of the plasma may react or if it participates actively in the reaction. The present work deals with the microwave (MW) plasma interaction of CH_4 in the presence of a catalyst. The plasma was produced in a quartz tube with a microwave (MW) discharge provided by a surfatron launcher. Herein, the main difference with previous designs[5,6] consists on the geometry of the reactor, adapted to enable the incorporation of powdered catalysts in the glow discharge zone (see scheme), in order to allow a direct interaction between the plasma species and the catalyst surface. Also, the catalyst zone can be externally heated. Two types of catalysts have been used, a commercial SiO_2 powder from Aldrich with a 270 m^2g^{-1} specific surface area and a lanthanum substituted perovskite prepared by spray pyrolysis in our laboratory (specific surface area of 13 m^2g^{-1}). The investigated gas mixture consisted of N_2 or Ar as the carrier gas and CH_4 (3600 ppm) as minority component.

As a relevant result, it has been found that the plasma alone produces the almost complete removal of CH_4 that is transformed into CO, while the synergetic effect of combining plasmas and perovskites at low temperature produces the total oxidation of CH_4 to CO_2.[7]



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Characterization of CuO_x/TiO_2-ZrO_2 and CuO_xVO_x/TiO_2-ZrO_2 Catalysts and Decomposition of 2-Propanol

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We report the synthesis of CuO_x/TiO_2-ZrO_2 and CuO_xVO_x/TiO_2-ZrO_2 catalysts prepared by the sol-gel method, containing 1, 3, and 5 wt% of copper oxides and 0, 1, 3, and 5 wt% of copper oxides with 12 wt% of vanadium oxides, respectively. The solids were dried at 100°C for 24 hrs and calcined at 400°C for another 24 hrs in an open-air atmosphere. The samples were characterized by X-Ray diffraction (XRD), surface area (BET), temperature programmed reduction (TPR), and electron paramagnetic resonance (EPR) spectroscopy. In order to study the acid-base character of the catalytic sites, we have monitored the decomposition of 2-propanol. The XRD diffraction patterns of the samples with calcinations at 400°C show only an amorphous phase for all the catalysts. The BET surface areas of the samples are around 230 m^2/g. TPR results of the CuO_x/TiO_2-ZrO_2 samples show two different copper temperatures reduction and for the CuO_xVO_x/TiO_2-ZrO_2 samples the reduction consumption are wider and achieved at higher temperatures. By the EPR technique we have identified two Cu^{2+} ions sites in CuO_x/TiO_2-ZrO_2 series and one V^{4+} ion site in sample VO_x/TiO_2-ZrO_2 with no copper, and three EPR signals in CuO_xVO_x/TiO_2-ZrO_2 sample with 1% of copper, two of these sites belongs to Cu^{2+} ions and the third one correspond to a very scarcely EPR signal of V^{4+} ions. The two others CuO_xVO_x/TiO_2-ZrO_2 samples (3 and 5% of copper oxides), are characterized by two Cu^{2+} ions sites. Spectra simulations of the EPR measurements at 400, 300 and 77 K give EPR hyperfine parameters characteristic of isolated Cu^{2+} and V^{4+} ions in octahedral environments and clusters of copper ions. The 2-propanol decomposition shows that the acid properties of CuO_xVO_x/TiO_2-ZrO_2 catalysts are superior that those of CuO_x/TiO_2-ZrO_2 samples. The introduction of copper into VO_x/TiO_2-ZrO_2 modifies the acid-base properties of the catalysts, inducing a change in isopropanol decomposition activity and selectivity.[1]

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[1] We acknowledge support from COFAA-IPN.

Vanadium-Zirconium Mixed Oxides as Oxidative Dehydrogenation Catalysts

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Introduction. In previous reports, it has been demonstrated that the tetrahedral superficial VO_4 units are the principal responsible species for the oxidative dehydrogenation process, while the presence of V_2O_5 characterized by bidentated V=O species promote the deep oxidation process. In the present work we report a combined impregnation-precipitation method to obtain a VOx-ZrO_2 mixed oxide to improve the formation of superficial VO_4 species, in order to avoid the undesirable reaction of deep oxidation.

Experimental Procedure. Vanadium-zirconium mixed oxide (VZrO) were prepared by addition of zirconium oxide to a slightly basic hot solution of ammonium metavanadate (in different quantities in order to obtain 15, 30, 45 and 65 wt% of VOx) with a continuous stirring for 1 h, followed by solvent evaporation and dried at 95 °C over night. The resulting solids were crushed and calcined at 600 °C. The textural properties were measured at 77 K in a Micromeritics ASAP-200 using N_2 physisorption, X-ray diffraction of the calcined samples were recorded at room temperature in a Phillips Xpert difractometer and spectroscopic measurements were performed with a EPR (Jeol JER-RES3X) and a FTIR (Nicolet 750).

Results and Discussion. From the textural analysis was observed that the BET specific area increases by the vanadium incorporation, simultaneously both specific area and pore volume gradually decreases, and additionally by the hysteresis loops it was founded the absence of microporous structures. XRD analyses of pure ZrO_2 shows the presence of a monoclinic phase only. In V-Zr oxides, the vanadium addition stabilize the tetragonal phase of ZrO_2 , but no V_2O_5 phase was detected. In the infrared spectra of 60, 45, 30 and 15 VZrO samples were identified a series of bands at 859 characteristic to 3 stretch of $(VO_4)3$, the vibrations at 691 and 456 due to ν_{as} and ν_a of V-O-V bond like orthovanadates. EPR measurements of the 60, 45, 30 and 15 VZrO samples showed two different axial signals of isoleted V^{4+} ions with hiperfine interactions. A third broad paramagnetic axial EPR signal with an averaged $g = 1.964$ and without hyperfine interaction was also observed, this signal has been assigned to VO^{2+} clusters (V-O-V). In similar way, another narrow symmetric signal attributed to Zr^{3+} ions was determined and characterized by a $g = 1.978$ and $\Delta H = 1.66$ mT. These results are consistent with XRD and FTIR data.

In this work, was established that supported V_2O_5, forms a layer structure with the exposed (010) plane and which is not found in VZrO samples. Additionally, it has been observed that the V=O bound shows a characteristic infrared stretching frequency at about 1020 cm^{-1} (V=O), which is not present in our samples. Finally, it was found that at VOx content higher than 20% the ZrV_2O_7 formation is promoted, which is considered as active phase for oxidative dehydrogenation of propane.[1]

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[1] We aknowlwgde support from COFAA-IPN

Catalysis on Distorted Nanoparticles

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Building nanoarchitectures by controlling atomic assembly to achieve manipulation of material properties has opened opportunities for improving catalyst activity, selectivity and stability. The present work presents a novel platform to prepare distorted metallic and oxide nanoparticles, together with results of their catalytic behavior.

Carbon nanofibers (CNF) have many unique properties, and one of the most outstanding features for CNF is the presence of a large number of edges, which in turn constitute sites that are readily available for chemical reaction or physical interactions. Engineering carbon nanofibers makes it possible to control the arrangement of the carbon atoms in terms of primary and secondary structures, which opens unprecedented opportunities to tailor the properties of both the CNF surface and supported metal nanoparticles. The progress of development of CNF as a hierarchical platform in catalyst development will be reported. This platform can be used to manipulate electronic, mechanical, and structural properties of the catalysts in order to meet the requirements for specific reactions towards better activity, selectivity and stability.

A wide range of CNF-supported metals such as Ni, Co, Cu, Au, Pd, and Pt catalysts have been studied by the Catalysis Group at NTNU. Four typical structures, platelet, fishbone, multi-walled tubes and stacked cup have been tested as catalysts or catalyst supports. We have observed microstrain in Ni nanoparticles induced by the CNF surfaces, which had a significant effect on the activity of Ni nanoparticles during ethane hydrogenolysis.[1] Molecular dynamics simulations (MD) indicates that adatom migration caused by bonding with carbon atoms on the edge of the CNF is compensated by a rearrangement of the atomic structure of the cluster, leading to an enlargement of the mean bond length, which is in good agreement with experimental observations. The simulation points out that the degree of distortion depending on the graphite sheet orientation of the CNFs and the properties of the nanoparticles. A larger degree of distortion was found on platelet than on herringbone, and Ni than Pt. Further evidence of the effect of CNF is provided by a recent EXAFS study where a distortion of TiO_2 nanoparticles supported on CNF is observed. The changes in geometric and electronic properties of metal nanoparticles will result in enhanced activity and selectivity for certain reactions, and in some cases, the stability. The properties of CNF-supported catalysts are further studied by various techniques such as chemisorption, XRD, HRTEM, EXAFS, XPS etc., in order to understand the relationship between the catalyst properties and the CNF structures.The catalysis on distorted nanoparticles have been studied in F-T synthesis on Co/CNF,[2] CO oxidation on Au/TiO_2/CNF[3] and hydrogen/CO oxidation on Pt/CNFs. All the results have shown that the graphite sheet orientation of the CNF has a significant effect on the catalyst activity and selectivity. In conclusion, the systems studied shows that it is possible to manipulate the geometric and electronic properties of nanoparticles by tuning the graphite orientation of the CNF. This provides an excellent platform for rational catalyst design for different reaction systems.

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A Quantitative Determination of Reaction Mechanisms from Density Functional Theory Calculations: Fischer-Tropsch Synthesis on Co(0001)

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The Fischer-Tropsch (FT) synthesis is of importance in utilizing natural resources. Its mechanism is still under heavy debate, especially for the C-C coupling reactions responsible for chain growth due to its complex nature. In this work, we systematically investigate the mechanism of the C-C coupling reactions using density functional theory. The activation energies of C-C coupling and carbon hydrogenation reactions on both flat and stepped surfaces are calculated and analysed. It is found that the ratio of reaction rates between step sites and flat sites is related to the difference of transition state energies between both sites as well as the ratio of vacancy coverage at steps to that on terraces, independent on initial state energies. Moreover, coverages of adsorbed C_1 species are estimated based on quasi-equilibrium approximation and reaction rates of all possible C-C coupling pathways on different sites are quantitatively evaluated. The results suggest that the reactions of CH_2+CH_2 and CH_3+C at steps are most likely to be the key C-C coupling steps in FT synthesis. The quantitative approach used to determine the mechanism in this work may be extended to other catalytic systems.

Dynamics and Kinetic Consequences of Oxygen Assisted Methane Activation on Rh and Pt Metal and Metal-Oxide Cluster

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C-H bond activation on Group VIII metal (Rh, Pt, Ru, Ir, Ni) clusters has been well established as the kinetically relevant elementary step in catalytic reforming and decomposition reactions. The forward turnover rates for CH_4 reforming are first order in CH_4 concentrations, independent of co-reactant identity, and are identical to the initial CH_4 decomposition rates. A normal CD_4/CH_4 kinetic isotope effect was observed, as also measured for CH_4 decomposition. These results suggest that the reaction proceed through activating the C-H bond activation on clean metal surface as the kinetically relevant step. Active oxygen atoms, derived from CO_2 and H_2O co-reactants, do not assist the C-H bond activation. In contrast, when O_2 is used as the oxidant, turnover rates measured are significantly higher than the rates of reforming and decomposition reactions. Above a certain O_2 partial pressure, CH_4-O_2 turnover rates remain first order in CH_4 and independent of O_2 partial pressures. The regime where rates are independent of O_2 partial pressure depends on both the metal identities and reaction temperatures. At 873K, turnover rates are independent of O_2 pressure above 0.2 kPa O_2 on Rh and over a wider range (up to 2.5 kPa O_2) on Pt catalysts. On Rh catalyst, kinetic analysis carried out in this O_2 independent regime shows a 35 fold increase in the first order rate constant, when comparing to the rate constants measured for CH_4 reforming and decomposition reactions. Despite the significant differences in rates, a normal CD_4/CH_4 kinetic isotope effect (1.8 at 813K) measured confirms that C-H activation remains as the kinetically relevant step. The C-H bond activation energy, however, is lowered from 108 to 55 kJ/mol in the present of O_2. Under these O_2 partial pressures (>0.2kPa), in-situ X-ray absorption studies show that Rh present as Rh (III) state in the form of Rh_2O_3 clusters. Since the turnover rates are independent of O_2 concentrations in this regime, it is concluded that the Rh_2O_3 surface is saturated with $O^\star$, and these $O^\star$ species enhanced the C-H activation. Small Rh_2O_3, with a higher surface fraction of coordinatively unsaturated defect sites, exhibited a higher CH_4 turnover rates than the stable Rh_2O_3 spread onto Al2O3 support that have been treated to higher temperatures.

During O_2 depletion, the CH_4 turnover rates acquired a negative kinetic order in O_2 and increase suddenly within a narrow range of O_2 pressure. The negative O_2 dependence observed here suggests that the surface is no longer saturated with reactive $O^\star$ intermediates. Exposed metal surface partially covered with $O^\star$ is much more reactive than both the bare metal surface and the $O^\star$ saturated surface, leading to the observed unusual increase in rates during O_2 depletion. It is believed that these vacancies formed site pair with $O^\star$ and are much more reactive than both the $O^\star$ saturated surface and the uncovered metal surface, leading to the high turnover rates observed. A complete kinetic and mechanistic interpretation of elementary steps will be presented to elucidate the dynamic shift of the most abundance surface intermediates (MASI) during CH_4-O_2 reaction.

Synthesis of Dimethyl Carbonate from Carbon Dioxide and Methanol: Comparison of Homogeneous and Heterogeneous Catalyst

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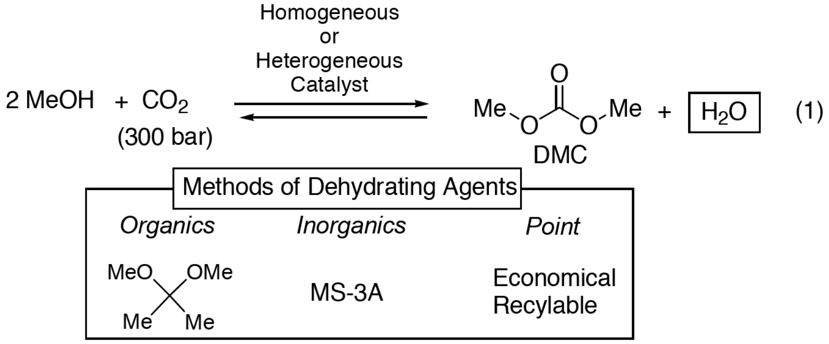
Conversion of carbon dioxide is very fascinating due to its environmentally benign nature (nontoxic, noncorrsive, abundant, and non-flammable). In particular, carbon dioxide (CO_2) is useful as a phosgene substitute.[1] For example, CO_2 can be transformed to various organic carbonates. Dialkyl carbonates (e.g. dimethyl carbonate) are commercially important compounds, and are used as electrolytes in lithium ion batteries, as aprotic polar solvents, as a fuel additive, and as intermediates for producing polycarbonates and fine chemicals.

$ScCO_2$ is efficiently converted to dimethyl carbonate (DMC) via the reaction with methanol in the presence of homogeneous or heterogeneous catalyst. The removal of water is the key to accomplishing the high conversion by shifting the equilibrium to DMC. Dehydration is successfully carried out by adding a dialkyl actal as a recyclable organic dehydrating agents or circulating the reaction mixture through a dehydrating tube packed with zeolite (MS-3A) (eq 1).[2] Moreover, adding a very small amount of an acidic co-catalyst greatly improves the reaction rate. Under the effective dehydration conditions, the DMC yield is almost linearly dependent on the reaction time, catalyst amount, and CO_2 pressure.



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Iron(III)-Catalyzed Intermolecular Addition of Carboxylic Acids and Alcohols to Olefins

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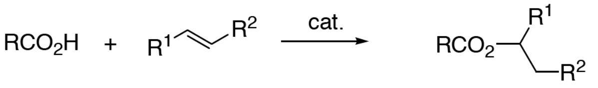
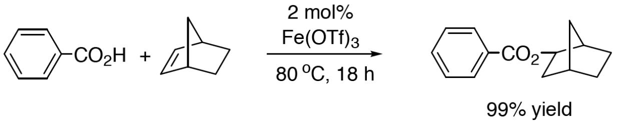
Ester formation is a key reaction in organic synthesis. The addition of carboxylic acids to alkenes is an especially attractive green procedure because the reaction is coproduct-free unlike common esterifications, which generally need coproducts such as water or HCl removed (eq 1). Conventional procedure uses a relatively large amount of sulfuric acid as a catalyst and requires its neutralization before the purification of the ester (eq 2).[1] The addition of carboxylic acids with alkenes has also been catalyzed by precious metal complexes such as platinum and silver.[2] Herein, we report the efficient catalysis for using iron-based catalysts (eq 2).

$$\mathrm{RCOX} + \mathrm{R'OH} \xrightarrow{\text{cat.}} \underset{(\mathrm{X} = \mathrm{OH\ or\ halogen})}{\mathrm{RCO_2R'} + \mathrm{HX}} \qquad (1)$$



(2)

The effect of the catalyst structure was investigated for the reaction of benzoic acid and norbornene (eq 3). We found that the addition of a catalytic amount of silver triflate dramatically accelerates the reaction. The active species is presumably in situ formed $Fe(OTf)_3$. The isolated $Fe(OTf)_3$ exhibited nearly the same catalytic activities as the $Fe(OTf)_3$ *in situ* formed from $FeCl_3$ and Ag(OTf).



(3)

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Pt/SBA-15 Catalyst: The Effect of the Preparation Route on the Pt Nanocrystalline Size

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We report the application of two functionalization pathways used in order to load SBA-15 with Pt. The first method is the inclusion method (IM), which involves the preparation of Pt nanoparticles in aqueous solution, capped in a protective polymer, and subsequently utilized for the synthesis of SBA-15, giving the Pt/SBA-15 catalyst as a result. The second method applied is the deposition-precipitation method (DP). Through both investigated methods we were able to prepare active catalysts for toluene hydrogenation with a low metal loading, albeit with different Pt particle size. In addition to the results obtained from catalystic testing, we report on the characterization of the samples in order to give more insight into the impact of the functionalization pathways on the parent SBA-15 as well as to further characterize the properties of Pt/SBA-15. For the IM, the main emphasis is on characterizing the Pt nanoparticles in the aqueous solution (TEM, UV-Vis spectroscopy, Dynamic Light Scattering), while for the DP method we have used mehods providing information on the functionalized solids (TPR, UV-Vis diffuse reflectance, NIR). Furthermore, the support properties are investigated using XRD, N2 sorption, ^{29}Si MAS NMR, while chemisorption measurements and TEM are used to give information on the Pt nano-crystalline size on the Pt/SBA-15 catalyst. The results indicate that both preparation methods result in a narrow Pt nanoparticle size, but the DP-method gives the smaller Pt entities in the Pt/SBA-15 catalyst.

New Carbohydrate Derivative Diphosphite Ligands for Metal Nanoparticles Stabilization and Asymmetric Catalysis

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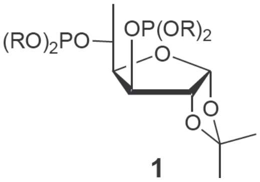
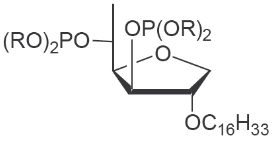
Designing and synthesising new ligands is a key step in the practical development of asymmetric catalysis. Carbohydrate derivatives have been used as synthons to obtain chiral ligands for catalysis. The presence of hydroxyl functions in carbohydrates makes it easy to prepare oxygenated phosphorous functions such as phosphinites, phosphonites and phosphites.[1]

This communication describes the synthesis of new diphosphite ligands designed and systematically modified to be used in asymmetric catalysis and stabilization of metal nanoparticles. In particular the diphosphites **1-3**, provide high regioselectivites and enantioselectivities in the rhodium catalyzed asymmetric hydroformylation of vinylarenes.



1



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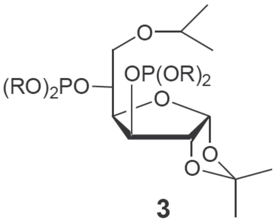

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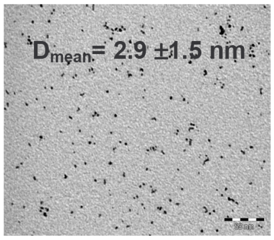
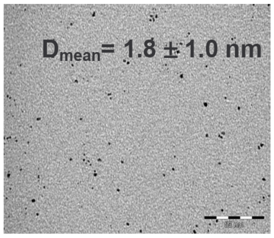
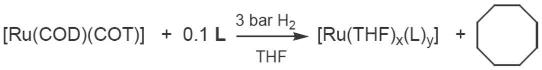
Metal nanoparticles can be prepared from organometallic complexes containing olefinic ligands through their reduction under H_2 and stabilisation in the presence of ligands.[2] We present here the use of diphosphite ligands to stabilize nanoparticles to be applied in asymmetric catalysis. Pd nanoparticles ligands have been prepared from $[Pd_2(dba)_3]$ and tested in asymmetric allylic alkylation reaction.[3] Rh nanoparticles have been synthesized using $[Rh(\mu\text{-}OMe)(COD)]_2$ and $[Rh(\eta^3\text{-}C_3H_5)_3]$ as precursors and tested in asymmetric hydroformylation. Ru nanoparticles have been synthesized using [Rh(COD)(COT)] as precursor, to be tested in asymmetric hydrogenation. Modifications in the diphosphite influence the properties of the nanoparticles (Figure 1) and the catalytic results.



L=1



L=2



$$[Ru(COD)(COT)] + 0.1\ \mathbf{L} \xrightarrow[THF]{3\ bar\ H_2} [Ru(THF)_x(L)_y] + $$

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Polar Double Bond Hydrogenation Performed by the Shvo Catalyst: A Computational Study

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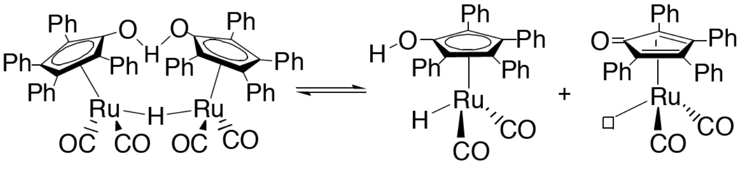
The $\{[2,3,4,5\text{-}Ph_4(\eta^5\text{-}C_4CO)]_2H\}Ru_2(CO)_4(\mu\text{-}H)$ complex or Shvo catalyst[1] has been applied successfully in a broad range of homogeneous reactions.[2] Once heated it produces the A and B species, which are able to perform reduction and oxidation reactions, respectively. The active species in hydrogenation is A, having two hydrogens of opposite acidic and hydridic properties able to perform hydrogenation of polar double bonds.

There are mainly two mechanisms proposed in the literature for polar double bond hydrogenation, both of them involving the concerted transfer of the active hydrogens of the catalyst. The first one proposes and outer-sphere mechanism where the hydrogenation takes place outside the coordination sphere of the metal.[3] Conversely, the other one suggests an inner-sphere mechanism where previously to the hydrogenation occurs the substrate coordination via the $\eta^5 \rightarrow \eta^3$ ring slippage of the CpOH ring.[4]

Here, a theoretical study of the different proposed mechanisms in carbonyl hydrogenation is presented.[5] Stepwise mechanisms involving the CO leaving or the $\eta^5 \rightarrow \eta^2$ CpOH ring slippage prior to substrate coordination have been also evaluated.



1 **A** **B**

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The Transformation of $BaCO_3$ to BaO as an Initial Step in NO_x Storage on $Pt/Ba/Al_2O_3$ Catalysts

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NO_x storage and Reduction (NSR) is a promising technology for the reduction of NO_x in the exhausts of lean-burn and diesel engines. The concept is based on the incorporation of a NO_x storage component, typically barium oxide, in the catalyst to store NO_x as nitrates for relatively long lean periods and subsequently release, and reduce NO_x under short rich periods. Extensive investigations have been performed to understand the performance of barium-based NO_x storage catalysts and to suppose mechanisms for the storage and reduction processes. However, some fundamental issues are still debated one of which is the nature (or phase) of barium-sites on which the storage of NO_x takes place.

In this work, transient in-situ infrared spectroscopy (DRIFT) and flow reactor experiments were performed to answer the question regarding the phase of the barium sites on which NO_x storage takes place. The outlet gas components from the DRIFT cell as well as from the flow reactor were analyzed by means of mass spectrometry and the surface morphology of new prepared samples and samples used in NSR experiments were studied using electron microscopy (SEM-EDS).

The transient NO_x storage (with NO_2) and reduction (with NO_2 + H_2) experiments were performed at 200, 350 and 390°C after pre-treating the catalyst with CO_2 to transform the BaO sites to $BaCO_3$. The DRIFT data confirms the formation of nitrates on both alumina and barium sites during lean conditions at all investigated temperatures. The formation of nitrates was accompanied by the release of CO_2 from the sample indicating that the storage of NO_x is initiated by the decarbonation of barium carbonate sites (i.e. $BaCO_3$ transformation to BaO). The amount of released CO_2 during lean periods corresponded to about 1/3 of the amount of stored NO_x. During rich conditions, the stored nitrates were released, decomposed and reduced over the Pt sites. However, negative absorption peaks were observed at regions where IR bands corresponding to barium carbonates usually appear. The appearance of these negative bands is most likely due to disappearance of barium carbonates as a consequence of the replacement of barium carbonate with barium nitrate during lean conditions. The intensity of these negative bands was significantly lower during the second NSR cycle, while no negative peaks were observed after three NSR cycles probably due to the transformation of all barium sites which were available for NO_x storage to BaO.

SEM-EDS analysis showed that platinum is evenly distributed over the entire sample surface, while the distribution of barium is more uneven. Additionally, agglomerates of barium particles were found in the sample which was used in NSR experiments. The agglomeration of barium particles is most likely a consequence of the dynamic property of barium-containing phases during NSR processes.

Chymotrypsin Activity at Single Enzyme Level: Spontaneous and pH-induced Deactivation

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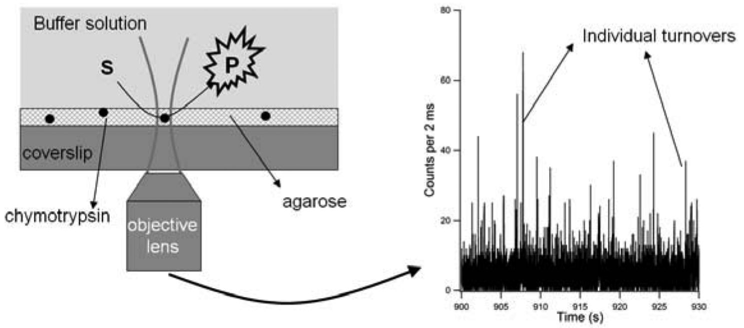
The last decade in situ single molecule fluorescence spectroscopy (SMFS) introduced a revolution in enzymology. By studying individual biocatalysts with single turnover precision, enzymatic activity has been associated with new effects such as static disorder,[1] dynamic disorder[2] and memory effects.[3] These observations lead to a new hypothesis of a fluctuating enzyme which during its catalytic action constantly interconverts between several thermodynamically favored sub-states, each with their own catalytic parameters.[4,5]

Until now research was mainly focused on observing enzymes in optimal working conditions. A lot of interesting information can however be obtained by looking at the response – and more in particular at the time resolved activity – of single enzymes on external stimuli.

The present research monitors the activity of single α-chymotrypsin enzymes, from which the activity and conformational dynamics have been already extensively studied on the ensemble level, towards a specific home-made profluorescent rhodamine 110-derivative.[6] Upon enzymatic hydrolysis, the liberated strongly fluorescent rhodamine 110 is easily tracked with confocal fluorescence microscopy. Prior to the catalytic experiments, the enzyme is immobilized in an agarose polymer (see figure).



The results for chymotrypsin at its optimal pH show a complex dynamic behavior in line with the individual kinetic behavior of other enzymes. In addition, a hitherto unknown spontaneous deactivation process at optimal working conditions is observed distinct from the known pH-induced deactivation. Their respective mechanisms will be dealt with in more detail in the presentation. Interestingly, the pH-induced deactivation seems to be susceptible to static disorder effects, since not all individual enzymes respond similarly to the applied triggers.

To conclude, the SMFS research approach is not restricted to enzymatic research. Recently our group applied fluorescence microscopy for space- and time-resolved investigation of heterogeneous chemocatalysts such as zeolite and layered double hydroxide crystals in action.[7,8,9]

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[1] i.e. differences in time-averaged activity between individual enzymes

[2] i.e. time dependent activity fluctuations within a single enzyme

[3] i.e. correlation of the time scales of successive turnover events

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[8] M.B.J. Roeffaers et al. *Nature* 439 (2006) 572.

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In-situ X-ray Adsorption Spectroscopy (XAS) of Mono-dispersed Co Nanoparticles: Implications for Co Based Catalysis

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This work presents the investigation of mono-dispersed Co nanoparticles in H_2 at elevated temperatures using *in-situ* X-ray adsorption spectroscopy (XAS). Mono-dispersed Co nanoparticles synthesized from a carbonyl precursor ($Co_2(CO)_8$) were deposited on a gold foil using Langmuir-Blodgett method. High-resolution scanning electron microscopy (SEM) images showed that the nanoparticles were packed on the gold surface as a single layer. X-ray photoelectron spectroscopy (XPS) revealed that Co nanoparticles were oxidized to CoO during deposition. Reduction of the oxidized Co nanoparticles to metallic Co was then investigated *in-situ* by XAS (Co L-edge) in the presence of 1 bar H_2 at various temperatures up to 300°C, using a specially designed gas-flow cell. During the reduction in H_2, the capping ligands on the nanoparticles were also removed, as supported by O K-edge spectra in XAS. On the other hand, the nanoparticles retained the same morphology after *in-situ* XAS measurements, as revealed by SEM. These results imply a promising way to study the catalysis of Co nanoparticles using an *in-situ* method.

Degradation of Phenol in Aqueous Solutions: Comparing the Homogeneous Photochemical Process with Heterogeneous Photocatalysis using Nanostructured Photocatalysts

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Titanium dioxide (TiO_2) has been widely used as photocatalyst, either for treatment of waste waters,[1] or gaseous effluents.[2] Three major limitations are normally quite restrictive to the efficient use of TiO_2: a) low photonic yield of the degradation process, b) a band gap energy of 3.2 eV requiring excitation in the UV region for activation of the process; and c) in the case of liquid phase treatment, there are but inadequate systems for supporting the TiO_2 particles, leading mainly to the use of suspensions, which requires a final filtration step in order to separate the photocatalyst from the liquid. As result an intense research is currently ongoing in order to develop systems able to overcome these drawbacks. Recently, it was recognized that activated carbon may have some beneficial effects in the photocatalytic activity of TiO_2. Following these observations granular or powder activated carbon and carbon nanotubes have been used to produce biphasic photocatalytic systems.[3,4] Production and characterization of novel nanostructured catalysts of this type, for use in the described processes, are subject of research at the boundary between homogeneous and heterogeneous catalysis. Nanoparticles possess interesting electronic, optical, and catalytic properties that differ from those of the bulk materials. In this study, TiO_2 was prepared following an acid-catalyzed sol-gel method using titanium isopropoxide as precursor. The xerogel calcination temperature was controlled in order to optimise surface and morphological properties of the catalysts. Commercial carbon nanotubes (CNT) were introduced in the matrix during aging of the gel to develop a strong interaction between the phases.

In phenol photodegradation experiments different light sources were used in a discrete range of wavelengths (254, 313, 366, 405 and 436 nm). In the UV range, phenol concentration decays consistently with a close to first order reaction rate law, reaching essentially zero concentration at the end of the experiment. Above 366 nm no conversion of phenol is observed in the homogeneous process.

The heterogeneous photocatalytic process was more efficient than the homogeneous neat photolysis and was operating over the full range of wavelengths. Additionally, CNT/TiO_2 nanostructured catalysts exhibit higher activities than TiO_2 alone. In general, the smaller the particles are, the larger is their surface to volume ratio and more efficient becomes the process specially in the nanometer size range. Because heterogeneous catalysis depends on surface properties, the use of nanoscaled catalysts opens up a wide range of possibilities for improving catalytic activity and selectivity. The use of composites also opens the possibilities in what concerns the development of efficient structures to support the photoactive phase.

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Nano-Structured Membrane Catalysis

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This report summarizes our explorations on the application of the nano-structured anodic aluminum oxide (AAO) membrane in heterogeneous catalysis. The procedures for growing the AAO membrane in the center of an aluminum disc have been developed by appropriately masking the disks perimeter during the anodization and the following etching step. The remaining aluminum ring connects seamlessly to the AAO membrane and serves as a support for convenient handling and sealing. The supported AAO membrane can be sealed gas tight in a flow reactor so that the nanopores on the membrane function as parallel arrays of tubular reactors when the reactants are pushed through. Loading a catalytic material onto the walls of the nanopores turns the AAO membrane described above into a unique catalytic system. This membrane system provides some possibilities that can hardly be achieved with a conventional powder bed. For example, its open, one-dimensional channel structure facilitates the deposition of coatings and catalytically active materials by the Atomic Layer Deposition (ALD). The combination of AAO and ALD allows for flexible controls over a lot of parameters of the membrane catalytic system, such as the size and shape of the pores, the compositions of the support and the catalytic species, or even the locations of the catalysts inside the pores.

Vanadium oxides (VO_x) species, which are used as the catalysts in the oxidative dehydrogenation (ODH) reactions, are coated on the AAO membrane by ALD. In the ODH reaction of cyclohexane, the membrane catalytic system shows better performances than does the same catalyst in the form of a powder with respect to both the activity and the selectivity to the partial oxidation product. This test result demonstrates the advantages of the membrane catalytic system in terms of overcoming the bypass and diffusion problems, reducing the residence times, and the possible capability of prohibiting the undesired gas phase reactions.

The catalytic behaviors of the VO_x supported on the AAO membrane have been systematically studied in the ODH of cyclohexane. It is proved that the loading of the VO_x has remarkable influences on the activity as well as the selectivity of the catalyst. Compared to the traditional incipient wetness impregnation method, the ALD turns out to be a more effective and controllable way to load the catalytic species. The reaction path is studied by comparing the ODH reactions starting from cyclohexane, cyclohexene and benzene respectively. The experiment results reveal that the production of the deep oxidation products (benzene and CO_x) may either go through a sequential path or parallel paths, depending on the experiment conditions and the nature of the catalyst.

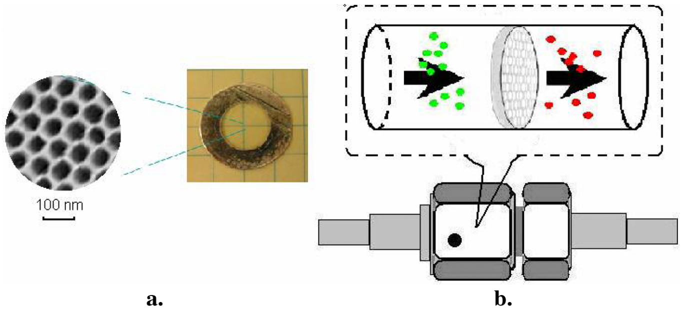

Figure 1. a) The AAO membrane mounted on the aluminum ring support
b) The flow reactor with the AAO membrane sealed inside

Homogeneous and Heterogeneous Catalytic Norbornadiene Allylation: Common Features and Specifics

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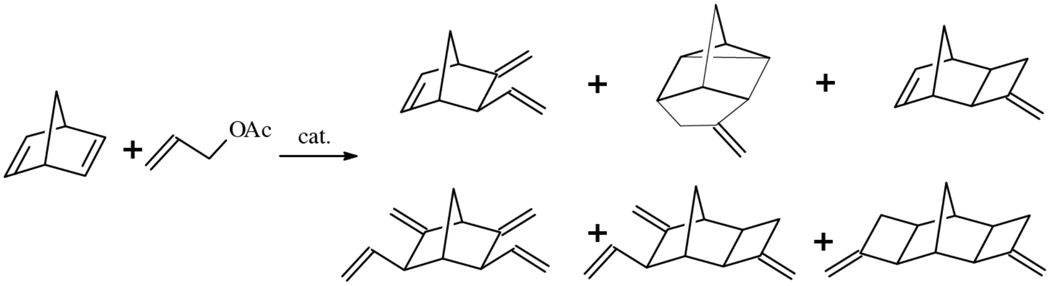
Nonconventional allylation of norbornenes and norbornadiene (NBD) is the unique synthetic method allowing to introduce methylen-, vinyl- and methylenecyclobutane fragments in NBD structure.[1,2]



Phosphite nickel complexes show high catalytic activity and also high regio- and stereoselectivity only in the complete absence of oxygen. Phosphine palladium complexes carry out catalytic process with high parameters in normal conditions.

On the basis of X-ray spectroscopy and kinetic data it was shown, that nickel and palladium have qualitative analogies in this reaction. The effective charge on metal should be in the range from +0.4 up to +0.8. The ratio of stereoisomers and the number of catalytic cycles depends on the metal - ligands ratio.

The reaction mechanism was offered for homogeneous and heterogeneous catalysts.[3] β-Hydride transfer with participation both allylic and NBD fragments was confirmed by isotope methods. Ways of improving of the reaction parameters – usage of non-traditional reaction media (ionic liquids) and claster catalysts – had been investigated.

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Influence of Heterogeneous and Homogeneous Catalysts on the Ring-opening Reaction of 1,2-Epoxydodecane with Acetic Anhydride

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The ring opening reaction of oxiranes to the corresponding alcohols is a useful organic reaction[1] and the acetylation of alcohols is a fundamental process for protecting hydroxyl groups.[2] Therefore to open the epoxide and form the corresponding diacetate compound instead of diol in one step is interesting not only as building blocks, but also as synthetic intermediates.[3]

Ring opening reaction of 1,2-epoxydodecane with acetic anhydride to the corresponding diacetate was studied:

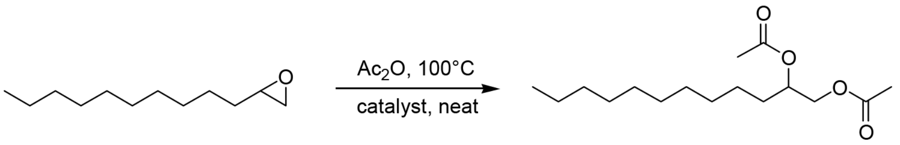

Figure 1. Ring-opening reaction of 1,2-epoxydodecane with acetic anhydride

Quaternary ammonium salts were found to be excellent catalysts for the acetylation reaction of the epoxide with acetic anhydride when their activity was compared to different chloride salts and polymer supported catalysts. After the preliminary studies (optimisation of the conditions) we extended this reaction to other acylating agents like anhydrides and acids which need longer reaction times. Use of other substrates, varies the reaction time as a function of their reactivity.

Since our aim is to find a heterogeneous recyclable catalyst with good activity we explored different acidic and basic catalysts. For better comparison homogeneous (left Table) and heterogeneous (right Table) catalysts were screened as well:

Table 1: Influence of the nature of homogeneous (3h) and heterogeneous (24h) catalyst on the acylation

Catalyst	Yield(%)	Catalyst	Yield(%)
$Bu_4N^+Cl^-$	82	Amberlyst A-26	17
H_3PO_4	55	HY	45
K_2CO_3	58	CaO	57

The environmental benign green character of these reactions is that there is no need for the addition of solvent. Therefore we can work in so called solvent free conditions and the heterogeneous catalysts can be recovered.

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CO Oxidation Reactions on SnO_x/CeO_2 Catalysts: Structure and Catalytic Activity

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The effects of preparation conditions on structural and physicochemical properties of SnO_x/CeO_2 catalysts were investigated by using high resolution transmission electron microscopy (HRTEM), scanning TEM combined with energy dispersive spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD). The catalytic reactions, $CO+O_2$ and CO+NO were performed at atmospheric pressure under gas flow in a specially designed micro reactor with quadrupol mass spectrometry (QMS) detection. A small amount of catalyst (typically 2 mg) was dispersed on a flat, heated 13x13 mm SiO_2/Si(100) wafer substrate. The gas mixture NO(7.5%) + CO(7.5%) + Ar(85%) or CO(7.5%) + O_2(3.75%) + He(88.75%) flowed at a flow rate of 40 ml/min through a 100 μm narrow space over the catalyst. Good thermal contact of catalyst ensured a reliable control of the catalyst temperature permitting to determine activation energies of reactions.

Two types of catalysts were prepared. The CeO_2 nanopowder particles (20-50 nm) were impregnated with tin acetyl acetate dissolved in toluene. The catalyst was calcined in O_2 and then reduced in hydrogen. The second type of catalyst was prepared by impregnating alumina particles or nanoporous alumina flat substrate with tin acetate dissolved in benzene and/or ceria acetate dissolved in water. This catalyst was calcined in O_2 with Ar and then reduced in pure H_2.

The catalysts showed higher activity for NO reduction by CO and CO oxidation reactions relative to pure ceria and tin oxide. XRD showed traces of a tin metallic phase appearing with reduction temperature increase. TEM analysis showed tin oxide particles (2-10 nm) grown on ceria particle surface. XPS study revealed that ceria has a mixed valence character with higher content of the Ce^{3+} phase with higher reduction temperature.

The high catalytic activity of the SnO_x/CeO_2 catalysts might be explained by strong Ce-Sn interaction and Sn-Ce charge transfer that leads to weakening of cerium-oxygen bond and consequently to the formation of oxygen deficient active sites on the ceria surface.

Formation and Structure of Au-TiO$_2$ Nanostructures inside Mesoporous SBA-15

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The Au sol (d=6 nm) derived Au/SiO$_2$ sample decorated by amorphous TiO$_2$ were established to possess enhanced catalytic activity in the CO oxidation compared to the TiO$_2$ (P25) supported analogue.[1,2] The Au/TiO$_2$ nanostructures were aimed at forming in the mesopore system of SBA-15 to mimic the 3D nano-system. Different preparation procedures were used and compared to reach stable, well dispersed system with great Au-TiO$_2$ interface.

SBA-15 was prepared by the hydrothermal treatment of TEOS with P123 block copolymer in acidic media, the template was removed by calcination at 450°C in oxygen for 5 h. 5 wt% TiO$_2$ was introduced by surface hydroxyl initialized hydrolysis of Ti-isopropoxide in anhydrous ethanol under reflux followed by evaporation of liquid, drying and calcination in air at 400°C for 4h (sample denoted by *TiSBA*). Gold was deposited on three different ways using HAuCl$_4$ precursor: (i) by deposition precipitation using Na$_2$CO$_3$ (*AuTiSBA_DP*), (ii) by adsorption of NaBH$_4$ reduced, PVA stabilised Au colloid (*AuTiSBA_PVA*) and (iii) by NaBH$_4$ reduction of Au precursor in presence of PDDA in the suspension of the support (*AuTiSBA_PDDA*). Au/5wt%TiO$_2$/SiO$_2$ reference sample (*AuTiSiO$_2$_DP*) was prepared using high surface area (546 m^2/g) amorphous silica by similar TiO$_2$ introduction and DP of Au. Au/SBA-15 references (*AuSBA_PVA, AuSBA_PDDA*) were made by gold deposition type (ii) and (iii) on SBA-15. The samples were characterized by BET meaurements, transmission electron microscopy (TEM) with EDS and catalytic CO oxidation reaction after 400°C calcination for removal of organic residues.

The original 610 m^2/g surface area of SBA-15 decreased to 556 m^2/g by introduction of TiO$_2$ and the pore size (5.6 nm) did not change significantly. TiO$_2$ could not be detected by XRD and could not be seen on TEM images, either, but according to EDS it was well distributed on the samples. The Au particle size was very similar (5.1-5.6 nm) in case of as prepared *AuTiSBA_DP, AuTiSBA_PDDA* and *AuSBA_PDDA* and was stable during catalytic reaction and the preceding calcination treatment. On the contrary, for the amourphous SiO$_2$ supported *AuTiSiO$_2$_DP* the as prepared Au mean diameter (2.1 nm) increased tremendously (11 nm) during calcination and CO oxidation test. In the sol derived samples (*AuSBA_PVA, AuTiSBA_PVA*) the original Au size was smaller (2.7 nm), while it increased to smaller extent (4.0 nm) during calcination and catalytic test. The activity order in CO oxidation was $AuTiSiO_2\_DP > AuTiSBA\_PVA > AuSBA\_PVA > AuTiSiO_2\_DP > AuTiSBA\_PDDA > AuSBA\_PDDA$. The activity is strongly affected by the length of Au/TiO$_2$ perimeter, formation of that is discussed in terms of the surface charges of the components during the preparation. To sum up, in the SBA-15 the Au particles are more stable resulting in the change in activity.[3]

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Effect of Different Sulfates on the Performance of Sulfated V_2O_5/TiO_2 for the Selective Oxidation of Methanol

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Recently, we found that the conversion of methanol to dimethoxymethane (DMM) over V_2O_5/TiO_2 could be greatly improved by doping with $Ti(SO_4)_2$.[1] In this work, the V_2O_5/TiO_2 and sulfated V_2O_5/TiO_2 catalysts were characterized with different techniques such as XPS, XRD, temperature programmed-reduction (TPR), Raman spectroscopy and microcalorimetric adsorption of ammonium in order to correlate the structural and surface properties of the catalysts with the catalytic behavior.

$Ti(SO_4)_2$, $(NH_4)_2SO_4$ and K_2SO_4 were added respectively into the 10%V_2O_5/TiO_2 and the catalytic results for the oxidation of methanol over the catalysts at 433 K were presented in Table 1. The data showed that great amount of formaldehyde was produced over the V_2O_5/TiO_2 with only 11% selectivity to DMM. The addition of $Ti(SO_4)_2$ or $(NH_4)_2SO_4$ significantly increased the conversion of methanol and selectivity to DMM, while the addition of K_2SO_4 greatly inhibited the oxidation of methanol to DMM. The amount of SO_4^{2-} was only 0.5% or 1.5% in the calcined catalysts when 5% or 10% SO_4^{2-} was added in the form of $Ti(SO_4)_2$, while the amount of SO_4^{2-} in the calcined catalyst was 5% when 5% SO_4^{2-} was added in the form of K_2SO_4. The results of XPS revealed the bidentate sulfate anions (BE (S_{2p})=169.0 eV) in the V_2O_5/TiO_2 doped with $Ti(SO_4)_2$,[2] and K_2SO_4 (BE (S_{2p})=168.4 eV) in V_2O_5/TiO_2 doped with K_2SO_4. The addition of any sulfate did not seem to change the binding energy of V_{2p}. The addition of a sulfate decreased the surface area of the catalyst, especially when K_2SO_4 was added. V_2O_5 was monolayerly dispersed on TiO_2 in the 10% V_2O_5/TiO_2 as indicated by Raman spectroscopy. Crystalline V_2O_5 was found in the sulfated V_2O_5/TiO_2 catalysts as evidenced by the band of Raman shift at 995 cm^{-1}.

The results of microcalorimetric adsorption of NH_3 showed that the number and the strength of surface acid sites were slightly increased by doping with 10%$Ti(SO_4)_2$ for the V_2O_5/TiO_2 catalysts. The TPR profiles of sulfated V_2O_5/TiO_2 were quite different for the catalysts modified with $Ti(SO_4)_2$ and K_2SO_4. The main reduction peak for the V_2O_5/TiO_2 doped with K_2SO_4 was 150 K higher than that doped with $Ti(SO_4)_2$, indicating the decreased redox ability of the catalyst doped with K_2SO_4.

Table 1. Selective oxidation of methanol to DMM at 433 K over 10% V_2O_5/TiO_2 doped with $Ti(SO_4)_2$, $(NH_4)_2SO_4$ and K_2SO_4, respectively[a].

	S_{BET}	MeOH	Selectivity /%				SO_4^{2-} (wt%)		Surface S
Catalyst	$/m^2 \cdot g^{-1}$	conv. /%	DMM	FA[n]	MF[c]	DME[d]	Added	Analyzed[f]	atoms /%[g]
10VTi	92	40.7	10.9	61.1	27.5	0.5	0	0.04	n.d.[h]
10VTi-5$Ti(SO_4)_2$	82	60.0	88.6	1.2	9.8	0.4	5	0.5	n.d.
10VTi-10$Ti(SO_4)_2$	72	64.2	87.5	1.3	10.6	0.6	10	1.5	0.8
10VTi-5$(NH_4)_2SO_4$	N/A[e]	55.8	88.8	1.4	9.3	0.5	5	N/A	N/A
10VTi-5K_2SO_4	42	5.6	35.1	63.1	1.8	0	5	5.2	1.1

[a]Feed conditions: methanol/O_2/N_2=2/6/30 ml·min^{-1}, catalyst loading: 0.2 g. [b]FA=formaldehyde. [c]MF=methyl formate. [d]DME=dimethyl ether. [e]Not available. [f] Analyzed by XRF. [g] by XPS. [h]Not detectable.

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It is Possible to Enhance Both Intrinsic Activity and Enantioselectivity of Single Site Hydrogenation Catalysts by Anchoring: The Case of Ru-MAB Complexes Supported on Mesoporous Silica

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Contrary to the standard belief, supporting a homogeneous single site catalyst has the potential of improving not only the ease of separation, but the intrinsic nature of the catalytic step. This is particularly interesting in the case of chiral catalysis, where the issues of activity and molecular selectivity merge. In a noteworthy example, we reported previously[1] that it was possible to reach >97% of enantiomeric excess during room temperature chiral hydrogenation of the double bond of substrates such as itaconic acid and α-acetamidocinnamic acid, in all cases with a 100% yield. This was accomplished by covalent bonding of a Ruthenium-based organometallic complex containing an amine-based ligand, (S)-6,6'-dimethyl-2,2'-diaminodiphenyl (MAB), to the surface of an MCM-41 material. By comparison, the homogeneous reaction resulted in 65-70% ee.

In order to understand the underlying reason behind this phenomenon, it is necessary to properly characterize the dynamics of the reaction itself, as well as the catalyst. In this work, we report kinetic studies with the homogeneous complex, as well as with the complex supported on MCM-41 or SBA-15. We discuss also detailed characterization studies using MAS-NMR, XAS, FTIR and UV-Vis, together with DFT molecular simulation.

Contrary to what we expected, there was a significant variation in the kinetic behaviour of the catalyst. Use of the complex under homogeneous conditions resulted in a sigmoidal conversion vs. time shape, and an ee of roughly 65-70% depending on the substrate used. By comparison, the tethered chiral catalyst had practically no induction period and followed a first order reaction rate equation with an ee of practically 100%. The ee was constant throughout the reaction. The rate of reaction followed the sequence: (S or R)-MAB-Ru-SBA-15 > (S or R)-MAB-Ru-MCM-41 > homogeneous (S or R)-MAB-Ru complex.

A question that arises is whether or not the structure of the complex is retained during the preparation procedure. In general, this question is not frequently asked or answered in the literature, and it is of importance in order to improve the strategies and to attain high efficiency in the use of expensive complexes, and in order to control the support effect. Characterization of our catalysts with the different techniques mentioned before showed that the structure of the complex was preserved upon anchoring. The analysis of the EXAFS spectra gathered at the Campinas synchrotron in Brazil provided an excellent match between the simulated structures of the homogeneous and supported complexes. The EXAFS simulations were based on the spectra of model compounds coupled with DFT simulations. The spectra of spent catalysts did not show the presence of Ru-Ru bonds, and differed slightly from the spectra of fresh samples, apparently as a result of some changes in the ligand sphere.

To conclude, we present a structural model that explains the observed enhancements in both ee and reactivity as a result of anchoring, and that provides a framework for further use of this effect.

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Immobilization of $MoO_2(OSi(CH_3)_3)_2$ Species in a Ligand-modified Layered Double Hydroxide

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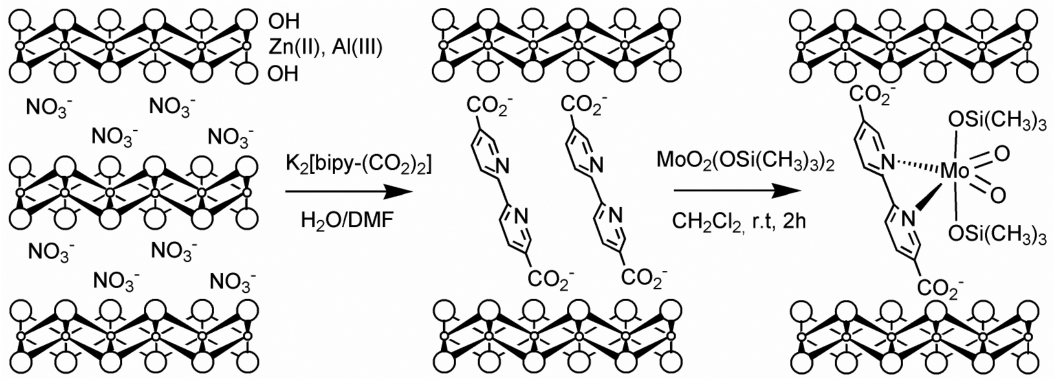
High-valent d^0 transition metal complexes, such as V^{V}, Mo^{VI} and Re^{VII}, have been extensively investigated as catalysts for liquid-phase olefin epoxidation, often employing *tert*-butylhydroperoxide (TBHP) as the oxidant. Despite the good results obtained for oxomolybdenum(VI) complexes in homogeneous catalysis, considerable attention has also been focused on developing heterogeneous catalysts. We recently described the heterogenization of oxomolybdenum species by treatment of a layered double hydroxide (LDH) pillared by 2,2'-bipyridine-5,5'-dicarboxylate (bdc) anions with the complex $MoO_2Cl_2(THF)_2$ [1]. EXAFS studies of the Mo-containing LDH indicated the formation of unidentate-bridged entities of the type $[O_2MoOMoO_2]$ with a metal-metal separation of 3.29 Å. The material was active as a heterogeneous catalyst for the epoxidation of *cis*-cyclooctene, 1-octene and *trans*-2-octene with TBHP, yielding the corresponding epoxides as the only products.

In this communication we describe the application of the LDH pillared by bdc anions as a solid ligand for the immobilization of the dioxomolybdenum(VI) complex $MoO_2(OSi(CH_3)_3)_2$ (Figure). This work was undertaken because it is well known that tetracoordinate complexes of the type $MoO_2(OR)_2$ readily form stable adducts with bidentate Lewis base ligands, giving hexacoordinate (distorted octahedral) complexes such as $MoO_2(Ot\text{-}Bu)_2(bpy)$ and $MoO_2(OSiPh_3)_2(bpy)$ (bpy = 2,2'-bipyridine)[2].



The final hybrid material represented in the Figure has been fully characterized (by powder XRD, Mo K-edge EXAFS, thermal analysis and vibrational spectroscopy) and tested in catalytic olefin epoxidation. The results will be discussed in this communication.

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The Transformations of Donor Ligands During Copper Complexes Catalyzed Organic Reactions

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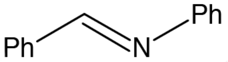
It is established that donor components of catalytically active systems on the basis of copper complexes (such as amines and aminoalcohols) can participate in different stages of radical reactions. The reactions under consideration were as follows: carbon tetrachloride addition to multiple bonds and oxidative coupling of thiols. Mercaptan oxidation in isooctane media can be catalyzed by complexes of copper with donors at the presence of which copper ions exist both in univalent and divalent states. The ligands of that kind are: simple aliphatic and aromatic amines, monoethanolamine. The oxidation of dodecane-1-thiol and pentane-1-thiol in isooctane proceeds with noticeable rate only when there present the excess of the donor ligand. And at the same time cymbate decrease of thiol and donor concentration takes place. The chromatography-mass spectrometry investigation of the system displayed, thatwhile the reaction passes benzylamine mainly converts into the Schiff base (see figure), which forms as the result of amine oxidation by oxygen in the presence of copper ions. If such a reaction doesnt take place thiol oxidation in isooctane doesnt proceed either. Other donors, able to transform in such a way are inactive in catalysis, because they stabilize copper in divalent state selectively. There was no activity also in the presence of donors, capable of reducing copper to univalent state (triphenylphosphine and aliphatic thiol).

Complexes of transition metals with donor ligands are active in carbon tetrachloride addition to alkenes; at that strong donors catalyze the process even at the absence of metal. Aromatic aminoalcohols (the analogues of the nature aminoalcohol ephedrine) were found to be the most active in catalysis. The investigation of the system by means of EPR-spectroscopy and chromatography-mass spectrometry permitted to find out, that the donor ligands in this reaction take part in the stages of chain origin and chain transfer. As the result the process flows rapidly and the selectivity is high. Such a results earlier could be obtained only when metal containing catalysts where used.[1]



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[1] This work was supported by RFBR grant # 06-03-32394-a.

Heterogeneous and Homogeneous Contributions in the Reaction of Total Oxidation of Benzene Using Oxides Type Catalysts Cu-Cr Supported on Al_2O_3+SiO_2

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Supported mixture metal oxide system, Cu-Cr on Al_2O_3+ SiO_2 were prepared and studied. They exhibited catalytic activity in the complete oxidation of benzene in a laboratory installation with continuum flux and the reaction products were chromatographic analyzed.

The utilized reactor was designed specially to simulate the industrial reactors of total oxidation with pre-heating of the reacting mixture but without pre-heating flame. The reaction is initiated in the narrow catalyst layer and is continued in the gas-phase, inside the enclosure having the reaction temperature. The reactor in use is a system made from two series tubular reactors: the first one, catalytic heterogeneous, can operate as a differential reactor (for conversion ≤ 0.1), or as an integral reactor (for conversion >0.1);the second one, non-catalytic, operates as an integral reactor.

The kinetic analysis of contributions: homogeneous or heterogeneous and on the other hand, total oxidation or partial oxidation, to experimental conversion is a complex problem. One can evidence these contributions using a simplifying kinetic analysis. In this analysis we used the following hypothesis, suggested by conversions vs. temperatures plots:

1. For low contact times (high spatial velocities) one can use the ideal tubular reactor model, and the catalytic process contribution prevails.
2. The hypothesis described before is valid even at lower temperatures, where conversions are low too. Looking for a kinetic regime, where catalytic reaction is velocity determinant is justified in this temperature domain.
3. When temperature grows, the diffusion regime might be important. Also, the non-catalytic process can be important, but it might be neglected for low contact times.

The preliminary analysis of the oxidation results is based on the selection of the experimental domains where the assumption of higher importance of the heterogeneous reaction versus the global process is valid.

The homogeneous process contribution to the total conversion is more and more important when the reaction temperature increases.

The differential analysis

The experimental data for low conversion, was used to compute the apparent kinetic constants. The activation energy suggests the dominant process taking place, together with the temperature range: the total oxidation and broking of aromatic cycle of benzene (E= 40Kcal/mol). Obviously, using the integral reactor model for the whole conversion and temperature range can clarify this problem.

Integral analysis

The apparent kinetic constants corresponding to the integral reactor model were computed using Microsoft Excel and suitable equation, based on similar plots and 3-4 experimental points (for low contact time values) for every temperature. The conversion integral was computed using the trapezium method. The activation energy for benzene in the kinetic regime(weak dependence of activation energy on reaction order) is in good agreement with the value obtained from work function measurements.

Recyclable, Magnetic, Solid Acid Catalysts: Sulfonic Acid Functionalized Silica Coated Nanoparticles

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Recent years have seen increased interest in the use of magnetic nanoparticles (MNPs) as catalyst supports. Several advantageous characteristics of the MNPs make them promising candidates as a catalyst support: the ability to be easily dispersed into and recovered from solution, high thermal stability, high surface area to volume ratios, and the capacity for surface modifications.[1] Literature describes several examples of catalyzed reactions via enzymes, transition metal complexes, and organics supported on MNPs. However, no report of MNP supported sulfonic acids exists currently. Four different immobilized sulfonic acids on silica coated MNPs were examined in this work.

Superparamagnetic $CoFe_2O_4$ nanoparticles were prepared[2] and silica coated (SiMNP)[3] according to modified literature procedures. Sulfonic acid functionalities were post-grafted onto the SiMNP via four methods. These include the ring opening of fluorinated sulfonic acid sultones (SiMNP-FSO_3H)[4] and via perfluorosulfonic acid silanes (SiMNP-$SiFSO_3H$).[5] These methods were chosen to highlight a range of electronically diverse sulfonic acids. Attempts to immobilize sulfonic acid sites on non-silica coated MNP via the oxidation of supported thiols were thwarted for various reasons. Upon coating, transmission electron microscopy (TEM) images displayed silica coated aggregates ranging in size from 100 nm to 1 μm. Despite the heterogeneity in particle size, the SiMNP were still suitable for surface modification.

The deprotection of benzaldehyde was chosen as a simple benchmark reaction for evaluation and comparison of the synthesized acid catalysts (Figure 1). The SiMNP-$SiFSO_3H$ catalyst was found to generate the highest rates of the four catalysts, reaching conversions of >95% in under 5 minutes for 1 mol% catalyst and after 60 minutes for 0.1 mol% catalyst. Magnetic recovery tests confirmed surface bound sulfonic acids in three of four cases. The SiMNP-FSO_3H catalyst was found to be inactive upon reuse. This presumably occurred from leaching of the fluorinated sulfonic acid into solution resulting from cleavage of the Si-O-C bond by water present in the reaction mixture. The potential and limitations of the various magnetic, solid acid catalysts and comparisons to other homogeneous and heterogeneous sulfonic acids will be discussed.

This work illustrates the use of a hybrid organic/inorganic catalyst, creating a magnetic, solid acid catalyst. Taking advantage of the ability of MNPs to be dispersed into solution and easily recovered, similar acidic nanoparticle catalysts could potentially be utilized in a variety of organic transformations where diffusion limitations of traditional heterogeneous catalyst supports slow reaction kinetics.

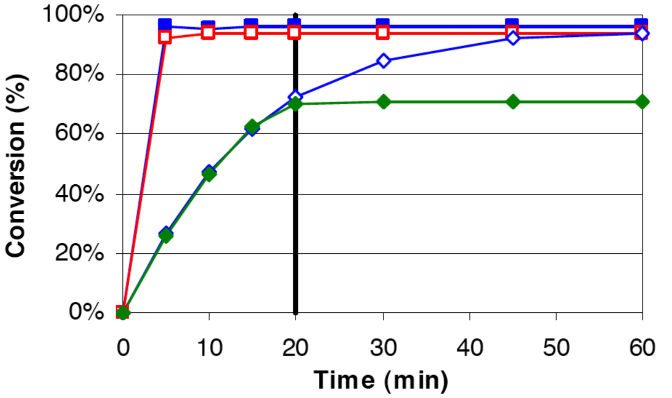

Figure 1 – Reaction conversion data for SiMNP-$SiFSO_3H$ catalyst: initial at 1 mol% (■), recycle at 1 mol% (□), initial at 0.1 mol% (◇), and recovery test at 0.1 mol% (◆).

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Deactivation Mechanisms in Gold Based Low Temperature Water Gas Shift Catalysts

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Although recent results on gold supported CeO_2 based supports[1,2,3] have displayed promising results for the WGS reaction, there is a difficulty in preparing highly active gold catalysts which do not deactivate.[4] For these systems the deactivation has been associated with the formation of carbonates[5] or formates,[6] the sintering of Au[4] and the loss of oxide surface area.[7] However, there has been no consensus, to date. We have demonstrated that the active site of gold in a range of Au/$CeZrO_4$ catalysts is likely to be associated with the interface between gold clusters and the oxide support[3]. The present paper reports on the use of in situ EXAFS, TAP, DRIFTS, high pressure XPS coupled with DFT calculations to elucidate the mechanism by which these highly active Au/$CeZrO_4$ catalysts for low temperature WGS deactivate.

Excellent low temperature WGS activity was found for the 2% Au/$CeZrO_4$ catalysts with the equilibrium conversion reached at 200°C. However, on increasing the WGS reaction temperature above 250°C, significant deactivation was observed with the temperature for 50% conversion rising from 140°C to 220°C. A similar decrease in activity was also observed if the temperature was maintained at 200°C with the catalyst showing a gradual deactivation over a period of 30 h. The rate of deactivation was determined by the water content and under high humidity (>10% water) rapid loss of activity was found. Using a CO multipulse characterization of the catalyst, TAP was employed to study the number of active sites and the rate constants for CO removal. Over the 2% Au/$CeZrO_4$ catalyst the results mimicked the WGS activity results with a large drop from apparent rate constant between 250 and 300°C from 2000 s^{-1} to 1000 s^{-1}.

EXAFS of the fresh catalyst showed that the local structure around the gold is dominated by the presence of oxygen co-ordination at ∼2 Åwhich is consistent with bond distances found in a gold oxide. Additional features at 3-4 Åwere also found and were fitted to cerium co-ordination in the second shell. Under the WGS reaction conditions, the in-situ EXAFS showed that the gold transforms into Au^0 state forming metallic clusters of ∼50 atoms. Importantly, despite the change in activity of the catalyst on thermal cycling no agglomeration of the metal particles was observed and the 1st shell co-ordination remained at ∼6. From the XANES data, on exposure to air at 150°C following WGS at 100°C, significant reoxidation occurred with 15% of the gold found to be reoxidisable. Exposure to higher temperatures under WGS conditions (350°C) followed by exposure to air at 150°C showed that less gold can be reoxidised (<5%). High pressure XPS on the 2% Au/$CeZrO_4$ catalyst under reaction conditions at 150°C and 300°C also showed the presence of Au^0 in good agreement with the XANES. However, at higher temperature a 50% decrease in intensity of the gold 4f XPS peaks was observed. In-situ DRIFTS studies also indicated that the Au^0 is where the CO adsorbs. Under WGS conditions a single band at 2096 cm^{-1} was found which has previously been assigned to a CO-Au^0 species.[8] This feature is found to reduce in intensity with increasing reaction time.

Both thermal and hydrothermal deactivation mechanisms are thought to be the result of the Au particle dewetting and the loss of metal-support interaction. This is in excellent agreement with DFT results which indicate that the presence of surface hydroxyl groups destabilise gold clusters and that, even in the absence of hydroxyls, the gold cluster-support interaction is less favourable than gold-gold interactions.

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Homogeneous Versus Colloidal Effect Using Palladium Catalysts: A Key-lock Matching between Metal, Stabiliser and Substrate

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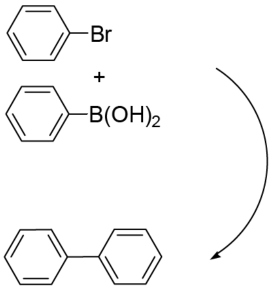
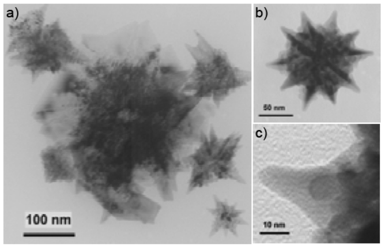
For metal-catalyzed processes, many studies have been reported to establish the true nature of the catalyst. From the point of view of the reactivity, it is more appropriated to classify catalysts as homogeneous or heterogeneous depending on whether the substrate interacts with one or many types of active sites.[1] Recently, tests commonly used to evaluate the nature of the catalyst have been reviewed.[2] However, when metal nanoparticles are involved, it is even more difficult to conclude about the catalyst nature, because they are placed at the frontier between classical homogeneous and heterogeneous catalysts.[3]

In the last years, we have been interested in the study of the catalytic effect of metallic nanoparticles used as catalytic precursors in several processes, like Pd-catalysed C-C bond formation (allylic alkylation,[4] Suzuki coupling[5] or cyclopropanation[6]) and Ru-catalysed arene hydrogenation.[7]

In this communication, an overview of our research concerning the catalytic effect of palladium nanoparticles stabilised by ligands in C-C bond formation processes, will be exhibited. Specific activities and selectivities observed in some reactions allow the distinction between molecular and colloidal nature of the catalytic species involved. In addition, ligand-free nanoparticles stabilised in ionic liquids have led to outstanding catalysts, showing an excellent activity without leaching of metal up to ten recycling runs.



Pd-catalysed Suzuki coupling.



TEM images of Pd dispersed in [BMI][PF$_6$]: a) representative micrograph; b) isolated "star"; c) a "branch" view.

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Supported Ionic Liquid Phase Catalysis on Carbon Nanotubes

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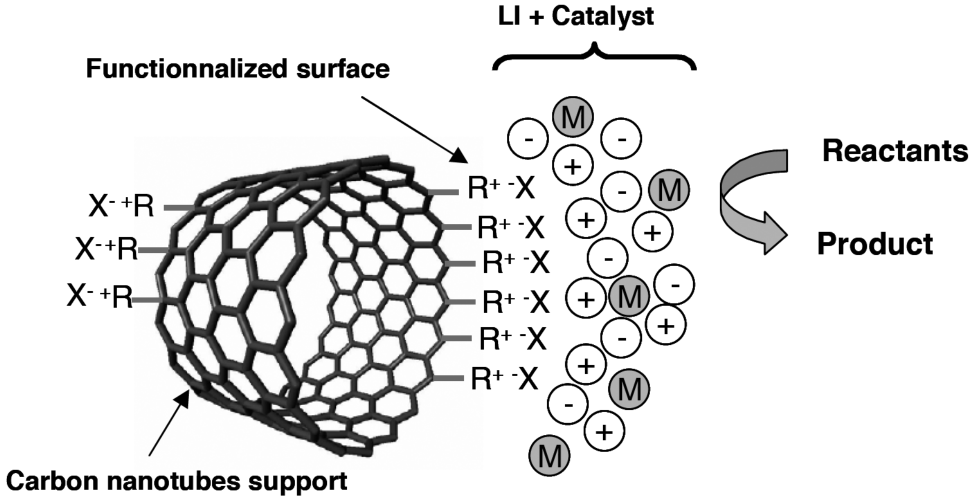
Recently ionic liquids have attracted significant attention in the homogeneous catalysis community as an alternative green reaction medium. Based on their highly charged nature these ionic phases are ideal for biphasic reactions with organic substrates and enable easy catalyst separation. Their ionic character confers to these media a spatial organization on several nanometers that induce peculiar solvation phenomena and specific reactivity which can be linked either to confinement effects in this organized structures or to molecular interactions.[1] However, these solvents remains expensive and the fact to support them should permit to reduce significantly the volumes used and to recover easily the catalyst which will be immobilized in the ionic liquid phase. Up to now, the supported ionic liquid phase catalysis has been performed on classical mesoporous supports such as silica. We will present preliminary results obtained when using multi-walled carbon nanotubes as support. These supports that present a very open macrostructure with large mesoporosity permit to avoid mass transfer limitation in the support porosity and increase reaction kinetics. The following scheme shows the approach we have followed to prepare the catalytic systems: i) carbon nanotubes functionnalization to improve the compatibility with the ionic liquid phase, and ii) stabilization of the catalyst in the ionic liquid phase, this latter forming a film around the nanotubes.



Catalysts preparation and catalytic activity of rhodium based catalysts in a test reaction (hexane hydrogenation) will be presented.

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On the Origin of the High Activity/Selectivity of PtRu/Carbon Nanotubes Catalysts for the Selective Hydrogenation of Cinnamaldehyde

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The increasing needs for catalytic materials for very selective reactions have allowed the development of well defined, nanostructured catalysts. Carbon nanotubes, spearhead of nanotechnologies, have already been successfully used in heterogeneous catalysis, often in hydrogenation reactions. Indeed, carbon materials are currently used in fine chemicals industry to support precious metals for this kind of reaction. Unfortunately, a lack of systematic comparison with traditional activated carbon supported catalysts has to be noted.[1] Additionally, studies dealing with the detailed characterization of catalyst nanoparticle structure, size and composition, characteristics that might influence activity and/or selectivity, are relatively scarce.

The present communication reports the use of multi-walled carbon nanotubes (MWCNTs) as catalyst support for bimetallic Pt-Ru nanoparticles for the selective hydrogenation of cinnamaldehyde, and the characterization of the most active and selective system.

Carbon nanotubes based catalysts (Pt, Ru and Pt-Ru) were prepared and compared to their counterparts on activated carbon for the selective reduction of cinnamaldehyde to its unsaturated alcohol. As MWCNTS surface is not reactive enough, the carbon supports were oxidized prior to metals impregnation, in order to develop oxygen containing surface groups to act as anchoring sites for the precursors. Metals were deposited on the supports by means of a surface organometallic approach, using $[\mathrm{Pt(CH_3)_2}(\eta^4\text{-}\mathrm{C_8H_{12}})]$ and $[\mathrm{Ru}(\eta^4\text{-}\mathrm{C_8H_{12}})(\eta^6\text{-}\mathrm{C_8H_{10}})]$ as precursors. This method allows the preparation of highly dispersed nanoparticles. The use of mesoporous nanostructured support that limits mass transfer limitations allows significantly better activity than microporous activated carbon. As far as selectivity is concerned, monometallic systems supported on activated carbon are more selective towards cinnamyl alcohol formation. However, the use of a Pt-Ru bimetallic system on MWCNTs permits to reach higher selectivities than with the monometallic ones. Finally, we demonstrate that, for MWCNTs supported bimetallic catalysts, high temperatures catalyst activation does promote significantly the selectivity towards cinnamyl alcohol.[2] The role of this high temperature treatment, which may affect the electrical conductivity of the support, the mean particle size, the nanoparticles structure and the cinnamaldehyde equilibrium adsorption will be discussed through a detailed characterization (XPS, WAXS, IR, HTEM, EXAFS) of the catalytic system, in order to rationalize the obtained results.

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Removal of Ag Ions by Selective Wet Etching from Shape Controlled Pt Nanoparticles Leads to Highly Active Hydrogenation Catalysts

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Many recent studies have shown that the shape of metal nanoparticles can be controlled by appropriate selection and concentration of ligand or by addition of foreign molecules or metal ions. Recently, we found that ∼9 nm platinum cubes, cuboctahedra, and octahedra can be synthesized by varying the concentration of silver nitrate.[1] In this reaction, poly(vinylpyrrolidone) (PVP) is the ligand and ethylene glycol is the solvent and reducing agent while silver ions are believed to play a roll in altering the relative growth rates of Pt crystal faces. Shape-dependent catalytic properties were studied by loading the nanoparticles into a mesoporous silica support by a nanoparaticle encapsulation method.[2] The catalysis was found to be dominated by the silver content and therefore shape-related catalytic properties could not be accertained.[3] In order to continue studies with this system and understand the mechanism of shape control, we have developed a method of selectively etching the silver from the Pt-Ag nanoparticles using nitric acid. We find that <15% silver is etched from the nanoparticles by nitric acid concentrations of 6M or less, while >85% of the silver is etched from the particles by nitric acid concentrations of 7M and higher. Turnover frequency (TOF) measurements for ethylene hydrogenation coincide with the etching efficiency; catalysts etched using 6M nitric acid show an increase in TOF from 0.1 to 0.7 while catalysts etched using 7M nitric acid and greater have a TOF >25. The nanoparticles show no change in size or shape as studied by TEM and XRD. The influence of the etching procedure on the nanoparticles and PVP was additionally studied using FTIR and by studying CO bound to the platinum surface by diffuse reflectance FTIR. Shape-dependent catalytic properties are currently being studied using these samples.

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New Efficient Ruthenium Complexes for the Catalytic Murai Reaction

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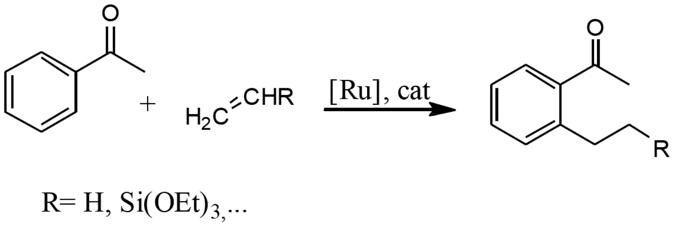
The Murai reaction is one of the best systems to achieve catalytic C-H activation, leading to the fonctionalization of a wide variety of substrates.[1] A representative example is given in the following scheme. Alkene insertion into the C-H aromatic bound is catalyzed by ruthenium complexes.



From the first examples presented by Murai with $RuH_2(PPh_3)_3(CO)$, a few other ruthenium complexes[2] have been tested, but all of them need high temperature for the catalysis to proceed. We have developed ruthenium complexes ($RuH_2(H_2)_2(PR_3)_2$; $PR_3 = PCy_3$, $PCyp_3$), that are able to perform such a reaction under smooth conditions (room temperature).[3,4,5]

In this poster, we will present our last results with a series of ruthenium complexes.[6] In-situ monitoring of the catalytic reaction and stoichiometric studies will allow us to analyze the effect of the different parameters and to discuss the mechanism of this process.

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Structure and Reactivity of Chromocene Confined into Nanovoids with a Different Polarity: From Organometallic Chemistry to Catalysis

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$CrCp_2$ supported on silica, which is a modification of the well known Cr/SiO_2 Phillips catalyst,[1] is highly active in ethylene polymerization (Union Carbide catalyst).[2] The structure of the active sites resulting from the reaction of $CrCp_2$ with the silanol groups of the silica surface, and their reaction with the ethylene monomer are not completely understood. The experimental approach recently applied to give an insight into the structure of the active sites and into the reaction mechanism of the parent Cr/SiO_2 catalyst,[3] does not give the same successful results in the case of the $CrCp_2/SiO_2$ system, whose complexity mainly arises from the tendency of $CrCp_2$ to cluster. For this reason, in fact, the majority of the spectroscopic techniques give information on the dominating but inactive $CrCp_2$ clusters, and not on the grafted and active species.

It is clear that, in order to clarify the structure and the reactivity of $CrCp_2$ and to allow a direct comparison with theoretical calculations, it is necessary to be in presence of molecularly dispersed $CrCp_2$ species. In this contribution we discuss the effect of $CrCp_2$ confinement into the nanovoids of two porous matrices characterized by a different polarity: a nanoporous polystyrene and a Na-Y zeolite. The structural, vibrational and optical properties of molecular $CrCp_2$ hosted inside these two matrices and its reactivity towards different molecules (CO, NO, H_2O, CH_3OH, etc.) is fully characterized by means of several spectroscopic techniques (FTIR, Raman, UV-Vis DRS, EXAFS, etc.) and compared to the theoretical results obtained by DFT calculations, adopting several Hamiltonians (e.g. BP86, B3LYP) and using the Gaussian03 software.

The confined $CrCp_2$ molecules show an enhanced reactivity with respect to the corresponding bulk or with the $CrCp_2$ in solution. As an example, in the $CrCp_2$/PS system, reversible $CrCp_2^{\cdots}(CO)$ complexes are formed in mild conditions (room temperature and PCO = 100-300 Torr), in contrast to the drastic conditions required in toluene solution (below 0°C and PCO = 1-10 bar).[4] The $CrCp_2$ molecules confined inside the ionic environment of the Na-Y zeolite show a much higher reactivity towards CO, in that the $CrCp_2^{\cdots}(CO)$ complexes immediately loose a Cp ring and form tri-carbonyl species stabilized by the zeolitic walls.

The conclusion arising from this work is that the $CrCp_2$/nanoporous systems can be considered as materials having a model character, useful to understand the structure and reactivity of the more complex real $CrCp_2/SiO_2$ catalyst. Finally, these offer a good opportunity to verify the potentialities of DFT calculations in predicting the properties of open shell metallocenes. The here presented approach, the peculiarity of which consists in the possibility to characterize an organometallic complex by working in heterogeneous standard experimental conditions (i.e. without using gaseous matrices or solvents), is an outstanding example of the possibility to connect together organometallic (homogeneous) chemistry with heterogeneous catalysis.[5]

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[5] We thank C. Prestipino, M. Tromp and A. Quadrelli, for the friendly and important help during the EXAFS experiments. The financial support of NoE IDECAT is acknowledged.

Functionalization of High Surface Area Nanoporous Polystyrenes by Means of an Organometallic Approach: New Materials Exploitable for Catalytic Applications

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In the recent years metal-containing polymers are becoming very attractive owing to their possible applications as catalysts for organic synthesis.[1] The vast majority of these systems are microporous polystyrenes (PS) functionalized with several groups and characterized by a very low surface-area, where the reactive sites are accessible to the reactants only upon swelling by the solvent.[2] These systems allow a nominally heterogeneous reaction to proceed in a microscopically homogeneous solution-like environment.[3] Much more challenging is the functionalization of nanoporous macroreticular PSs (usually 20-40% cross-linked), characterized by a very high surface area (501000 m^2g^{-1}) and an open texture with different pore-size distributions. The development of easy methods to immobilize metal species into these polymers, by mantaining in the same time their porous structure, will allow their application to catalytic reactions also in the absence of a swellable solvent. Furthermore, functionalized nanoporous PS with a high surface area could be extremely interesting in the field of H_2 storage, since the transition metal able to adsorb H_2 provides a higher capacity of hydrogen storage in more favorable conditions, with respect to those required by the non- functionalized polymers.[4]

In this contribution we report our first results obtained in the field of functionalization of nanoporous PSs by means of an organometallic approach. Two commercial (Aldrich) nanoporous PSs have been investigated, differing in composition, hydrophilic character and surface area: (i) a poly(4-ethylstyrene-co-divinylbenzene) in the following PS, showing a BET surface area of 1000 m^2g^{-1}, and (ii) a poly(4-vinlypyridine), in the following PS-N, 25% cross-linked with divinylbenzene, showing a surface area of 60 m^2g^{-1}. PS is highly hydrophobic, while in PS-N the presence of the pyridine unit determine its hydrophilic character.

Cr has been successfully incorporated inside PS by a simple chemical vapor deposition method starting from $Cr(CO)_6$, by following an approach similar to that adopted in the preparation of inorganic-organic hybrid materials.[5] FTIR and UV-Vis spectroscopies demonstrate that, by heating $Cr(CO)_6$/PS at 150°C, Cr is immobilized on the benzene groups of the PS in the form of [$(C_6H_6)Cr(CO)_3$] complexes. As $(C_6H_6)Cr(CO)_3$ molecular solid easily sublimate under moderate vacuum, the stability up to 200°C of $(C_6H_6)Cr(CO)_3$ complexes hosted inside the PS nano-cavities is ascribed to a stabilization effect of the hosting matrix. This functionalized PS could be used in the development of unique heterogeneous catalysts, since the arenetricarbonyl complexes exhibit effective catalytic activity for some reactions, such as the hydrogenation of polyunsaturates into cis-unsaturated products.

The PS-N matrix has been successfully functionalized with Cu(II), by impregnation with aqueous solutions of $CuCl_2$ or $Cu(NO_3)_2$. In both cases, the inclusion of Cu strongly perturbed the vibrational properties of the PS-N related with the pyridine groups. The Cu(II) cations inserted from $Cu(NO_3)_2$ precursor are reduced to Cu(I) by treatment in CO (or H_2) at 150°C. As Cu(I) ions hosted in zeolites are able to adsorb H_2 even at RT,[6] the insertion of Cu(I) species inside the lighter PSN hosting matrix can result in a promising H_2 storage material.

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Selective Oxidation of Allylic Alcohols over Platinum Group Metal Catalysts

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The selective oxidation of allylic alcohols to their corresponding aldehydes finds widespread application in the fine chemicals, agrochemicals and food industries in the production of valuable chemical intermediates. Heterogeneous catalysts offer alternative clean chemical technologies for replacing current stoichiometric processes which utilise hazardous oxidants and often generate large quantities of toxic waste.[1]

Carbon and oxide-supported Platinum Group Metals (PGMs) are highly selective catalysts for the direct aerobic selective oxidation of such alcohols, but suffer rapid deactivation on-stream.[2,3] Fundamental issues, such as the nature of the active phase and the origin of such deactivation, remain intensely debated, due to the complexity of the reaction system and lack of detailed operando studies. While a number of sources for this deactivation are proposed in the literature, the most widely debated route concerns the oxidation state and possible over-oxidation of the PGM. For a long time the view has been held that reduced, metallic surface sites are the active phase, and that surface oxidation must be minimised.

Here we present the first systematic study of the relationship between surface oxidation state and catalytic reactivity in the oxidation of crotyl and cinnamyl alcohols over Pd/Al_2O_3 catalysts. Operando EXAFS (Figure 1) and surface sensitive XPS measurements reveal that *highly oxidised Pd nanoparticles* exhibit activities an order of magnitude greater than their metallic counterparts (Figure 2), and that deactivation is accompanied by PdOx *reduction.*[4]

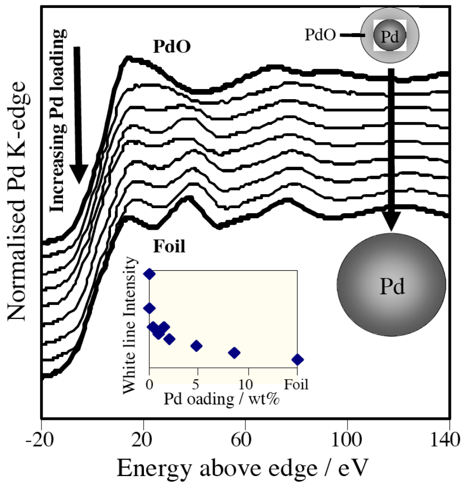

Figure 1: Pd K-edge EXAFS of Pd/Al_2O_3 catalysts as a function of palladium loading.

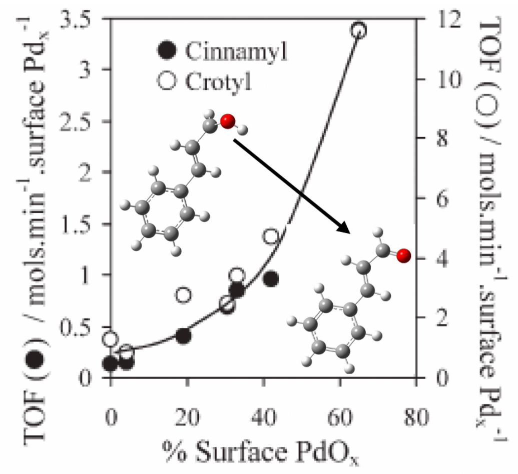

Figure 2: Reaction rate dependence of allylic alcohol oxidation on palladium oxide surface concentration.

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Highly Selective Hydroformylation of Vinylarenes by a Rhodium Complex Entrapped within a Silica Sol-gel Matrix Modified with an Ionic Liquid

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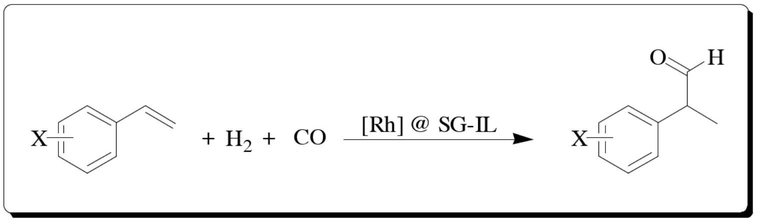
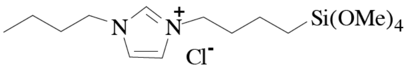
Although the ratio between linear and branched aldehydes formed in the hydroformylation of alkanes can sometimes be tuned by selection of the appropriate catalysts, solvents and reaction conditions, only a few cases have been reported in which either the linear or, in particular the branched produces are formed in a really very high selectivity.[1,2] We have now found that a rhodium catalyst prepared from $Rh(cod)Cl[Ph_2P(3\text{-}C_6H_4SO_3)]^- Na^+$, co-entrapped within a combined silica sol-gel matrix of $Si(OMe)_4$ (TMOS) and the silylated ionic liquid N-butyl-*N*'-(trimethoxysilyl)butylimidiazolium chloride (BTBIC) promotes at 50°C within 12 h, under 7 atm. H_2 and 7 atm. CO, nearly quantitative conversion of styrenes $XC_6H_4CH{=}CH_2$ (where X= NO_2, F, Cl, Br, Me or OMe) as well as 1-vinylnaphthalene, into the respective branched aldehydes in excellent yield and selectivity.

In the absence of the ionic liquid the branched and linear arylpropanals are formed in a non-selective fashion. The reaction was studied in different solvents at a variety of temperatures within matrices of different ratios between the rhodium and the ionic liquid components. The highest selectivity was obtained when the reactions were conducted in *n*-heptane and the molar ratio of TMOS:BTBIC: Rh complex was 25:1:0.054. The immobilized catalyst was recycled at least four times without decrease the catalytic activity and the selectivity.[3]



[Rh] @ SG-IL: $\{Rh(cod)Cl[Ph_2P(3\text{-}C_6H_4SO_3)]^- Na^+\}$ @ silica sol-gel

modified with



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Fixed-Bed Reactor Cascades using Homogeneous Catalysts Immobilized via Supported Ionic Liquid Phase (SILP) Technology

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Homogeneous transition metal catalyst immobilization remains one of the challenges for large scale industrial processes like hydroformylation. The high price of ligand and rhodium metal requires complete catalyst recovery and easy product separation. In the Ruhrchemie/Rhône-Poulenc (RCH/RP) process catalyst immobilization is achieved via aqueous biphasic catalysis. With the aid of ionic liquids the applicability of this elegant separation technique has been extended to higher alkenes. However, mass transport limitations due to low solubility of syngas remain a problem for efficient catalyst utilization.

By dispersing a thin film of a non-volatile ionic liquid catalyst solution onto the high inner surface of a porous material, so called Supported Ionic Liquid Phase (SILP) catalysts are obtained.[1] These SILP systems showed excellent stability and activity in gas-phase propene[2] and butene[3] hydroformylation.

In this work we extend the use of SILP catalyst for the important hydroformylation of Raffinate II, a technical mixture of butenes. With the help of fixed-bed SILP catalysts a reaction sequence has been established in which the internal butenes were isomerized and hydroformylated in two designated reactors as shown in Figure 1.

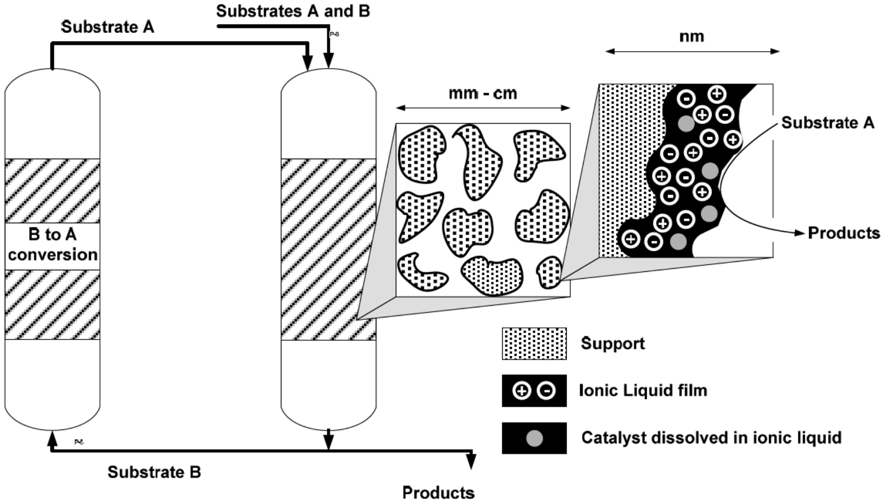

Figure 1. Schematic representation of a novel, fixed-bed SILP catalyzed reaction sequence.

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Ultrasound-assisted Membrane Reaction – A Novel Way to Fabricate Metal Nanoparticles: Application in Nanocatalysts Preparation

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Many attempts have been made in fabricating well-defined metal nanoparticles for their application in many fields. In order to synthesize well-defined monodisperse nanoparticles, control over the nucleation and growth process is essential. In the past year, a promising method, i.e. ultrasound-assisted membrane reaction, has been developed in our laboratory, which is helpful for nucleation and growth process control.

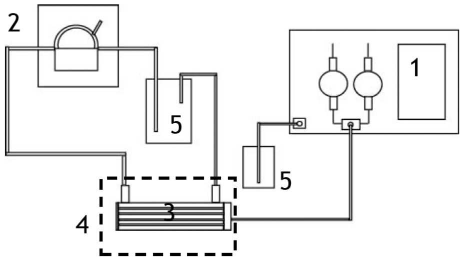

Figure 1. Schematic of experimental apparatus; 1. Constant Fow Pump 2. Peristaltic Pump, 3. Membrane Reactor, 4. Ultrasonic bath, 5. Beaker.

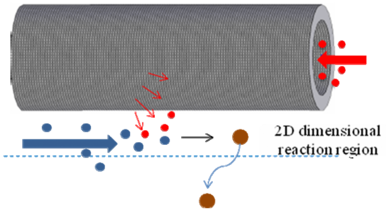

Figure 2. the process of metal nanoparticles generation; red dot: BH_4^-; blue dot: metal ions; brown dot: metal nanoparticles.

Figure 1 demonstrates the setup of the experimental apparatus. Preparation of metal nanoparticles can be carried out as follow: $NaBH_4$ solution with a desired volume and concentration is injected into the lumens of UF membrane microtubes by a constant flow pump. At same time, an aqueous solution of metal ions and poly(*N*-vinyl-2-pyrrolidone) (PVP) is recycled through the membrane reactor, which is dipped in an ultrasonic bath, by a peristaltic pump. As described in Figure 2, when $NaBH_4$ solution diffuses through the microholes of the membrane into tube reactor, metal ions reduction occurs, and metal nanopaticles are generated immediately in the 2D dimensional region that locates near to the outside surface of the membranes, and then the metal nanoparticles can be moved away from the reduction region by ultrasonic force and the growth of metal nanoparticles is hindered, resulting the production of metal particles with considerable uniform size distribution and well-defined boundary. In this process, the reduction rate and concentration of metal ions as well as reductant in the 2D reduction region can be controlled precisely by regulating the flow rates of the two solutions via the constant flow pump and peristaltic pump, respectively.

Upon the novel method, Ag, Pt, Rh, Au, RhAu nanoparticles were synthesized, which showed considerable uniform in particles size distribution and well-defined crystal boundary. The nanocatalysts of Au/TiO_2, $Pt/\gamma\text{-}Al_2O_3$, $Rh/\gamma\text{-}Al_2O_3$, $Rh_{0.5}Au_{0.5}/\gamma\text{-}Al_2O_3$ were also fabricated successfully. The CO+NO reaction and CO oxidation were investigated over some selective samples. The results indicated that the nanocatalysts possess of better catalytic activities than the catalysts prepared by wet impregnation method.

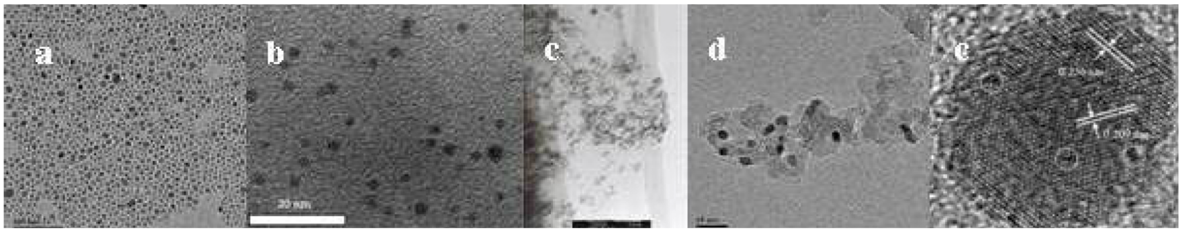

Figure 3. TEM images of Ag (a), Au (b) and Rh (c) nanoparticles and Pt (d) monodisperse nanoparticles on $\gamma\text{-}Al_2O_3$ as well as HRTEM of Ag (C) nanoparticle.

Ultrasound-assisted Membrane Reaction – A Promising Method for Nanocatalyst Preparation: A Comparative Study of Pt (0.5wt%)/γ-Al_2O_3 Nanocatalysts for NO+CO Reaction

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It is well-known that activity and selectivity of catalysts by supported metals on support are strongly dependent on the nature of metal particles, e.g. shape, size, size distribution, and morphology. Conventional preparation based on wet impregnation and chemical reduction often can not provide precise control of metal size and shape. Recently, a promising method, i.e. ultrasound-assisted membrane reaction (UAMR), has been developed in our laboratory, which can generate monodisperse metal nanoparticles in colloid and on supports.

Figure 1 demonstrates the setup of the experimental apparatus. The Pt/γ-Al_2O_3 nanocatalyst was prepared as follow: 50 ml $NaBH_4$ solution with the concentration of 0.028mol L^{-1} in water was injected into the lumens of UF membrane microtubes (= 2 mm) at a constant rate of 1.5 ml min^{-1} by a constant flow pump. At same time, an aqueous slurry containing desired amount of γ-Al_2O_3 powder and H_2PtCl_6 was recycled at the flow rate of 500 ml min^{-1} through the membrane reactor, which was dipped in an ultrasonic bath with the temperature of 40°C, by a peristaltic pump. After the injection of $NaBH_4$ solution, the slurry was filtered, dried at 60°C overnight, and calcined at 550°C in air for 3 h. The reference samples were prepared by the wet impregnation and conventional chemical reduction methods, respectively. Figure 3 represents the TEM images of Pt/γ-Al_2O_3 nanocatalysts. The Pt nanoparticles on γ-Al_2O_3 prepared via UAMR exhibited monodisperse with well-defined size of 3.2±0.4 nm. In the case of conventional chemical reduction, the synthesized Pt nanoparticles showed illegible crystal boundary.When the Pt was loaded on γ-Al_2O_3 by wet impregnation, no distinguishable Pt particles were found. Similarly to the TEM images, the Pt/γ-Al_2O_3 nanocatalysts fabricated via the three routes possessed of different catalytic performance on NO+CO reaction. The light-off temperatures for NO conversion (50%) were 290, 305, and 338°C, indicating the monodisperse of Pt nanoparticles on γ-Al_2O_3 was of benefit to improve the activity of the catalyst. The Pt/γ-Al_2O_3 nanocatalysts were also characterized by XRD, XPS, BET, TPR, and CO-TPD techniques and some meaningful results were obtained.

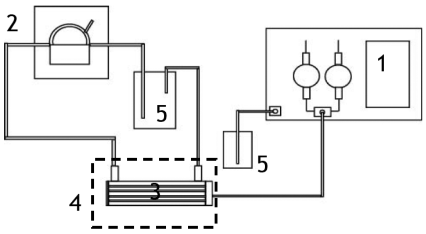

Figure 1. Schematic of experimental apparatus; 1. Constant Flow Pump. 2. Peristaltic Pump, 3. Membrane Reactor, 4. Ultrasonic bath, 5. Beaker.

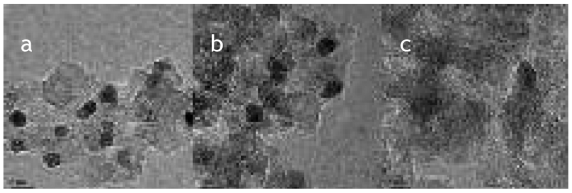

Figure 2. TEM images of Pt/γ-Al_2O_3 nanocatalysts prepared by (a) Ultrasound-assisted Membrane Reaction, (b) conventional chemical reduction, and (c) wet impregnation methods.

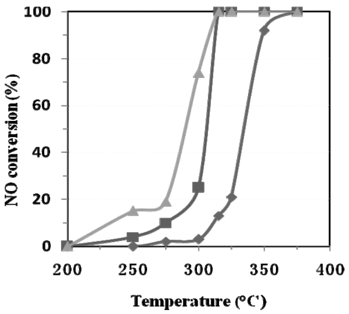

Figure 3. The activity of NO+CO reaction over the Pt/γ-Al_2O_3 nanocatalysts prepared by (▲) Ultrasound-assisted Membrane Reaction, (■) chemical reduction, and (◆) wet impregnation methods.

Sonophotocatalytic Degradation of Methyl Orange in Aqueous Solutions

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Recently, the introduction of ultrasound to assist the photocatalytic degradation process has attracted considerable attention, as the photocatalytic oxidation could be enhanced in the presence of the ultrasonic irradiation. It is well known that the primary radicals produced during cavitation have the potential to decompose organic molecules or the primary intermediates generated during photocatalysis for the degradation of pollutants. This new methodology, sonophotocatalysis (a combination of sonolysis and photocatalysis) is expected to be a better oxidation technique for enhancing the efficiency of environmental remediation process compared to the individual methods.

In our study, the orthogonal array method was adapted to establish the correlation between operation parameters and the performances of sonolysis, photocatalysis and sonophotocatalysis. Our results suggest that the efficiency of sonophotocatalytic degradation is significantly controlled by the frequency, power of the applied acoustic field and the ambient pH of the aqueous solution. The efficiency of degradation is correlated with the rate of production of the highly reactive radicals, which in turn is influenced by the applied ultrasound irradiation; 213kHz and 355kHz are the optimal frequencies for maximum degradation efficiency compared to 647 and 1056kHz. The investigation of pH value effect shows that the pH plays a key role in governing the adsorbed amount of methyl orange on TiO_2.

The chromatographic analysis of methyl orange solutions during sonication showed that there is no significant synergistic feature on the degradation of parent organic compound. However, the synergistic effect of combined oxidation system has been observed in the reduction of the products generated from methyl orange degradation process. Our results also show that the sonophotocatalytic technique is likely to lead to a complete mineralization of organic pollutants in aqueous solutions.

Direct Synthesis of Mesoporous $TiO_2$and its Catalytic Performance in DBT Desulfurization

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Synthesis of mesoporous titanium dioxide materials (TiO_2) with high catalytic activity in dibenzothiophene (DBT) desulfurization was investigated. Phosphotungstic acid (PWA) was used as the catalyst, and a series of different quaternary ammonium bromides were tested as the structure-directing agent. Octadecyltrimethylammonium bromide (STAB) was found to be the best structure-directing agent to obtain the mesoporous structure. The nitrogen adsorption/desorption isotherms exhibit the characteristics of mesoporous structure. The FTIR spectrum and XRD results suggest that there is no indication of PWA crystalline form in TiO_2 materials. TEM results indicate the disordered wormhole-like mesostructure without discernible long-range order is formed by the agglomerization of TiO_2 nanoparticles.

The TiO_2 materials exhibit good performance in DBT oxidation using H_2O_2 (30%) as the oxidant. DBT removal from a 300 ppm DBT mixture was as high as 98%within 2 min reaction with an oil/H_2O_2 volume ratio of 50:1. No DBT removal was detected at the absence of H_2O_2, suggesting that DBT removal was due to the catalytic oxidation rather than adsorptiver emoval. It is estimated that TiO_2 catalysts show good catalytic activity because PWA is introduced into TiO_2 structures rather than existing in free solid acid. The mesoporous structure has remarkable effect on DBT desulfurization. Larger pore volume and pore size will facilitate DBT mass transfer and therefore the rate of DBT oxidation.

Heterogeneous Catalysis by Highly Active Supported Pd for the Heck Reaction

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A series of ligand-free Pd supported on oxide catalysts have been studied toward the Heck coupling of bromobenzene and styrene. The uses of SiO_2 and TiO_2 as supports result in lower Pd leaching. Calcination treatment of Pd compound supported on oxide leads to an unusual catalyst system. PdII/oxide that generates in-situ fine supported Pd particles during the Heck reaction, exhibits incomparable advantages over conventional Pd^0/oxide. The catalytic activities over Pd^{II}/SiO_2 and Pd^{II}/TiO_2 can approach those of homogeneous Pd catalysts. Pd catalyst precursors show a strong effect on the activities of both homogeneous and heterogeneous catalysts. Supported Pd particles display an obvious nano effect on the Heck reaction. The efficiency of the base on the catalysis has the order as $Na_2CO_3 > NaOAc > NaHCO_3 > Ca(OH)_2 > Mg(OH)_2 > NEt_3 > K_3PO_4$. Comparative reaction kinetic studies suggest that in the Heck reaction using either Pd^0/SiO_2 or Pd^{II}/SiO_2 as a pre-catalyst, actual catalysis is dominated by the supported Pd particles in a mixed catalyst system comprising leached Pd in solution and Pd particles supported on SiO_2. Although leached Pd in solution alone even at a low concentration is very active, its catalysis is affected by the presence of the supported Pd particles. At a low concentration of leached Pd, homogeneous catalysis by leached Pd is negligible and the Heck reaction takes place virtually on the supported Pd particles. During the Heck reaction, it seems that leached Pd in solution in a mixed catalyst system acts slightly only at initial stage and does no more in a steady state.

SERS and Gas-Phase Pre-Treatment Studies of PVP-Coated Rhodium and Platinum Nanoparticle Catalysts

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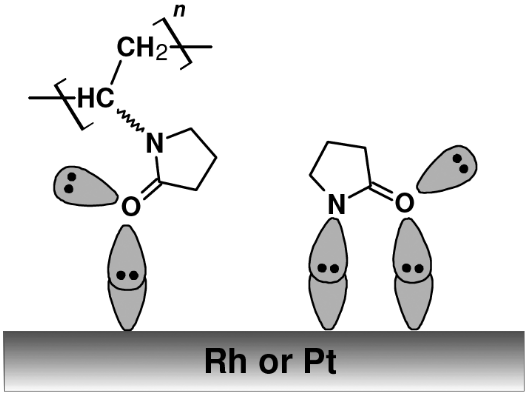
Poly(vinylpyrrolidone) (PVP)-capped platinum and rhodium nanoparticles (2-12nm) prepared by solution-phase syntheses have been studied by Surface-Enhanced Raman Spectroscopy (SERS) to determine the nature of the PVP-M interaction in both the reduced and oxidized states. This reveals a distinct difference in the behavior of the two systems, that may be rationalized based on differences in accessible oxidation states of Pt versus Rh. In addition, degradation of PVP upon gas-phase redox treatment has been observed. The data obtained from SERS studies shows close correlation to the catalytic performance (turnover rates) of the nanoparticle catalysts (supported on SBA-15 mesoporous silica) achieved after reductive, oxidative or mixed pre-treatment conditions. In addition, results from a model pre-treatment study with the pyrrolidinone monomer are also discussed.[1]



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[1] *J. Phys. Chem. C* 111 (2007) 6288.

Mechanochemical Engineering of Nanoparticles to Design, Optimize and Control Catalyst Selectivity

Joe Hutchins, Eric Peterson, Morgan Reed, Dan Rutman, Eddie Gaston, David L. Cocke

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A heterogeneous catalysts performance is critically dependent on the process of its creation. Heterogeneous catalysts are generally created sequentially (ex. synthesis, stabilization, and activation) which require elevated temperatures. Mechanochemistry and mechanochemical processing offer the relatively unexploited potential for the creation of unique catalysts at nearly ambient temperatures for in situ synthesis, stabilization and activation while allowing for the possibility of additional requisite thermal treatments. This approach can offer unrestricted compositions, large surface areas, high surface energies, incorporation of heterogeneous catalysts components and nanostructures that are difficult to achieve by other technologies. Mechanochemistry offers rudimentary approaches to yield metal matrix composites, oxide matrix metal composites, nonmetal catalysts such as refractory compounds (borides, carbides, nitrides, silicides, etc.), intermetallics, bi- and multicomponent alloys, amorphous materials, immobilized homogeneous and enzyme catalysts, and functional composites for a multitude of specific reactions. The relative simplicity of the syntheses of nanostructure model catalytic systems allows both the rapid production and study with systems of modern materials and surface characterization tools. The principles of mechanochemical engineering are outlined with results from recent studies of nanostructured non-metallic and immobilized homogeneous catalyst systems.

Platinum Nanoparticle (Core)- Hollow Porous Carbon (Shell) Composite as A Heterogeneous Catalyst in Hydrogenation Reactions

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Tsukasa Torimoto[‡], Matsumura, Michio[†]

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Studies on syntheses and catalysis of metal nanoparticles (MNPs) have attracted much attention because their specific properties are distinct from bulk metals, e.g., a high surface energy and a high surface-to-volume ratio, leading to inducing unique abilities in organic reactions.[1] These MNP catalysts are usually preserved by organic ligands such as polymers and surfactants to prevent coalescence and used in homogeneous systems similar to the metal complex catalysts. One of the current interests in designing high-performance practical catalysts is the heterogenization of MNPs by fixing them on organic and inorganic solid surfaces. Thus, numerous supported MNPs have been prepared by various methods, e.g., grafting of in situ generated MNPs and adsorption of organic capped MNPs, and have been proved to catalyze a variety of reactions.[2] However, since these supported MNPs are still encountered with inevitable propensity of coalescence as mentioned above, they are also used in the presence of organic stabilizing and/or capping agents in most cases. Our research interest has, therefore, been focused on evaluation of catalytic functions of "naked" MNPs heterogenized by a solid support.

The creation of core-shell structure is a technique to stabilize MNP cores in the solid shell such as carbon and silica without the use of organic ligands. For the use as catalyst, the promising structure in such core-shell approach is achieved by encapsulating a core MNP by a hollow porous shell whose size is larger than the core particle to form a "rattle-type" nanostructure which enables the stabilization of naked core nanoparticles.[3] In the present study, we have fabricated ligand-free platinum nanoparticle of 2 nm in diameter encapsulated in hollow porous carbon shell of 30-40 nm in diameter (Pt@*hm*C) as a typical catalyst (Figure 1).[4] Since the carbon shell not only acts as a barrier to prevent the coalescence between Pt particles but provides a void space where organic transformation occurs on a naked surface of Pt nanoparticle, the Pt@*hm*C particle has found to work as a robust and reusable heterogeneous catalyst for hydrogenation reactions.

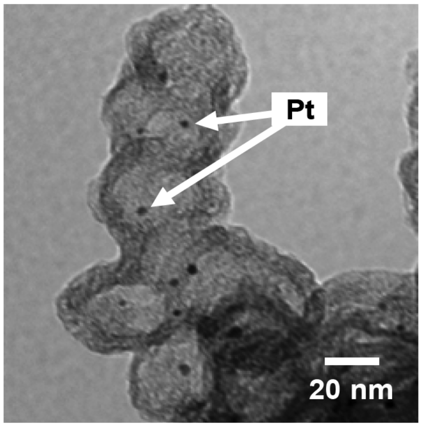

Figure 1. A TEM image of Pt@*hm*C.

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Characterisation and Catalytic Studies of MoV Oxide Catalysts Prepared by Homogeneous Precipitation Method

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Binary MoV oxide catalysts were synthesized using homogeneous precipitation method. The catalyst physicochemical properties were further optimised by adding organic species in the preparation mixture. The synthesized precursors were subsequently calcined at different temperatures. Resulting materials were characterised using X-ray Diffraction (XRD), BET surface area, Thermal Gravimetry Analysis (TGA), Scanning Electron Microscopy (SEM) and Temperature Programmed Reduction in hydrogen (TPR). The catalytic activities of the catalysts were evaluated in a fixed-bed reactor for the selective oxidation of propane to acrylic acid. The specific activity of the catalyst was found increased with ease of reducibility of the catalyst which in turn was strongly affected by the calcination temperature. Addition of organic species further improves the reducing property of the oxides, hence influence the catalytic activity.

Highly Efficient Environmentally Clean Liquid Phase Oxidation of Organic Compounds Using Tetraphenoxy Vanadylphthalocycnine as Recyclable Heterogeneous Catalyst

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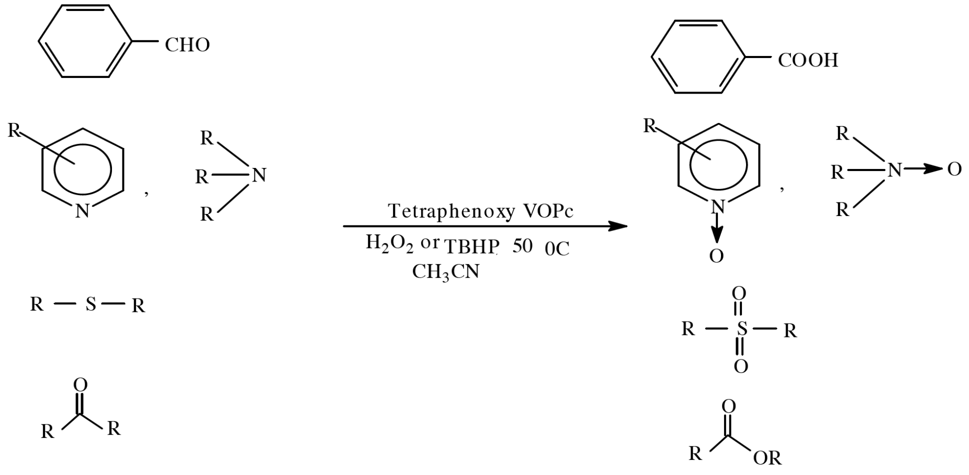
Green chemistry is becoming a powerful tool and replacement of traditional metallic oxidants, which lead to the production of huge amounts of undesirable heavy metal wastes with catalytic processes using clean oxidants like O_2, H_2O_2 and TBHP is gaining increasing interest in present day oxidation chemistry. In particular, heterogeneous catalysts are preferred because of their inherent properties such as ease of separation of catalyst / product from reaction mixture, easy tunability, recyclability and high atom efficiency.[1] Metal phthalocyanines (MPcs), closely related to metal porphyrins in their structural and functional properties, are easily accessible, more stable to degradation than metal porphyrins and have found extensive applications as potential oxidation catalysts in recent years.[2] Being insoluble in common organic solvents they can be easily separated from reaction mixture by simple filtration and reuse with out further activation. Thus metallophthalocyanines behave as heterogeneous catalysts without the inherent limitation of leaching commonly associated with heterogeneous or heterogenized homogeneous catalysts. We report herein for the first time the use of tetraphenoxy vanadylphthalocyanine (VOPc) as an efficient, recyclable heterogeneous catalyst for oxidation of sulfides to sulfones, aldehydes to carbnoxylic acids, tertiary amines to N-oxides and Baeyer-Villiger oxidation of ketones/lactones to esters using hydrogen peroxide (30 wt %), tert. butylhydroperoxide (TBHP) as oxidants in acetonitrile at 50°C under mild reaction conditions.



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Preparation of Au/MO$_x$ Catalysts and Its Performance for Low Temperature CO Oxidation

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In this paper, gold supported on Ni, Co and Zr oxide were prepared respectively. The main aim of the research project was to investigate the properties, structure and state of gold supported on different Co, Ni and Zr oxide materials. BET, XRD, TPR and XPS were employed to evaluate the characteristic behavior of gold nanoparticles in various materials and CO catalytic oxidation was taken as the probe reaction.

Results and discussion. The property of the support influence the catalytic activity. The catalytic activity sequence was as follows: Au/a-Co_3O_4 > Au/Co_3O_4 > Au/a-NiO > Au/NiO > Au/ZrO_2 > Au/a-ZrO_2. Moreover, the gold supported on the uncalcined supports showed higher activity than that on corresponding calcined supports for Co and Ni based catalyst, which was similar to the result of Au/TiO_2 and Au/CeO_2 we have studied before. However, it was different for Zr based catalyst.

No reflections of gold could be detected at $2\theta=38.2, 44.4^\circ$ over all these catalysts from XRD results, indicating that the corresponding gold particles are too small to be detected by the instrument. For Co and Ni based catalyst, the difference between the gold supported on calcined and uncalcined supports, just lie in the particle size of support and surface area. However, for Au/ZrO_2 catalyst, the catalyst from the uncalcined support showed amorphous ZrO_2 and the catalyst from the calcined support showed tetragonal ZrO_2 phase and the result suggest that tetragonal ZrO_2 phase seem to be more benefit for improving activity than amorphous phase.

All the TPR in the examined temperature range results demonstrate that with the gold addition, the reduction occurs to low temperature. It is also found the temperature of reduction peak is related to the catalyst activity XPS result.indicated that Au^+ and Au^0 may coexist in all these catalysts and ionic gold was important in the reaction.[1]

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[1] This work is financially supported by the National Natural Science Foundation of China (20563003 and Natural Science Foundation of Inner Mongolia (200508010203).

Methods to Assess Leaching of Active Palladium from Immobilized Molecular Catalysts in Heck and Suzuki Couplings

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Palladium is ubiquitous as a catalyst in the development and synthesis of active pharmaceutical ingredients. A large number of supports and immobilization strategies have been employed to aid palladium recovery. In most cases, these solid precatalysts are assumed to act as active, heterogeneous catalysts. However, rarely are specific tests to elucidate the nature of the active species undertaken and in cases when they are used, relatively ambiguous methods, such as hot filtration tests and comparisons of reaction yields upon catalyst recycle are most often employed. There is a growing consensus that the majority of catalysis from immobilized palladium is actually from leached metal in Heck catalysis, which is usually determined after more rigorous testing has been employed.[1,2,3,4,5]

Herein we present an examination of several recently reported heterogeneous palladium pre-catalysts for Heck and Suzuki couplings. These include Pd-EnCat[6] and Pd(II) salts immobilized on alkylthiol-modified supports.[7,8,9] Our new data, when combined with previous reports, suggest that catalysis is predominantly and perhaps solely from leached metal and no definitive evidence is found for catalysis by palladium species immobilized on an alkylthiol surface or within an encapsulating polymer particle.[10,11] We also demonstrate how organic modified supports can be used as selective metal poisons, which can be used as a tool in the assessment of the presence of heterogeneous palladium catalysis.

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Oxidation of Higher Aliphatic Hydrocarbon, *n*-Hexadecane with Ozone using Various Catalyst Materials

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The selective oxidation of alkanes at room temperature and pressure conditions is one of the most important objectives of organic chemistry. Saturated hydrocarbons, alkanes, are known to exhibit very low reactivity with variety of reagents and reactivity could enhance only under high temperature and pressure conditions. The oxidation of higher alkanes is studied with at moderate reaction conditions with ozone, in the presence of various supported catalysts and zeolite materials impregnated with different cations to enhance the selectivity and extent of conversion during the oxidative ozonation of higher aliphatic hydrocarbon *n*-hexadecane, *n*-tetradecane and *n*-dodecane is investigated. Effective oxidation of the three higher hydrocarbons was achieved at (20 ± 1°C) and normal pressure conditions. The results of oxidation of higher aliphatic hydrocarbon, *n*-hexadecane with ozone are reported. The major reaction products are different aliphatic ketones with same carbon number and organic acids in little amounts, where oxygen is introduced into carbonaceous site within the product molecule, are 4-, 3- and 2-hexadecanones. The catalytic activities of different combination materials are compared with uncatalysed reactions.

Preparation and Characterization of Supported-Rh Catalysts for Ethylene Hydroformylation

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Hydroformylation is an important industrial process for the production of oxygen containing compounds, such as aldehyde, alcohol, diol and others from olefin compounds. It is known that the homogeneous rhodium catalysts derived from rhodium-ligand compounds show high activities in hydroformylation reactions. The use of homogeneous catalysts in the processes has disadvantages, such as separation problem, which need another equipment and difficulty in continuous process. Thus, many researchers recently have made effort to develop heterogeneous catalysts for the use in hydroformylation of olefins. Especially, many improved-results have been reported, regarding active metal compounds. However, support materials also are an important and essential element on catalytic reactions. In this work, a series of supported-Rh catalysts were prepared using a variety of supports and catalytic activity was examined for the use in the ethylene hydroformylation. The catalysts prepared were characterized by XRD, TPR, TPD and TEM. Results showed that the characteristics and catalytic activities of Rh catalysts were dramatically changed with the changes in the types of catalyst supports. This work provides a basis for the design and use of Rh-based catalysts as a heterogeneous catalyst for the olefin hydroformylation reactions.

Synthesis of 2-Adamantanone from 1-Adamantanol over Solid Heteropolyacids

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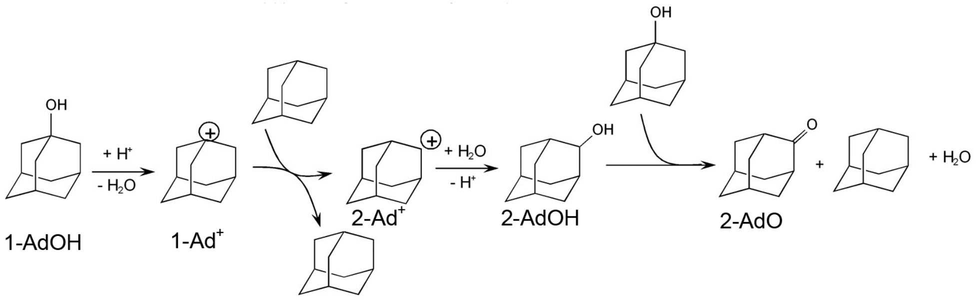
While 2-adamantanone is a useful raw material for photoresist materials, traditional process involving a transformation of 1-adamantanol (1-AdOH) into 2-adamantanone (2-AdO) using sulfuric acid as a catalyst is environmentally harmful. We herein report the environmentally benign synthesis of 2-AdO from 1-AdOH over solid heteropolyacids.

The synthesis of 2-AdO was conducted in a batch type reactor. A mixture of 1-AdOH (2.5 mmol), adamantane (AdH, 2.5 mmol), propionic acid (10 cm^3), and catalyst (0.5 g) was heated with stirring at 393 K for 4 h. The products were analyzed with an FID-GC.

Zeolites (H-BEA, H-MFI, and H-MOR), ion-exchange resin (Amberlyst 15 and Nafion-H), and SiO_2-Al_2O_3 were inactive for the formation of 2-AdO, while 1-adamantyl propanoate was formed. Supported heteropolyacid (40wt% $H_4SiW_{12}O_{40}/SiO_2$) and its Cs salt ($Cs_{2.5}H_{1.5}SiW_{12}O_{40}$) were also inactive. In contrast, unsupported solid heteropolyacids, $H_4SiW_{12}O_{40}$, and $H_3PW_{12}O_{40}$, gave 2-AdO with moderate yield. It is known that the reaction of polar molecules in the presence of a solid heteropolyacid catalyst proceed in the bulk phase, which is called pseudoliquid phase behavior. The results that 2-AdO was formed over only solid heteropolyacids indicate that the reaction took place in the bulk phase of the heteropolyacid.

In the absence of AdH, yield of 2-AdO was 14% over $H_4SiW_{12}O_{40}$. The addition of AdH enhanced the yield and the maximum yield (23%) was obtained at AdH/1-AdOH = 2. Hydride transfer from 1-adamantyl cation (1-Ad^+) to 2-adamantyl cation (2-Ad^+) is suggested to be a rate determining step[1]. The hydride transfer from AdH to 1-Ad^+ took place, which lead to the promotion of 2-Ad^+ formation (Figure 1), comparing with the reaction in the absence of AdH. This would result in the enhancement of the yield of 2-AdO when AdH was added in the reaction mixture.[2]



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Surface Studies on Supported Silver Catalysts Used for Ethylene Oxidation

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Silver is a unique catalyst for the oxidation of ethylene to ethylene oxide. The commercial catalyst usually consists of silver supported on alumina carrier of low surface area (< 1 m^2/gm), promoted by alkali, alkali metal and chloride ion from Ethylene Di-Chloride (EDC) feed which may interact near the top surface. As catalysis is a surface phenomenon, surface sensitive analytical technique ESCA has been used for Characterization of ethylene oxidation catalysts in fresh, used and spent forms. The study has been aimed at:

a) Estimation of silver dispersion on alumina support to identify a catalyst with best silver dispersion from a set of fresh catalysts
b) Identification of surface promoters used for improved performance of these catalysts
c) Identification of process contaminations on catalyst surface to look for possible reasons of underperformance of catalysts and
d) Identifying reasons of catalyst deactivation on its use in ethylene oxidation reaction.

This surface study may be helpful in selection of best catalyst for ethylene oxidation reaction, identifying few precautions in normal operation of a catalyst, understanding performance variations in catalysts including possible reasons of catalyst deactivation on its continuous use and also in development of improved catalyst.

Cobalt-Functionalised Mesoporous Silica Using Ionic Liquids – One-Pot Synthesis and Catalysis

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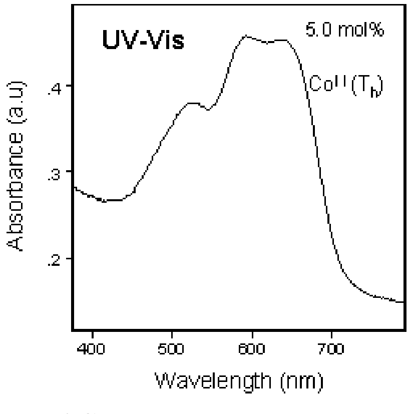
The ionic liquid 1-hexadecyl-3-methylimidazolium bromide has been utilized by Wang *et al*[1] as a templating agent in the synthesis of mesoporous silica. In the present study, we investigate the scope of the ionic liquid to act simultaneously as the template, directing the formation of the mesoporous silica, and as a ligand, stabilizing metal ions to be incorporated during the gel phase in a similar manner to that reported earlier.[2]

In particular, we studied the incorporation of Co^{2+} species. As such Co/silica materials hold great promise as heterogeneous oxidation catalysts for the conversion of cyclohexane to cyclohexanol and cyclohexanone.[3,4] One of the principle issues with this type of catalyst is that of selectivity and leaching, both thought to be negatively affected by extraframework cobalt species[3]. Thus, the target of our investigation was to probe if the ionic liquid could prevent or suppress the formation of such species.

The materials synthesized have been fully characterized using XRD, UV-Vis, N_2 adsorption-desorption measurements, HR-TEM and elemental analyses. They were found to have average pore sizes of 4.6 nm, pore volumes from 0.54 - 0.83 cm^3/g and surface areas from 515 - 708 m^2/g. UV-Vis analyses indicate that the cobalt ions have been incorporated into the framework after calcination (even at 5 mol% Co), as illustrated by the UV-Vis spectrum – a spectrum typical of tetrahedrally coordinated cobalt ions.[5] A very unusual result for such high metal loadings.

Following the procedure of Anand et al[3], the catalytic performances of the materials were tested in the liquid phase oxidation of cyclohexane under an inert atmosphere using t-butyl hydroperoxide as the initiator and oxidant for the reaction (65 mol% cyclohexane and 35 mol% TBHP). Using a mesoporous Co-silicate (0.4 mol% of Co) a conversion of 12% and a selectivity of >90% for the mono-oxygenated products and <4% for the diacids was obtained over a period of 6 hours at 70°C. The Co-silicate materials presented here perform better in terms of conversion and selectivity towards mono-oxygenated products than previously reported Co-silicates (conversion 8%, selectivity 89%)[3].



UV-Vis spectrum of Co-silicate sample with 5mol% Co content

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Supported Catalysts Prepared by Atomic Layer Deposition, Impregnation and Organometallic Method: Raman Spectroscopic Difference

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The membrane catalysts, produced by a combination of anodic aluminum oxidation (AAO) and atomic layer deposition (ALD) consist of an assembly of identical pores having nanometer dimensions.[1,2] With this assembly, each reagent molecule traverses highly aligned, parallel pores with narrow porediameter distributions. A variety of catalytic active species (e.g., VO_x) and support materials (e.g., Al_2O_3, TiO_2, Nb_2O_5) can be incorporated on the surface of the pore walls.

Nanostructured membrane catalysts generally show better catalytic performance than the standard powder catalysts prepared by the impregnation method. Among the membrane catalysts, the VO_x/TiO_2/AAO membrane catalyst showed higher activity than the VO_x/Al_2O_3/AAO or VO_x/Nb_2O_5/AAO catalyst in the Oxidative Dehydrogenation (ODH) of propane. However, the VO_x/Al_2O_3/AAO catalyst showed the highest selectivity to propylene than the other catalysts, suggesting that the nature of the oxide support significantly affects the activity and selectivity. And, 1-monolayer (1-ML) VO_x/TiO_2/AAO membrane catalyst where 1-ML VO_x was prepared by organometallic method (precursor: $[(\mu\text{-}\eta^3\text{- } C_5Me_5O_3)VO]_2$) showed higher selectivity to cyclehexene from cyclohexane than other 1-ML VO_x/TiO_2/AAO membrane catalysts where the VO_x were prepared by ALD or impregnation method.

The structure of the (catalytically active) surface species on the support could be rather different when a different support is used. And, the structure (or the crystalline phase) of the support prepared by ALD could also be quite different from that of the typical support (e.g., γ-alumina, anatase TiO_2, etc.) despite of the same composition of the support. These two factors are the main reasons for the difference in catalytic performance between the different preparation methods.

To understand the difference in the structure of the surface species and the support affecting the catalytic activity and selectivity, we have been using multiwavelength Raman or Resonance Raman spectroscopy. The ability to select the excitation wavelength in Raman spectroscopy makes it possible to control the species detected by avoiding or taking advantage of the resonance enhancement effect as well as to minimize fluorescence interference. Here we present Raman spectroscopic difference on the surface vanadia and the support when are prepared differently: (1) ALD, (2) the wet-impregnation, and (3) the organometallic method.

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Preparation and Characterization of Copper Oxide/Alumina-ceria Catalysts for the Preferential Oxidation of Carbon Monoxide

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Hydrogen is well known to be a potential candidate for an alternative energy source. Many of researches for the use of hydrogen as a fuel have been focused on the use of proton exchange membrane fuel cell. However, safety and storage of hydrogen should be considered for the commercial application. Thus, as an alternative way, hydrogen could be generated from natural gas, gasoline or alcohols using a reformer. In case of hydrogen production using a reformer, a significant amount of carbon monoxide (CO) is produced as a by-product with hydrogen. CO partially converts to carbon dioxide via water gas shift (WGS) reaction. However, thermodynamically it is difficult to reduce the concentration of CO below 0.5% via WGS reaction. This amount of CO is still high because the common fuel cell catalyst (Pt) is easily poisoned by CO. CO can be removed by the preferential oxidation process. In this work, we prepared a series of copper oxide/alumina-ceria catalysts with change in loading amount of copper oxide and ceria for the preferential oxidation of CO and evaluated the characteristics and activities of prepared catalysts. Results showed that the catalyst activity was increased with the increase in the loading amount of copper oxide and ceria up to certain points. However, catalysts with excess loading of copper oxide and ceria showed low activity due to the destruction of catalyst structure and decrease in metal dispersion. For the preparation of catalysts, the single step method was used. It has advantages, such as well-dispersed metal particles with simple preparation process. Interestingly, the catalysts prepared here showed higher surface area and better metal dispersion than those of catalysts prepared by impregnation method.

Design and Catalysis of a Coordinatively Unsaturated Ru Complex Catalyst Supported on SiO_2 for Selective Oxidation of Aldehydes

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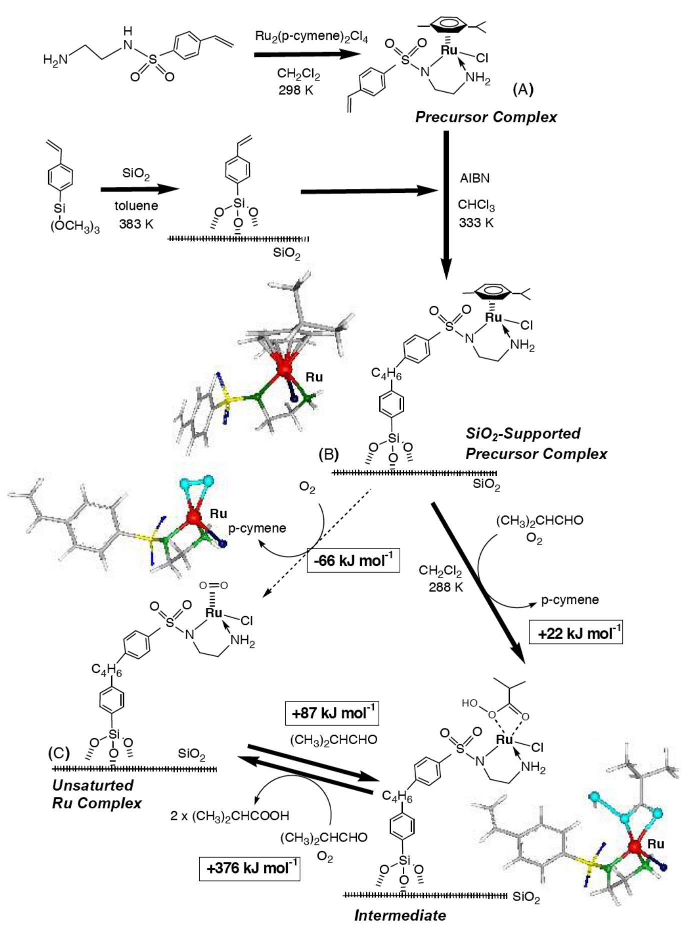
Immobilization of metal complexes on support surfaces is still the state of the art in the assimilative field between homogeneous and heterogeneous catalysis. The potential of immobilized metal-complex catalysts remarkably interplays with the nature of support surface resulting in significant rate enhancements and novel catalytic performances that homogeneous analogue complexes do not exhibit. We succeeded in preparing a novel unsaturated Rudiamine complex on a SiO_2 surface. A p-cymene ligand of the supported Ru complex was selectively removed by isobutyraldehyde (IBA) and the obtained coordinatively-unsaturated Ru-monomer complex exhibited good catalytic performances for the selective oxidation of aldehydes.

A SiO_2-supported Ru complex was prepared in three steps as illustrated in Scheme 1. A Ru-monomer precursor (A) was synthesized by *N*-surfonyl-1,2-ethylenediamine and $Ru_2(p\text{-cymene})_2Cl_4$. A SiO_2 surface was modified with *p*-styryltrimethoxysilane and its styryl moiety was reacted with (A) with a styryl group at the surface, forming an supported Ru complex (B) with a saturated Ru center coordinated with a *p*-cymene ligand (Scheme 1). The immobilized Ru complex (B) converted to an active unsaturated complex (C) in the presence of IBA and O_2. The structures of the supported Ru complexes were characterized by means of solid-state NMR, XPS, FT-IR, DR-UV/VIS, XRF, XAFS, and DFT calculations. The elimination of the coordinated *p*-cymene ligand stoichiometrically proceeded at the surface, and the obtained unsaturated Ru complex was stable in air. DFT calculations showed that the exothermic reaction mechanism for the selective elimination of the *p*-cymene ligand from the Ru site as shown in Scheme 1.

The selective oxidation of various aldehydes to corresponding carboxylic acids was examined at 288 K in CH_2Cl_2 under an atmospheric pressure of O_2. While homogenous complex (A) had no catalytic activity, the unsaturated Ru complex on SiO_2 (C) exhibited high activity and selectivity for the selective oxidation at 288 K. The relationship between the active structure at the surface and the catalytic performance for the selective oxidation will be presented.



Catalysts Based on Electrically Conducting Polymer Polyaniline: Tunable Selectivity in the Selective Hydrogenation of the α,β-unsaturated Aldehyde Citral

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Electrically conducting polymers (ECP) perpetually fascinate scientists for their unique electronic, optic and magnetic properties;[1] utilization in catalysis, however, is scarcely reported.[2] Conductivity in these materials is provided by electrons; in the case of polyaniline (PANI), its electric behavior is determined by the set of different substructures, which contain defined fractions of optionally protonated benzenoid or quinonoid blocks (fig. 1).

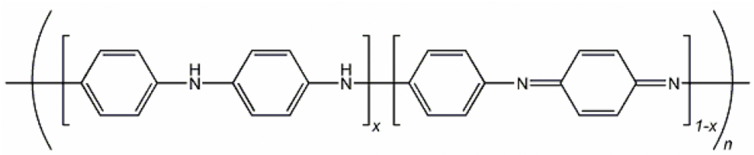

Figure 1. General structure of polyaniline.

The achievement of high selectivities (typical for homogeneous catalysts) remains a challenge in preparation of heterogeneous catalysts.[3] Ambitious model reactions for investigation of new catalysts can be found in fine chemistry, especially in hydrogenation of citral, which can undergo transformation of its C=O- or the conjugated C=C-double bond forming citronellal or geraniol/nerol (fig. 2), while further hydrogenation leads to citronellol. As was shown earlier for cinnamaldehyde hydrogenation, influence of supports like graphite can foster formation of allylic alcohols even over Pt catalysts, and the phenomenon was described as a macroligand effect exerted by the support surface.[4] Applying two different preparation routes, we are now able to synthesize PANI supported Pt catalysts exhibiting complementary selectivity in citral hydrogenation by using the aforementioned macroligand concept. Immobilization of a preformed Pt sol affords a catalyst which produces mainly geraniol/nerol (S = 78%), the reason of which we ascribe to an electronic effect of the PANI support. At the same degree of conversion, the catalyst prepared by a deposition-precipitation-reduction (DPR) route affords mainly citronellal (S = 87%). Determined by TEM and XPS, the DPR catalyst consists of molecularly dispersed Pt species comparable to an immobilized homogeneous catalyst. Analogous investigations performed with gold[5] suggest that the described preparation concept can be expanded to other precious metals.

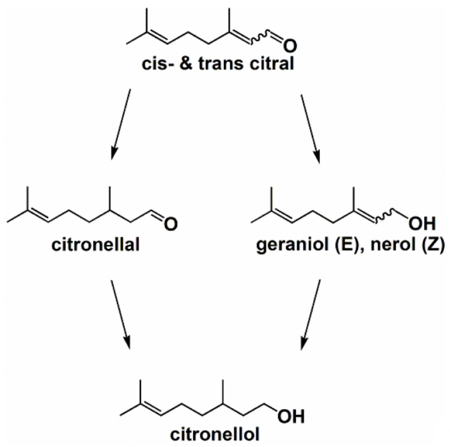

Figure 2. Simplified reaction network for citral hydrogenation.

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[4] P. Gallezot, D. Richard, *Catal. Rev. Sci. Eng.* 40 (1998) 81.

[5] F. Klasovsky, M. Steffan, J. Arras, P. Claus, *Chem. Commun.* (2007), submitted.

Supramolecular Strategies for Easy Recovery and Recycling of Homogeneous Catalysts

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The phenomenal growth of both population and prosperity levels world-wide is gradually leading to an increase in the demand for energy and consumer goods. The results of a number of studies have led to the conclusion that this growth can only continue on the long-term if in the next fifty years we improve a factor of twenty in efficiency on the use of resources, space and the environment. Chemistry in general, and catalysis in particular, is an important key to attain this improvement. Especially the production of fine chemicals generally entails the production of vast quantities of waste, and in these processes homogeneous transition metal catalysts, along with organocatalysis and enzyme technology, should play a key role in future processes.

We have been working on supramolecular strategies to make novel catalysts and to simplify catalyst recovery.[1] In this lecture we will elaborate on supramolecular catalyst recovery strategies developed in our lab. We recently reported the anchoring of transition metal catalyst to support by supramolecular interactions.[2] Dendrimers and silica materials with defined binding sites selectively bind guest molecules that are equipped with the complementary binding motif. In addition, these materials are also ideally suited for novel concepts such as reversed flow adsorption[3] This involves a concept in which the catalyst is reversibly adsorbed to a bed of adsorbent, enabling the easy separation between catalyst and products thereby avoiding tedious and waste-producing cleaning processes. Furthermore, the generic character of anchoring catalysts allows easy combination of currently non-compatible (bio, organo- and transition metal) catalysts, transforming them into powerful teams able to operate in one pot.

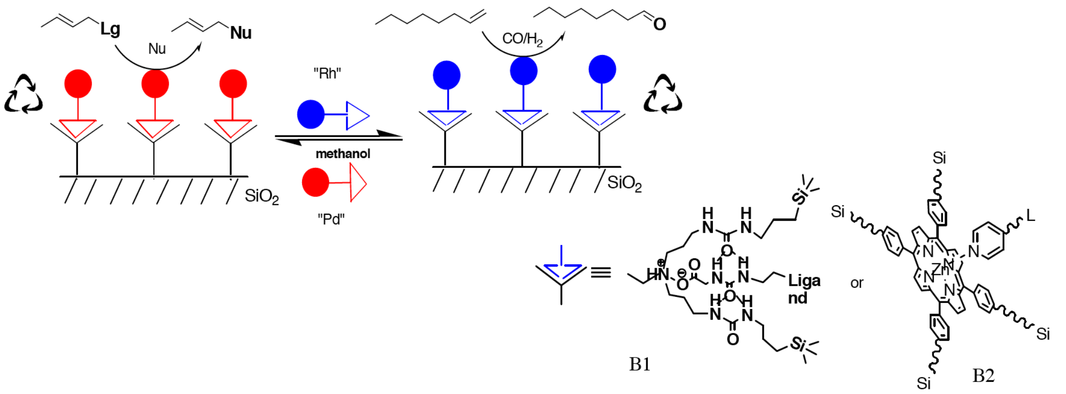

Figure 1. The concept of supramolecular anchoring

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Design and Stability of Surface Alloys for the Water-Gas-Shift Reaction

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Clean, cheap and efficient production of high-purity hydrogen is an essential prerequisite for the emerging hydrogen economy. The vast majority of the present hydrogen production comes from catalytic conversion of fossil fuel, which relies heavily on the Water-Gas-Shift (WGS) reaction:

$$H_2O + CO \rightarrow H_2 + CO_2$$

Here[1] we synthesize and characterize a new Cu/Pt(111) near-surface alloy which is found to be a promising candidate for an improved WGS-catalyst. In addition we use high-pressure Scanning tunneling microscopy (HP-STM) to examine the stability of this new Cu/Pt(111) near-surface alloy.

From the interplay of Scanning tunneling microscopy (STM), X-ray Photoelectron Spectroscopy (XPS), and Density functional theory (DFT) we show that a thermodynamically stable Cu/Pt NSA, with Cu preferentially located in the first subsurface layer, is formed upon evaporation of 1 ML of Cu onto Pt (111) at 800 K. Temperature-programmed desorption (TPD) and DFT studies show that the potential for CO poisoning of the Cu/Pt NSA is reduced compared to pure Pt. Furthermore we use DFT to analyze trends in catalytic activation of water, which is the rate-determining step for the WGS on several metal surfaces, and the binding of formate, a common spectator species blocking sites on Cu WGS catalysts. Very interestingly, OH-groups and formate is most weakly bound on our new Cu/Pt(111)-NSA and we thus expect a higher WGS-activity on this alloy. It is therefore, very likely that real Cu/Pt near-surface particles could be used as new and improved catalysts for the WGS reaction.

The WGS-reaction proceeds in high pressure of CO and it is therefore important to study the Cu/Pt(111)-NSA's stability in CO. Here we use fast scanning STM experiments in a high CO pressure to examine the stability of the Cu/Pt surface alloy. When the Cu/Pt(111)-NSA is exposed to high pressure of CO, small clusters are found to decorate large fractions of the surface and a moving reaction front is observed in STM movies. These clusters are always observed directly above the stress lines and it is therefore reasonable to assume that the small clusters contain Pt-atoms which have been expelled from the surface layer thereby reducing the stress in the surface. From these experiments we conclude that the Cu/Pt(111) NSA remains "stable" in high pressure of CO.

Iron doped Palladium based catalysts are also very interesting candidates for new improved WGS catalysts[2] and further studies in Pd/Fe-based catalysts are therefore interesting. We have therefore synthesized different model systems of Iron Oxide on Pd(111) and used scanning tunneling microscopy (STM) to show that the order of the oxides depend strongly on the preparation conditions. Furthermore we use TPD to study the different oxides interaction with CO, which is present in the WGS reaction.

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Study of Ni_2P Activation Using *in situ* Quick XAFS

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Nickel phosphide Ni_2P is a new material that has high activity for hydrodesulfurization (HDS) and hydrodenitrogenation (HDN). The activation of Ni_2P/K-USY was studied using in situ QXAFS (Quick X-ray Absorption Fine Structure). The activation could be divided into three stages.

The in situ QXAFS were performed at the NW10A beamline of KEK-IMMS-PF-AR (Institute for Material Structure Sciences Photon Factory Advanced Ring). The sample was pressed into a pellet and then set in a controlled-atmosphere cell, where it was heated to 773 K at 5 K/min and kept 2 hours under hydrogen flow (50 sccm). The gas products from the XAFS cell were monitored simultaneously using an IR gas detector. Each XAFS spectrum took 9 s to measure.

Figure 1 shows the production of water recorded by the IR detector. It shows that the activation took place in three stages. Figure 2 shows the Fourier Transforms of k^3-weighted EXAFS spectra. Two FT peaks were observed before activation (Time = 0). The first peak at ca. 0.18 nm corresponds to Ni-O bonds in the first shell and the other one at ca. 0.29 nm corresponds to Ni-Ni bonds in the second shell, which indicates that Ni_2P were oxidized and the structure similar to that of $Ni(OH)_2$ was formed before the activation. The position and shape of the first peak did not change in stages I and II, which indicates that the Ni was still oxidized. The second peak became weak in stage I and negligible in stage II, which indicates that $Ni(OH)_2$ crystal-like structure was converted into small Ni-O species by the release of weakly interacting oxygen in stage I. In stage III, the first peak started to shift to longer distance and a shoulder began to grow, which suggests that Ni and P were being reduced and that Ni_2P start to form.

In summary, the activation of Ni_2P was followed using in situ QXAFS and simultaneous gas analysis.

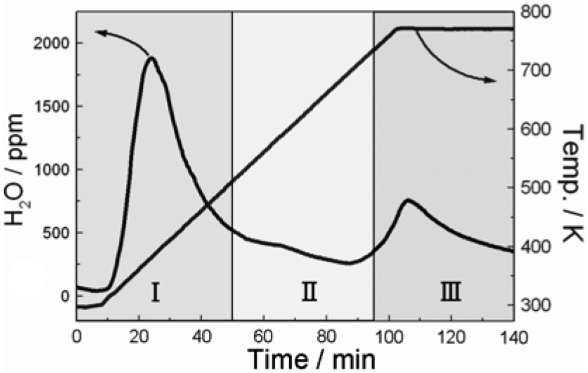

Figure 1: The amount of water in the gas products during activation process

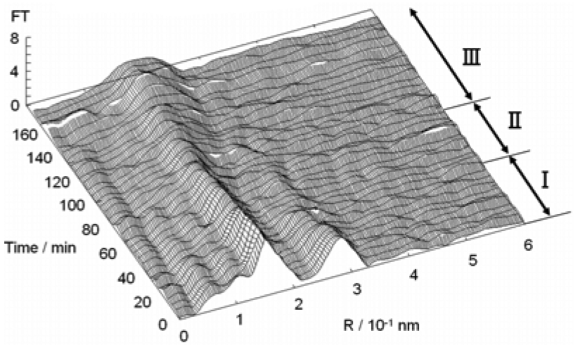

Figure 2: Fourier Transformed k^3-weighted EXAFS spectra during activation process.

The Origin of Self-Regulated Ni Clusters Growth on TiO_2(110)

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The three dimensional structure of Ni clusters on TiO_2(110) was investigated by PTRF-XAFS (Polarization dependent Total Reflection Fluorescence X-ray Absorption Fine Structure). Ni clusters were distorted $(110)_{fcc}$ structure at 1×10^{14} atoms/cm^2, where self-regulated cluster growth mode had been reported.[1] Ni-O interactions stabilized the distorted $(110)_{fcc}$ structure of Ni cluster.

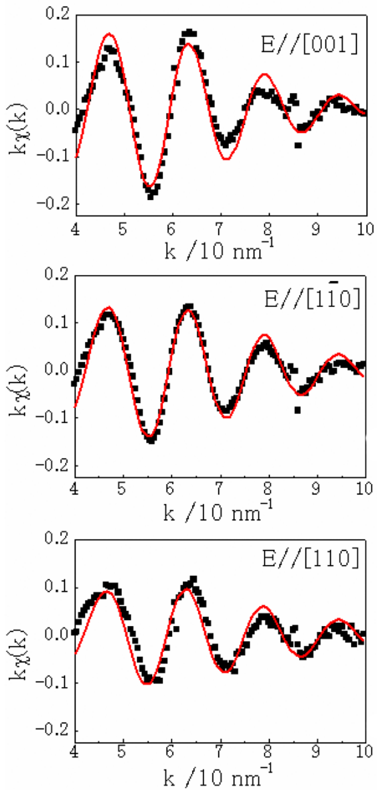

Figure 1. EXAFS spectra of Ni clusters on TiO_2(110). Dotted lines are observed and solid lines are calculated spectra.

Metal/oxide interaction is one of the important parameter for catalysis. Deposited metal clusters on oxide single crystals or films have been studied as model systems. One interesting feature is self-limiting (regulated) growth mode, where the size and shape of metal clusters little depend on the coverage. We found that Ni clusters deposited on TiO_2(110) showed the self-regulated growth mode at the initial stage of metal deposition up to 1×10^{14} atoms/cm^2.[1] PTRF-XAFS was applied to reveal the bond structure between Ni clusters and TiO_2(110).

Figure 1 (dotted lines) shows k-weighted PTRF-XAFS spectra at 1×10^{14} atoms/cm^2. Three spectra (two parallel to surface, E//[001], [110] and a normal to surface; E//[110]) were measured since TiO_2(110) is an anisotropic surface. We calculated spectra based on $(111)_{fcc}$, $(110)_{fcc}$, $(100)_{fcc}$ models. The calculated spectra based on distorted $(110)_{fcc}$ structure illustrated in Fig. 2 were in best agreement with experimental ones as shown in Fig.1. The distorted structure increased Ni atoms that can interact with surface oxygen around 0.24 nm.

In summary, the structure of Ni clusters was studied using the PTRF-XAFS. We found that Ni clusters were distorted $(110)_{fcc}$ structure at self-regulated growth mode. Ni clusters interact strongly with surface oxygen and the Ni-O interactions provide the self-regulated growth mode.

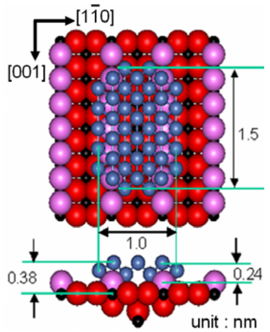

Figure 2. The proposed model of Ni cluster on TiO_2(110) at self-regulated growth mode.

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Structural Characterization and Imaging of Decarbonylated Molecular Osmium Cluster catalysts

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The dependence of catalytic activity on cluster size can be demonstrated in experiments with samples incorporating clusters of essentially uniform sizes, which can be prepared from molecular metal clusters such as $[\mathrm{Os}_{10}\mathrm{C(CO)}_{24}]^{2-}$, which can be formed on some supports (e.g., MgO) and then decarbonylated to give structures approximated as Os_{10}. We now report the preparation of such samples and their characterization by spectroscopy and transmission electron microscopy (TEM); we have tested the supported clusters for ethylene hydrogenation under mild conditions.

The catalyst was synthesized from $\mathrm{Os}_3(\mathrm{CO})_{12}$ in a *n*-pentane slurry at 298 K with MgO powder that had been calcined at 673 K. The sample was treated in He for 2 h and CO for 4 h at 548 K. This sample was later treated in He for 2 h at 733 K. The resultant sample had osmium content 2 wt%. The synthesis and sample handling were done with exclusion of air and moisture. A specially designed TEM sample holder was used to protect the samples. These samples were characterized by IR, EXAFS TEM and tested as catalysts for ethylene hydrogenation in a once-through flow reactor at 298 K and 1atm.

IR and EXAFS spectroscopy used to characterize the sample prepared by adsorption of $\mathrm{Os}_3(\mathrm{CO})_{12}$ on MgO indicated formation of $[\mathrm{Os}_{10}\mathrm{C(CO)}_{24}]^{2-}$. The Os-Os bond distance of 2.86 Å agrees well with the XRD value of 2.87 Å for the pure compound. These supported clusters were imaged by using TEM in dark field. A micrograph of the sample containing predominantly $[\mathrm{Os}_{10}\mathrm{C(CO)}_{24}]^{2-}$ includes strong scattering centers of nearly uniform size with diameters in the range 89 Å, indicative of the clusters.The sizes estimated from the EXAFS data and the TEM images match, indicating a successful synthesis of uniform supported molecular clusters. The metal-support interaction was investigated by using EELS (electron energy loss spectroscopy), and EELS spectrum imaging was performed.

The MgO support was investigated by electron diffraction, and the results indicate that the MgO was polycrystalline. EDX (Energy dispersive X-ray) analysis was used to determine the presence of osmium in the supported samples. Decarbonylation of the supported $[\mathrm{Os}_{10}\mathrm{C(CO)}_{24}]^{2-}$ was carried out by treatment in He. IR spectra in the CO region demonstrated the removal of the CO ligands starting at 573 K and nearly complete decarbonylation at 723 K. EXAFS analysis of the decarbonylated sample indicated the absence of contributions fromcarbonyl carbon and oxygen atoms. The first-shell Os–Os contribution indicates retention of the Os_{10} carbido metal frame. The data give evidence of an increased interaction between the clusters and MgO as a result of the decarbonylation, as indicated by two Os-support oxygen contributions at a distance of 2.15 Å and 1.73 Å. This result was supported by images demonstrating in-situ decarbonylation of $[\mathrm{Os}_{10}\mathrm{C(CO)}_{24}]^{2}$ at 373 and 673 K in He (0.002 Torr). Differences in the features characterizing the oxygen K edge were observed between supported samples and the MgO support, consistent with bonding of the clusters to the support through oxygen atoms.

The MgO-supported decarbonylated osmium clusters were found to be active for ethylene hydrogenation at 298 K. Calculations with standard methods show that the reaction was slow enough that the influence of transport phenomena on the rate was negligible, and conversions were differential. The catalytic activity of MgO-supported $[\mathrm{Os}_{10}\mathrm{C(CO)}_{24}]^{2-}$ was negligible, consistent with strong inhibition of catalysis by the CO ligands.

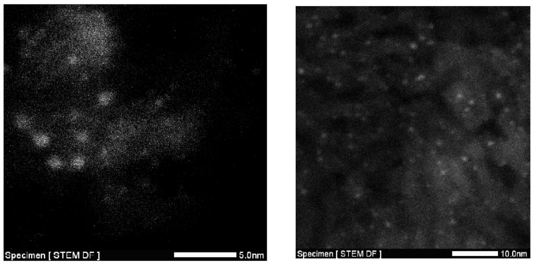

Figure 1. Z-contrast Dark field TEMimages A) [Os10C(CO)24]2- /MgO B) First images of Os10C metal frame decarbonylated at 450 C in He

Catalytic Oxidation of Organic Substances by Polymer-anchored Amino Acid Derived Tridentate Ligand Complexes of VO(IV) and Cu(II)

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A synthetic strategy was developed to covalently anchored 3-formyl salicylic acid on to chloromethylated polystyrene cross- linked with 5% divinylbenzene. Treatment of this chelating resin with two amino acid, DL-alanine and L-isoleucine form a shiff-base tridentate ligand (abbreviated as PS-Hfsal-ala and PS-Hsal-isol). The polymeric ligands contain tridentate ONO donor sites were treated with a solution of [$Cu(CH_3COO)_2 \cdot H_2O$], [$VO(acac)_2$], to form the corresponding metal complexes on the support. The metal complexes abbreviated as PS-[VO(fsal-ala)], PS-[Cu(fsal-ala)], PS-[VO(fsal-isol)] and PS-[Cu(fsal-isol)]. Structure of these immobilized complexes have been established on the basis of scanning electron micrographs, spectroscopic (Infrared and electronic), thermo gravimetric and elemental analyses studies. The catalytic oxidation of *p*-chloro toluene and cyclohexene were investigated using these complexes as catalyst in presence of eco friendly oxidant H_2O_2. Reaction conditions have been optimized by considering the concentration of oxidant, amount of catalyst, volume of solvent and temperature. Under optimized condition p-chloro toluene gives a maximum 13.34% conversion with four products, cyclohexene 98.6% conversion with four and two product respectively. In situ neat complexes of all the metal has been prepared to compare the spectral properties and catalytic activities. Recycling studies indicate that the catalyst can be recycled four times without any significant loss in their catalytic potential.

Study of Influence of Amines on Behavior of the Noyoris Catalyst Under Transfer Hydrogenation Conditions Studied by NMR

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Enantioselective hydrogenation is one of the most important catalytic methods in the synthetic organic chemistry both on the laboratory and the production scale. One of attractive methods for an asymmetric hydrogenation is the hydrogenation under transfer conditions. In 1995, Noyori, Ikariya, Hashiguchi and coworkers published a paper, reporting the TsDPEN-coordinated (TsDPEN = N-(*p*-toluenesulfonyl)-1,2-diphenylethylenediamine) Ru(II) complex (Ru-TsDPEN) to be an excellent catalyst for the asymmetric reduction of aromatic ketones and imines. A mixture of formic acid/triethylamine (2.5 HCOOH/TEA molar ratio) is frequently employed as both the solvent and hydrogen donor.

Special interest was focused on the study of the reaction pathway of 2-propanol/strong base mediated transfer hydrogenation in the literature, but nearly no attention was paid to study the HCOOH/TEA system. Therefore our work was focused on studies of a mechanism involved in the transfer hydrogenation using this system. It was used direct in situ NMR studies of Noyoris catalyst under variable temperature. The special attention was paid to the influence of amine in the course of the hydride formation and hydrogenation of imines by in-situ NMR. A range of amines with a combination of HCOOH was tested. To insight more deeply into the mechanism of hydride formation reaction with deuterated formic acid was used.[1]

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[1] The research was supported by the Grant Agency of the Czech Republic (Grant 104/06/0684)

Synthesis, Structure and Catalytic Activities of Cu(II)–N- or C-protected L-tyrosine Complexes Covalently Anchored onto Silica Gel or Merrifield Resin

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In order to satisfy the need for novel highly active, and, even more importantly, highly selective catalysts various strategies may be followed. One promising way may be to mimic the active sites of enzymes, the most effective catalysts of Mother Nature. To increase efficiency immobilization of these active site mimics looks advantageous. The activity and the selectivity may be further enhanced if the support resembles the protein skeleton of the enzyme as well. In this contribution we describe such a biomimetic approach: our work concerns the covalent anchoring of Cu(II)-N- or C-protected L-tyrosine complexes (as active site mimics) onto a rigid silica gel support or a swellable resin (as a mimic of the protein skeleton). Experimental conditions of the synthesis were varied and the structures of the anchored complexes as well as the activities of the obtained materials were also studied.

Covalent grafting was performed either with L-tyrosine methylester and B(ut)o(xy)c(arbonyl)-L-tyrosine at the N- and the C-terminal of the amino acid, respectively, through the reaction of the amino group (N-alkylation-like transformation) or the carboxylic group (esterification) with the chlorine of the chloropropylated silica gel or the benzylic chlorine of the Merrifield resin. Complexation followed the anchoring, applying either ligandum poor conditions (only the immobilized protected amino acids were available for coordination) or circumstances abundant in non-anchored appropriately protected amino acid molecules. Isopropanol, toluene and distilled water were used as solvents.

Structural information on each step of the synthesis procedure was obtained by midrange infrared spectroscopy, measuring diffuse reflectance and the superoxide dismutase activities of the catalysts were tested by the method of Beauchamp and Fridovich.[1] Merrifield resin was found to be a better support for the complexes, i.e. anchoring of the ligands through reactions with the benzylic chlorine was more effective than via the chlorine of the chloropropyl group of the silica gel. IR spectroscopic measurements revealed that varying the solvents did not influence the structure of the complexes dramatically under ligandum-poor conditions. The donor groups could be identified taking into account the conditions of complexation (basic conditions were always used), analyzing the IR spectra and chemical reasoning. Under ligandum poor conditions the anchored amino acids acted as bidentate ligands. Upon the addition of free protected tyrosine molecules in excess, the structure of the anchored complexes changed dramatically in some cases. Both the donor groups and the coordination number have changed.

The immobilized complexes prepared either in water or isopropanol were active in the superoxide dismutase reaction, while those prepared in toluene did not show any activity. The activity was higher when isopropanol was the applied solvent.

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[1] C. Beauchamp, I. Fridovich *Anal. Biochem.* 44 (1971) 276.

The Performance of a Biomimetic Oxidation Catalyst Immobilized on Gold and Silica Substrates

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Thiol-functionalized cobalt porphyrins[1] were used as a model system for investigating catalytic activity in homogeneous and heterogeneous oxidation catalysis. Self-assembled monolayers of thiol-functionalized cobalt porphyrins were prepared on a gold surface and served as heterogeneous catalysts. The immobilization of the molecules prevented the strong inactivation observed for their homogeneous congener. As a result, the turnover number per molecule in heterogeneous catalysis was at least 100 times higher than that of the corresponding homogeneous catalyst.[2] It is atypical for a heterogenized catalyst to outperform its homogeneous congener. The properties of the molecular layers were characterized on the molecular level by means of X-ray photoelectron spectroscopy (XPS) and scanning probe microscopy (SPM). The results demonstrate that the performance of these biomimetic catalysts can be dramatically improved if the catalyst arrangement can be controlled on the molecular level. In order to further investigate the influence of the substrate on the catalytic performance, monolayers of the cobalt porphyrins were grafted onto silica surfaces. The observed catalytic activity together with the surface analytical results are interpreted in relation to the supporting substrate. Preliminary results from this investigation (silicon wafer) show that the catalytic activity is similar to that of gold substrates.

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Selective Oxidation of Allylic Alcohols: from Single Crystal to Single Site

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The selective oxidation of alcohols finds widespread application in the fine chemical and food industries for the synthesis of valuable intermediates. These processes traditionally employ stoichiometric quantities of toxic or hazardous reagents, generating harmful waste with associated safety and disposal cost issues. Heterogeneous catalysts are a promising alternative clean technology offering both process advantages, in terms of catalyst separation/recovery and the use of cheap and safe oxidants such as dioxygen or even air, together with enhanced reaction selectivity.

Supported palladium is highly selective for the aerobic partial oxidation of allylic alcohols under mild conditions.[1,2] However, despite much promise these heterogeneous catalysts deactivate rapidly, hindering their commercialisation. A number of fundamental issues relating to the nature of the active phase, and origin of the deactivation process must be addressed in order to overcome this limitation. Furthermore poisoning may occur through the accumulation of irreversibly bound byproducts, surface corrosion and leaching of the active phase, or catalyst over-oxidation.[3]

Through combined surface science studies over model palladium surfaces, and corresponding X-ray measurements on dispersed Pd/Al_2O_3 catalysts, we have identified the active site in the selective oxidation of cinnamyl and crotyl alcohols to their respective aldehydes. XAS and XPS reveal that efficient oxidative dehydrogenation is crucially dependent on the presence of Pd(II) active sites, in the form of a metastable surface PdO.[4] Catalyst deactivation is associated with palladium oxide reduction;[5] this exposes metallic Pd(0) surface sites which are highly reactive towards aldehyde decarbonylation, and result in the accumulation of adsorbed CO/alkylidynes and associated selfpoisoning (Figure 1). Palladium nanoparticle sintering accompanies this Pd(II) → Pd(0) transition.

This insight has allowed us to develop exceptionally active heterogeneous Pd catalysts utilising a mesoporous alumina support to stabilise atomically dispersed Pd(II) centres. The result is a 10-fold activity enhancement (Figure 2) under mild reaction conditions, and catalytic materials offering new green chemical solutions to diverse industrial processes.

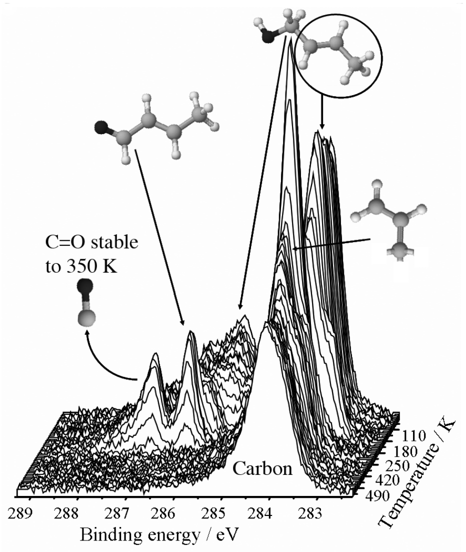

Figure 1: Operando C 1s XP spectra showing evolution of reacting crotyl alcohol adlayer over Pd(111) single-crystal.

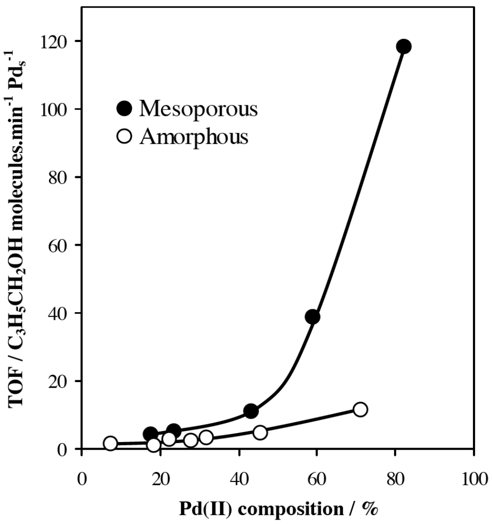

Figure 2: Correlation between surface Pd(II) content in dispersed Pd/Al_2O_3 catalysts and alcohol oxidation rate.

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Palladium and Nickle-catalyzed Carbonylation of Nitrobenzene for the Synthesis of N,N-diphenylurea

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N,N-diphenylurea (DPU) has been proposed as a convenient intermediate in the phosgene-free synthesis of diphenylmethane diisocyanate (MDI). The DPU can be synthesized effectively from nitrobenzene, aniline and carbon monoxide in the presence of a catalyst system comprising a palladium or nickel salt, a halogen promoter, and a ligand. This paper covers a detail account of the work.

The reactions were performed in a batch reactor. In a typical run, 300 mmol of aniline, 0.60 mmol of metal salt, 3.42 mmol of a ligand, 1.8 g of NEt_4Cl, and 70 ml of xylene were charged into the reactor. The gas phase was pressurized to 620 psig of CO. Then the reactor was heated to 120°C. After temperature stabilized, 50 mmol of nitrobenzene was pumped rapidly into the reactor. The reaction mixture was sampled during the reaction and liquid phase was analyzed quantitatively by a GC and MS.

DPU has been synthesized from nitrobenzene, aniline, and CO in a batch reactor at 80–160°C and 15–75 bar. Homogeneous catalyst systems containing of a palladium or nickel salt, an onium salt, and PPh_3 dissolved in xylene or toluene were found to be highly efficient, giving isolated urea yield up to 98% at 100% nitrobenzene conversion. The effects of catalyst composition and other reaction variables were studied. The presence of excess aniline was essential in order to reuse the catalyst system for new batches without appreciable loss of activity. By using deuterated nitrobenzene as a reactant, it was demonstrated that the reaction proceeded in two parallel routes:

1) $PhNO_2 + PhNH_2 + 3\ CO \rightarrow PhNHCONHPh + 2\ CO_2$
2) $PhNO_2 + 5\ PhNH_2 + 3\ CO \rightarrow 3\ PhNHCONHPh + 2\ H_2O$

The relative importance of these two routes depended strongly on the ratio of aniline-tonitrobenzene. Mechanisms are proposed that account for these reaction stoichiometries.

Effects of various ligands have been studied on catalytic activity. Both electronic and steric properties of a ligands had a profound effect. Compared to monodentate phosphines, bidentate ligands showed higher activity and promoted preferentially a path of the reaction network that involved steps in which the cis coordination of ligands to metal was desired. The use of a promoter NEt_4Cl was indispensable in the case of monodentate phosphines, yet inhibited the reaction if used with bidentate phosphines.

Shape-controlled Platinum Nanoparticles for Gas-phase Reaction Study

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Single crystalline platinum surface have been shown to exhibit distinctive catalytic activity and selectivity for different surface structures. Various shapes of platinum nanoparticles have different surface property, e.g. (100) surface for cube, mixture of (100) and (111) surfaces for cuboctahedra. Nanoparticles with the different surface property which result from morphology control can lead to better activity and selectivity for catalytic reaction.

Catalytically active platinum nanoparticles have been synthesized by using tetradecyltrimethylammonium(C14TAB) bromide as a surface stabilizing agent. Cubes, cuboctahedra, and porous particles were synthesized by manipulating reduction kinetics. The shape evolution from cuboctahedra to cubes was shown by controlling pH. Higher pH enables selective growth of (100) surface. The size of nanocubes was also controlled by changing reactant concentration and reaction time. 2-dimensional model catalyst was prepared by forming Langmuir-Blogette monolayer of these Pt nanoparticles. The catalytic activity was tested for this monolayer by using ethylene hydrogenation. Cube and cuboctahedra showed a similar activity, which is expected for surface insensitive reaction. The C14TAB-capped nanoparticles showed a superior catalytic activity (7.1 times) to the nanoparticles synthesized by polymeric capping agent (PVP, polyvinylpyrrolidone) and silver. The foreign metal ions such as silver or iron have been widely utilized for shape control of metallic nanoparticles. These foreign metal ions significantly degrade the catalytic activity of the nanoparticles. The activity of the C14TAB-capped Pt nanoparticles was further enhanced by H_2 treatment at mild temperature (110°C). The shape of nanoparticles was preserved after H_2 treatment and ethylene hydrogenation.

The effect of the shapes of nanoparticles was estimated for structure-sensitive reaction such as benzene hydrogenation. According to single crystalline study, (100) surface produces only cyclohexane as products while (111) surface produce cyclohexane and cyclohexene. The same trend was observed so that C14TAB-capped Pt cubes produce only cyclohexane while C14TAB-capped Pt cuboctahedra do cyclohexane and cyclohexene. When compared with the single crystalline study, these nanoparticles showed better TOF (3.5 times), lower activation energy, and better selectivity to cyclohexene (2.6 times). Interestingly, PVP-capped cubic nanoparticles synthesized using 1.1mol% silver produce cyclohexane and cyclohexene unlike C14TAB-capped cubes. The surface of PVP-capped cubic nanoparticles doesnt show the characteristic of (100) surface, emphasizing the importance of synthetic procedure of the nanoparticles for catalytic reaction study.

Titanium(IV) and Zirconium(IV) Sulfato Compounds in Oxygen-Rich Coordination Environments: Molecular Models of Sulfated Metal Oxides

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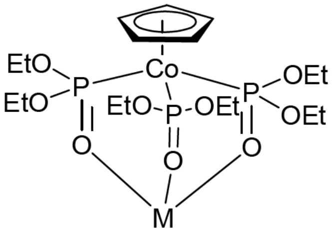
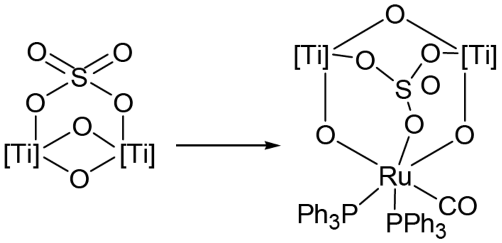
Sulfated zirconia (SZ) has attracted much attention due to its high catalytic activity for light alkane isomerization at low temperatures. It was reported that the use of a metal promoter, notably Pt, can enhance both the activity and stability of SZ. To better understand the nature of active sites and the organometallic reaction mechanisms of SZ-supported catalysts, we sought to develop molecular models based on polynuclear sulfato compounds in oxygen-rich coordination environments. The oxygen tripodal ligand $[(\eta^5\text{-C}_5\text{H}_5)\text{CoP(O)(OEt)}_{23}]$- ($\text{L}^-_{OEt}$) is a weak-field, π-donating ligand that can bind to hard metal ions tightly. Oxygen-rich polynuclear Ti(IV) and Zr(IV) L_{OEt} compounds may serve as models for metal oxide surfaces. We herein describe the synthesis, solid-state structures, and reactivity of Ti(IV) and Zr(IV) sulfato compounds supported by L^-_{OEt}.



$\text{L}_{OEt}\text{M} = [\text{M}]$



Hetero-bimetallic Catalytic Binuclear Elimination as an Origin for Synergism in Homogeneous Catalysis

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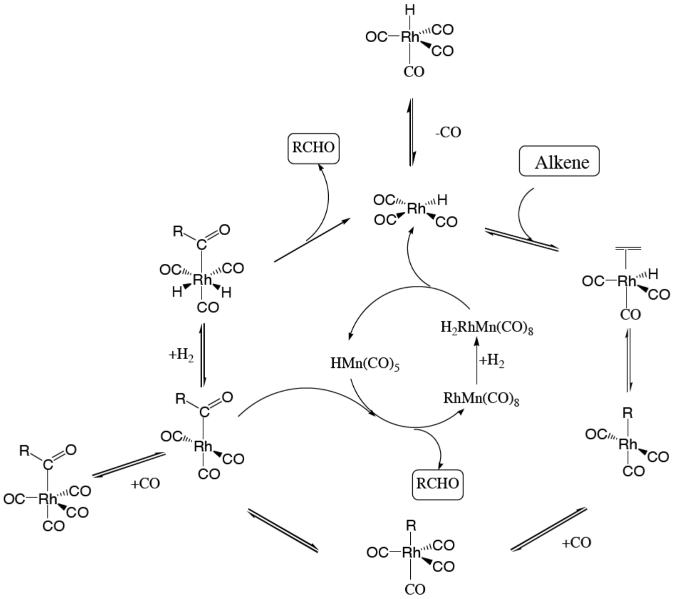
The observation of synergism in catalysis is not entirely uncommon. However, due to the rather widespread lack of detailed in-situ experimental studies, the phenomenological origins of synergism have remained to a considerable extent unproven. The present contribution reports on systematic studies of $Rh_4(CO)_{12}/HMn(CO)_5$ catalyzed hydroformylation of 3,3-dimethylbut-1- ene and cyclopentene with in situ FTIR monitoring using advanced signal processing techniques. The addition of manganese carbonyl hydride to the unmodified rhodium catalyzed hydroformylation leads to a significant increase in system activity. Detailed in situ spectroscopic information and the regressed linear-bilinear rate equation indicate that this increase in the rate of product formation is due to the existence of a bimetallic catalytic binuclear elimination reaction (CBER), where the reaction of manganese hydride with an acyl rhodium tetracarbonyl is the rate limiting step.



This contribution will address the in situ studies and signal processing, the identification of hetero-bimetallic CBER, and the importance of CBER to explain some types of non-linear kinetics. In CBER each metal performs a specific set of transformation and then interact to give product formation. This well-defined example of cooperativity between different metals, might have relevance / analogies / extensions to enzymatic systems and bimetallic heterogeneous catalytic systems.[1,2,3,4,5]

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The Activity and Characterization of MnOX Catalysts for Selective Catalytic Reduction of NO_X with NH_3 at Low Temperatures

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The low-temperature catalyst has recently attracted much attention because it can be placed downstream of the dust catcher and desulfurizer. Mn-based catalysts show good activity in NH_3-SCR at low temperatures, such as MnO_X/Al_2O_3,[1] MnO_X/TiO_2,[2] MnO_X/NaY.[3] MnO_X/AC[4] and MnO_X/USY.[5] In this work, a series of unsupported amorphous MnOX catalysts were prepared by three methods, their physical properties were characterized by BET, XRD, TEM etc, and the catalytic activities were evaluated in the temperature range of 50-150°C.

MnO_X catalysts were prepared by three methods, namely, Rheological phase reaction method (RP), Low temperature solid phase reaction method (SP), Co-precipitation method (CP). Hereafter the catalysts were designated as MnO_X (RP), MnO_X (SP) and MnO_X (CP), respectively. For comparison, MnO_X (CA) was also prepared by the citric acid method. The samples were characterized by BET, XRD, TPD and TEM. Catalytic activity tests were performed in a quartz tube reactor of 9 mm internal diameter in the flow of 500 ppm NO, 500 ppm NH_3, 3% O_2, 100 ppm SO_2 (when used) and 2.8 20% H_2O (when used), the total flow rate was fixed at 300 cm^3min^{-1}.

Figure 1 shows the XRD patterns of different MnO_X catalysts. The MnO_X catalyst prepared by the citric acid method has high crystallinity, while the MnO_X catalysts prepared by RP and SP and CP turned into an amorphous phase. Figure 2 shows the NO_X conversions over MnO_X catalysts. It is obvious that the catalytic activity of amorphous catalysts, which include MnO_X (SP), MnO_X (RP) and MnO_X (CP), are much better than the activity of MnO_X (CA). More than 98% NO_X conversion could be achieved at 80°C over the amorphous catalysts, and almost all of the NO_X can be converted in the range of 80∼150°C. In comparison, the amorphous catalysts with the MnO_X (CA), two obvious differences are the specific area and configuration, which may be the reasons why the amorphous catalysts have such superior low temperature catalytic activity. The catalyst stability and reaction mechanism are still investigating in our laboratory.

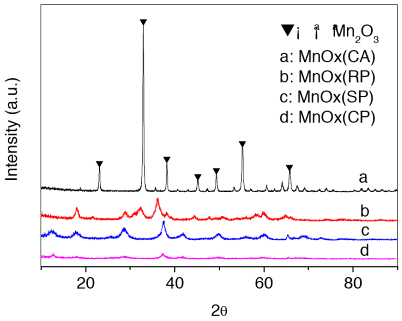

Figure 1. XRD patterns of MnO_X catalysts prepared by various methods

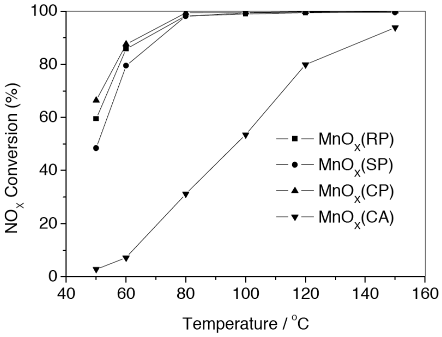

Figure 2. NO_X conversion over four MnO_X catalysts at different temperatures.

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Supported Rhodium Complexes on Highly Dealuminated Zeolite Y: Characterization During Catalysis of Ethylene Hydrogenation

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Typical supported metal catalysts consist of nonuniform nano-structures dispersed on supports. The nonuniformity has led to difficulties in the determination of structure-catalytic property relationships and understanding of the catalysts. In contrast, supported catalysts with virtually molecular structures, incorporating supported metal complexes, offer the advantages of simplicity and, in prospect, uniformity of structure to facilitate fundamental understanding. Our goals were to prepare and investigate well-defined and nearly uniform supported rhodium complex that is an active and stable catalyst and to determine relationships between catalyst structure (including the structure of the metal-support interface) and activity for a simple test reaction, hydrogenation of ethylene. The supported rhodium complex was synthesized from $Rh(C_2H_4)_2(acac)$ [acac is the bidentate ligand $CH_3COCHCOCH_3$] and highly dealuminated zeolite Y. The supported sample was characterized by IR, EXAFS, and ^{13}C MAS NMR spectroscopies, both in the as-synthesized form and in the working state.

The EXAFS spectrum of the as-synthesized sample gives no evidence of a Rh–Rh contribution, consistent with the presence of the rhodium as site-isolated mononuclear species, consistent with the IR data. The EXAFS data show that the Rh center was bonded to the support via 2 Rh–O bonds; the distance is 2.15 Å, consistent with a strong polar bond. The EXAFS Rh–C contribution (coordination number NRh-C = 3.8, distance RRh-C = 2.05 Å) indicates two ethylene ligands bonded to the Rh atoms, in agreement with the IR spectra. Thus, the supported rhodium complex is among the best-defined supported metal species.

When the initially prepared sample treated in flowing ethylene at 298 K and atmospheric pressure, no gas-phase products were observed. The EXAFS spectrum demonstrated that the rhodium complex was still mononuclear, with no evidence of Rh–Rh contribution. The supported Rh complex was bonded to two oxygen atoms of the support (NRh–O = 2.2, RRh–O = 2.10 Å). The supported Rh complex was tested as a catalyst for ethylene hydrogenation at 298 K and 760 Torr atmospheric pressure in a flow reactor/EXAFS cell. The EXAFS spectrum of the used catalyst shows the supported sample remained mononuclear, and the data indicate only Rh–O and Rh–C contributions. When the as-synthesized sample was treated in flowing H_2 at 298 K and amospheric pressure, gas was evolved and analyzed with a mass spectrometer; the data indicated ethane was formed immediately after beginning of the hydrogen flow. This result indicates that ethylene ligands on the rhodium were hydrogenated on the site-isolated Rh centers bonded to the support; these ligands are candidate catalytic reaction intermediates. The EXAFS spectrum of the sample after treatment in H_2 for 1 h indicated that the rhodium was slightly aggregated, with a Rh–Rh coordination number of 1.8 at a distance of 2.66 Å. However, EXAFS spectra of the working catalyst after ethylene was added to the gas stream show that the clusters had fragmented to again form mononuclear rhodium complexes; no Rh–Rh contribution was found, and the data indicated only bonding of the rhodium to the support and to hydrocarbon ligands (NRh–O = 2.0, RRh–O = 2.11 Å; NRh–C = 1.9, RRh–C = 2.28 Å). As a result, it is concluded that the mononuclear rhodium complex is stable under reaction condition and is the catalytically active species.

Support Effect in the Gold-catalyzed Aerobic Epoxidation of Stilbene

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When studying the liquid phase epoxidation of trans-stilbene in methylcyclohexane (MCH) over supported gold catalysts,[1] we found that the reference Au/TiO_2 from the World Gold Council (WGC) was more active and selective than the reference Au/C-WGC, even though it was less dispersed inside the reaction medium. However, the gold particle size was 3.5 nm over titania and 10.5 nm over carbon, so that it was impossible to conclude whether this was a support effect or a particle size effect.[2]

Here we look into the effect of the gold dispersion over TiO_2-P25. We also make use of a colloidal method developed by Comotti et al.[3] to prepare similar gold particle size distributions over various supports, especially high surface area titanias and carbons that disperse well in the apolar solvent. This allows us to assess the influence of the surface composition of the supports in this reaction.

The catalysts were prepared according to the method described in ref. 3, using commercially available titanias and carbons and poly(vinylalcohol) as the protecting agent. They were all calcined in air at 250°C for 4 h (except the carbon-supported ones) and characterized by ICP, TEM, XPS, UV-Vis. and TGA-DTA-MS before reaction. The supports were further characterized using TPD-MS. The catalytic tests were carried out in magnetically stirred glass batch reactors held at 80°C for 24 h in air at atmospheric pressure. The reaction mixtures consisted of substrate (*trans*-stilbene, 1 mmol), solvent (MCH, 20 mL), catalyst (2 μmol Au) and *tert*-butylhydroperoxide (TBHP, 0.05 mmol). *Trans*-stilbene conversion (C%), epoxide yield (Y%) and selectivity (S%) were determined by HPLC-product analysis.

With the colloidal method, the desired 1.0±0.2 wt% gold loadings are achieved on all supports (Table 1). The average gold particle size (3.0±0.2 nm) is similar on all pure anatase titania and carbon supports. Only for the mixed anatase/rutile TiO_2-P25, also used as support for the reference Au/TiO_2-WGC catalyst, does it reach 5.1 nm. This allows to study the influence of the gold dispersion over TiO_2-P25. Indeed, all trans-stilbene conversions, yields and selectivities for the epoxide obtained over the smaller gold particles (Au/TiO_2-WGC) are higher than those obtained over the larger particles.

Most of the other materials prepared by the colloidal route are more efficient than the reference gold catalysts for the epoxidation of trans-stilbene. Amongst them, the carbon-supported ones appear more active, although selectivities are similar. This could mean that Au^0 is more efficient than $Au^{\delta-}$ for producing the epoxide, since all gold particles supported on carbons are essentially metallic while those on titanias are slightly negatively charged. However, surface composition of the support seems to be critical too, with conversions and epoxide yields depending substantially on the type of support used. The role of the surface functionalization of the supports and the oxidation state of gold nanoparticles in the epoxidation mechanism will be discussed in correlation with TGA-DTA-MS, UV and TPD-MS data.

Table 1. Physico-chemical properties and catalytic behaviors of the materials

Catalyst	Au loading (wt%)	Average Au particle size (nm)	Au $4f_{7/2}$ binding energy (eV)	Au oxidation state	Catalytic properties		
					C%	Y%	S%
Au/TiO_2-P25	0.95	5.1±3.0	82.9	$Au^{\delta-}$	34	15	45
Au/TiO_2-WGC	1.5	3.7±1.5	83.0	$Au^{\delta-}$	44	27	61
Au/TiO_2-AK350	0.93	3.0±2.5	82.8	$Au^{\delta-}$	32	19	59
Au/TiO_2-PC500	1.10	2.9±2.4	83.1	$Au^{\delta-}$	43	28	64
Au/TiO_2-UV100	1.21	2.8±2.4	83.0	$Au^{\delta-}$	66	42	64
Au/C-WGC	0.98	10.5	84.1	Au^0	32	11	35
$Au/C_{Aldrich}$	0.97	3.0±1.7	84.1	Au^0	78	49	63
Au/C_{DGK}	0.85	2.7±1.4	84.1	Au^0	75	49	65
$Au/C_{PAK1420}$	0.94	3.2±1.4	84.1	Au^0	91	61	67

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Isomerization of D-glucose to D-fructose over Zeotype Solid Bases

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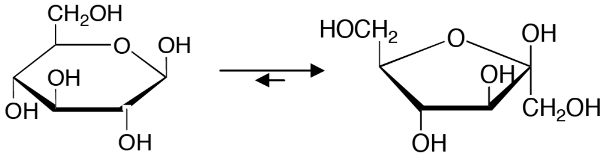
Glucose is an important monomer unit of the abundant natural polysaccharide, cellulose and is likely to become one of the most important starting chemicals as a result of the increasing dependence of the coming society on biomass resources for sustainability. One of the primary reactions of glucose is base-catalyzed isomerization to fructose, whereby the aldehyde glucose is converted into fructose, a ketohexose (see fiq.1). Fructose is the sweetest of the natural sugars and high fructose syrups are industrially produced for food applications via immobilized enzyme technology.[1] In biocatalytic processes, a chief benefit of using enzymes immobilized on solid supports is the simpler purification process after reaction and catalyst reutilization.[2,3] However, enzymes are very expensive, quite sensitive to process parameters, such as pH and temperature, and microbial growth may occur in the system. Alkaline aqueous solutions of hydroxide salts have been used for glucose isomerization in homogeneous phase,[4,5] but these homogeneous processes pose several safety, environmental and technical problems, warranting the search for alternative heterogeneous catalysts. Inorganic solid bases are interesting candidates, which may provide fair stability to mechanical, chemical and thermal demands.[6]

In this work, we wish to report on the aqueous phase isomerization of glucose into fructose over zeotype inorganic solids (silicates) containing non-framework or framework alkali metals at 100°C (1). Commercially available zeolite Na-X was used as reference catalyst for comparison. Fructose yields of 20-40% were obtained within 2 h reaction. These results are similar or better than that achieved with commercial zeolite Na-X or aqueous NaOH. Depending on the nature of the catalyst, different factors account for deactivation, such as loss of crystallinity, (Na,K) leaching and surface passivation.



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Sugar Stabilized Pd Nanoparticles Exhibiting High Catalytic Activities for Hydrodechlorination of Environmentally Deleterious Trichloroethylene

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Catalytic hydrodechlorination via Pd catalysts is an efficient way to destroy chlorinated hydrocarbon compounds in aqueous systems. In this paper, we present a straightforward and environmentally friendly aqueous phase synthesis of fairly small and nearly monodisperse Pd nanoparticles (mean size: 2.4 nm, standard deviation, SD: 0.5 nm) by employing a green, inexpensive, and biodegradable/biocompatible polysugar, sodium carboxymethyl cellulose (CMC), as a capping agent. The Pd nanoparticles exhibited rather high catalytic activity (observed pseudo-first-order reaction kinetic rate constant, $k_{obs} = 728\ \mathrm{L{\cdot}g_{\mathit{Pd}}^{-1}{\cdot}min^{-1}}$) for the hydrodechlorination of environmentally deleterious trichloroethene (TCE) in water. The high catalytic activity is due to both the extremely high particle surface area-to-volume ratio and the nature of the encapsulation performance of CMC molecules on the Pd nanoparticles surface that provides sufficient active site accessible for the reactants. Fourier transform IR (FT-IR) spectra indicate that CMC molecules interact with the Pd nanoparticles via both carboxyl ($\mathrm{COO^-}$) and hydroxyl (-OH) groups, thereby functioning to passivate the surface and suppress the growth of the Pd nanoparticles. In comparison with β-D glucose, another green capping agent that exhibits an ability to stabilize the particles via -OH groups, CMC molecules gives rise to smaller Pd nanoparticles in aqueous solution with narrower size distribution due to the additional interactions exerted from the $\mathrm{COO^-}$ groups of CMC molecules with Pd nanoparticles and significant electrostatic interaction between CMC molecules residing on the adjacent Pd nanoparticles. This work reveals that the capping ligand chemistry can signficantly affect the Pd nanoparticle catalytic activity for hydrodechlorination of TCE. The CMC capped Pd nanoparticles exhibited signficantly higher catalytic activity per unit surface area (or per surface atom) of the particles ($k_{SA} = 3.50\ \mathrm{L{\cdot}min^{-1}{\cdot}m^{-2}}$,TOF = 54.2 $\mathrm{min^{-1}}$) for hydrodechlorination of TCE compared to the β-D glucose capped Pd nanoparticles ($k_{SA} = 1.31\ \mathrm{L{\cdot}min^{-1}{\cdot}m^{-2}}$, TOF = 18.2 $\mathrm{min^{-1}}$). The nature of the molecular structure of CMC enables this polysugar to encapsulate the surface of Pd nanoparticles in a less compact fashion compared to the small molecule β-D glucose because of the signficant steric hinderance from the macromolecular CMC. This steric hindrance provides more active sites on the surface of the Pd nanoparticles accessible for the reactants during the catalytic hydrodechlorination of TCE. This work provides an insight into the influence of the capping ligand chemistry on metal nanoparticle catalysis.

γ-Al_2O_3-Supported Rhenium Clusters: Catalyst for Olefin Conversion

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Trirhenium clusters supported on γ-Al_2O_3 were prepared by adsorption $H_3Re_3(CO))12$. The supported clusters were decarbonylated at 400 and at 500°C in flowing H_2. The samples before and after treatment were characterized by EXAFS spectroscopy. Each sample was characterized by a Re-Re contribution with a coordination number of approximately 2 at distances R of 3.25 and 2.67 Å, respectively. These results indicate that the trirhenium framework in the original clusters was maintained during adsorption and decarbonylation. Furthermore, the presence of Re-O contributions in the EXAFS spectra of the decarbonylated sample at R = 2.07 Å indicates that the rhenium in the supported clusters was bonded to the support; this distance is indicative of cationic rhenium bonded to oxygen atoms of the support. The Re-Re distance in these samples, as well as the XANES spectra, provide additional evidence that the rhenium was cationic.

The supported rhenium catalysts were tested in a once-through tubular flow reactor for the following reactions: the conversion of propylene at 160 and at 180°C to ethylene and butenes, hydrogenation of ethylene at 25°C, and conversion of 1-heptene at 100-200°C to 2-heptene and 3-heptene.

EXAFS spectra of the catalyst used for propylene metathesis indicate that the rhenium was present in clusters smaller than those observed in the decarbonylated samples. A Re-O contribution at approximately 2.07 Å again indicates that the rhenium atoms were bonded to the support oxygen atoms and suggest that they are cationic in nature.

Immobilized RhI and RhIII Complexes on ZSM-5: In situ Infrared, Raman, and X-ray Absorption Spectroscopies Characterization

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Immobilized metal complexes on nanostructures with shape-selective properties and well-defined and highly uniform adsorption sites, such as zeolites or nanostructured metal oxides, have drawn wide attention because of their novel size-dependent properties and their potential applications for catalysis, biochemistry, fine and pharmaceutical chemistry, chemical sensing, microelectronic devices, and environmental technology.[1] There is a striking lack of understanding on the anchoring and stabilization processes of well-defined metal centers, due in part to the complexity and size of the metal particles that are used as precursors. Rhodium-based catalysts are commonly used, among many other reactions, for the partial oxidation of methane to form syngas.[2] However, the structure and stability of the rhodium active centers are not well understood. The anchoring of homogenous catalysts with simple structures on zeolites provides an opportunity to investigate well-defined active metal centers.[3] The goal of this research was to investigate the surface chemistry during the reaction of two well-defined rhodium precursors with different rhodium oxidation states and ZSM-5 with different Si/Al ratios and the formation of their corresponding well-defined active rhodium centers by using an ensemble of in-situ spectroscopic techniques. Syntheses and transfers of samples were performed with exclusion of air and moisture. The Rh/ZSM-5 samples, containing 1 wt% Rh, were synthesized by forming a slurry of either $Rh^{+}(CO)_2$(acac) (acac is $C_5H_7O_2$) or Rh^{3+}(acac) in toluene with ZSM-5 with Si/Al ratios of 23, 50, and 280. The samples were characterized by XRD and TEM before and after the immobilization of the rhodium centers. In situ characterization of the samples was performed by IR, Raman, and XAS during different temperature and flow treatments to determine the structure and stability of the well-defined rhodium centers. In this work, we will present infrared, Raman, and XAS spectra providing evidence of the formation of Rh^{+} and Rh^{3+} active sites and Al- and Si-acac surface species. Time-resolved XANES spectroscopy was used to characterize the oxidation states of the immobilized rhodium centers during flowing He, H_2, and CH_4 treatment. Similarly, EXAFS spectroscopy was used to postulate a structural model of the immobilized rhodium catalysts. A discussion on the influence of the zeolite Si/Al ratio on the immobilization of the rhodium precursors will be presented.

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Investigations on the Influence of Pd and Sb Loadings for Selective Acetoxylation of Toluene

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Aromatic esters are usually produced catalytically from alkyl benzenes at moderate temperatures in liquid phase employing homogeneous Pd containing catalysts. For instance, toluene in acetic acid gives benzyl acetate (BA) by a process called acetoxylation. BA is widely used in perfumery, food and chemical industries. This particular reaction, which is known for the past three decades, is mainly carried out until now in liquid phase and confined to batch reactors. Although high conversions achieved, there are yet several problems associated with these liquid phase studies such as easy deactivation, leaching of catalyst components, formation of secondary by-products etc. Thus, intensive efforts are being made continuously by various research groups to develop suitable heterogeneous catalysts and test their potential towards gas phase acetoxylation of toluene. On the other hand, literature survey reveals that no catalyst is successful in achieving better performance with good long-term stability. Against this background, we have initiated this work, investigated a variety of catalyst compositions and developed different Pd based heterogeneous catalysts in the past few years. In this contribution, we report some of the important results of our recent studies particularly the influence of varying Pd and Sb loadings on the catalytic performance of PdSb/TiO_2 solids.

Two series of TiO_2 (anatase) supported Pd-Sb catalysts with varying Pd and Sb contents were prepared by impregnation in two steps. In the 1st series, the metal content of Pd was varied from 0.5 to 20wt% by keeping Sb loading constant (8wt%). In the 2nd series, Sb loading was varied from 4 to 20wt% with fixed Pd content (10wt%). Catalytic testes were carried out in a fixed bed tubular stainless steel reactor at $T = 210°C$ and $p = 2$ bar. About 1 ml of catalyst particles is loaded into the reactor and activated in airflow at 300°C for 2 h prior to activity measurements. The molar ratios of the reactants such as toluene : acetic acid : oxygen : inert gas (Ar) = 1:4:3:16. The product stream was analysed on-line by GC using FID detector.

From previous investigations, it has been observed that the addition of Sb to Pd exhibited excellent performance compared to their individual monometallic solids, which gave mainly total oxidation products (i.e. CO_x). The conversion of toluene and the yield of BA achieved over monometallic catalysts are almost negligible ($\leq$2%). However, the combination of Pd and Sb not only enhanced the catalytic performance but also significantly suppressed the total oxidation. All these catalysts irrespective of composition exhibited very low initial activity, which is observed to increase progressively with time-on-stream. However, it is noteworthy that varying Pd and Sb loadings showed different influences on the catalytic performance. Activity increased continuously from 16 to > 90% with increase in Pd loading up to 20wt%, while the activity increased only up to 8wt% Sb (X-Tol=68%) and then decreased with further increase in Sb content. Selectivity of BA (ca. 85%) was found to be independent of X-Tol. The increase in the conversion of toluene with time-on-stream can be attributed to increase in Pd particle size during the course of the reaction. Both TEM and XPS gave complementary evidence for such increase in Pd particle size and changes in surface composition between fresh and spent solids of these two series. The catalysts belong to both these series are observed to undergo deactivation during time-on-stream due to coke deposits. However, they can be easily regenerated in air (250°C/2h) and the regenerated catalysts restored their maximum activity.

In conclusion, combination of Sb and Pd in PdSb/TiO_2 enhanced i) the catalytic activity, ii) selectivity and iii) remarkably suppressed the formation of COx. The loss of Pd and Sb concentration in the near-surface region, which is caused by coking during the course of reaction, is assumed to be the main reason for the loss of activity with time-on-stream. Growth of Pd particle size during the course of reaction is critical for better performance of the catalyst.

Immobilization of Metal Salen Complexes onto Mesoporous Silica and their Study in the Catalytic Epoxidation of Olefins

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Metal (e.g. Mn, Mo and V) Salen complexes were covalently immobilized on a mesoporous silica support to produce a stable heterogeneous catalyst for epoxidation reactions. Such a heterogenization leads to potential benefits, i.e. ease of separation and recycling of the catalyst. Peptide and ester bound immobilizations were performed to anchor the Salen complexes onto organo-modified silica frameworks. Peptide bound anchorage was found to be more effective with a metal Salen complex loading of about 0.25 mmol/g. The structures of the resulting heterogeneous catalysts were proven by elemental analysis, thermogravimetry as well as spectroscopic methods (e.g. FTIR, ICP OES, ESI MS and XPS). The results confirm the location of the metal Salen complexes inside the mesopores covalently connected to the silica support.

The catalytic activity of homogeneous and immobilized Mn, Mo and V-Salen complexes were studied in the epoxidation of olefins with peroxides as oxidants and found to be active. The influence of solvent, temperature, adduct proportion as well as presence of protic agents and possible side reactions were investigated for the epoxidation of cyclic olefins. A comparison of the results obtained for the homogeneous and the immobilized catalyst showed that there was no significant loss of the efficiency of epoxidation due to immobilization of the catalyst. The catalyst immobilized onto the silica surface could be used in manifold (>10) consecutive runs without significant leaching of the complex to the reaction mixture and maintained constant stability. Both homogeneous and immobilized Mo-Salen complexes exhibit higher catalytic activity in comparison to Mn and V-Salen complex systems due to rapid tert-butylhydroperoxide catalytic decomposition initiated by manganese and vanadium.

Low Temperature Microcalorimetry to Measure the Heat of Adsorption of Cyclohexene on Pt(111)

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The hydrogenation and dehydrogenation of cyclic hydrocarbons on platinum catalysts are important petrochemical reactions. We have used low temperature microcalorimetry measurements to determine the enthalpy of adsorption and sticking probability of cyclohexene on Pt(111) at 100K. Cyclohexene adsorbs intact at surface temperatures below 180K, but decomposes at higher temperatures via several intermediates, including benzene and hydrogen starting at ∼300K. Since cyclohexene adsorbs irreversibly on platinum, the traditional method to measure adsorption enthalpies, Temperature Programmed Desorption (TPD), cannot be used. Here we report the first direct measurement of the enthalpy of adsorption for a hydrocarbon on any single crystal surface at cryogenic temperatures. Low temperature microcalorimetry makes it possible to measure the heats of formation of important reaction intermediates that are frequently unstable at room temperature. One of the major challenges of conducting low temperature calorimetric studies for small heats of adsorption is getting the microcalorimeter to detect small temperature changes on the order of 10 milliKelvins with minimal noise. This study explores modifications to the microcalorimetry apparatus to detect small adsorption energies. The prototype molecule for this system is cyclohexene where only $\sim 2.5\text{x}10^{12}$ molecules are dosed per cm^2.

P-106

Adsorption of NO and SO_2 on the $Sn_{0.5}Ti_{0.5}O_2$ Catalyst Studied by *in-situ* FTIR Spectroscopy

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$Sn_{0.5}Ti_{0.5}O_2$ shows excellent catalytic performance for simultaneous reduction of SO_2 and NO by CO. The conversion of SO_2 is nearly 90% and the conversion of NO is above 98%. NO and SO_2 are selectively converted to N_2 and S. SO_2 shows a significant promoting effect on the activity of the $Sn_{0.5}Ti_{0.5}O_2$ catalyst for NO reduction by CO. In order to find out the mechanism of simultaneous reduction of SO_2 and NO by CO, the adsorption of NO and SO_2 on the $Sn_{0.5}Ti_{0.5}O_2$ Catalyst is investigated by in-situ FTIR.

Results

1. Adsorption of NO: The adsorption of NO at 100°C, 200°C, 300°C and 400°C respectively on $Sn_{0.5}Ti_{0.5}O_2$ activated at 400°C has been studied by FTIR spectroscopy (Figure 1). Three different types pf adsorbed species have been identified. At 100°C, the bands at 1603 and 1578cm^{-1}, which can be assigned to the bidentate NO_3^-, can be detected. Another two bands at 1287 and 1244cm^{-1} can be assigned to the monodentate NO_3^-.When the temperature is increased to 200°C, the bidentate NO_3^- at 1603 and 1578cm^{-1} become a little bit weaker and the monodentate NO_3^- at 1287 and 1244cm^{-1} convert to bridged NO_2^- at 1231cm^{-1}.On heating to higher temperatures of 300°C, all of the NO_3^- and NO_2^- bands disappear. At 400°C, three negative bands at 1520, 1430 and 1350cm^{-1} can be detected, which increases versus time corresponds to the decomposition of the carbonates on the surface of the $Sn_{0.5}Ti_{0.5}O_2$ catalyst. All of changes of the adsorbed species also can be detected in TPD-FTIR spectroscopy.

2. Adsorption of SO_2: The adsorption of SO_2 on $Sn_{0.5}Ti_{0.5}O_2$ has been investigated by FTIR spectroscopy (Figure 2). At lower temperature of 100 and 200°C, only very weak band at 1132cm^{-1} corresponds to SO_4^{2-} can be detected. Because SO_4^{2-} can substitute for CO_3^{2-} at lower temperature, the negative bands at 1550, 1430 and 1350cm^{-1} appear. At 300°C, a broad band at 1380-300cm^{-1} can be detected with strong intensity. The dominant adsorption is at 1330cm^{-1}. On heating to higher temperatures of 400°C, there is a pronounced increase in the intensity of the broad band and it shifts to higher frequency around 1400-1300cm^{-1}. The dominant adsorption also shifts to 1372cm^{-1}. One the other hand, at 400°C, part of the CO_3^{2-} are substituted by SO_4^{2-}, the rest begin to decompose. So the negative bands at 1530 and 1430cm^{-1} preferentially increase in intensity. But the negative band at 1350cm^{-1} is covered by the broad band of SO_2. The result of direct adsorption of SO_2 at 400°C on $Sn_{0.5}Ti_{0.5}O_2$ activated at 400°C proofs the above analysis.

Discussion

1. The adsorption of NO occurs at lower temperature. There is no adsorption can be detected at reaction temperature 400°C. So the reduction of NO by CO without SO_2 follows the Rideal mechanism.

2. Strong chemisorptions occurs between SO_2 and the surface of $Sn_{0.5}Ti_{0.5}O_2$. But high adsorption activation energy is required. So the adsorption only can be detected above 300°C. The adsorbed species of SO_2 on the surface of $Sn_{0.5}Ti_{0.5}O_2$ is the active site for NO reduction in the CO-SO_2-NO reaction, and through which SO_2 accomplishes its promoter role.

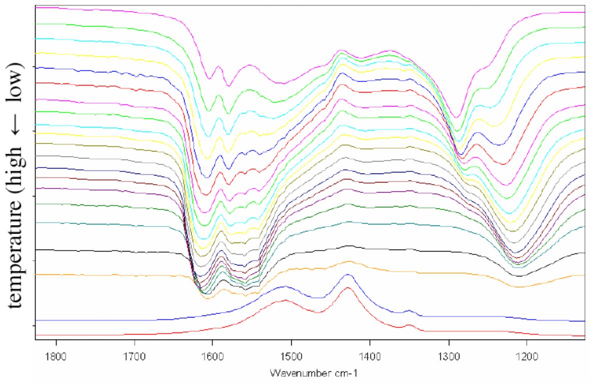

Figure 1. FTIR spectra of the adsorption of NO on $Sn_{0.5}Ti_{0.5}O_2$.

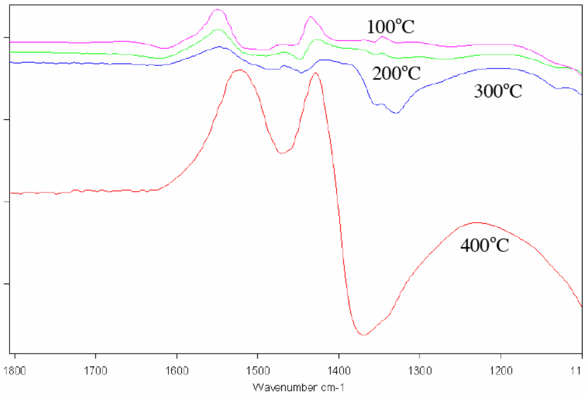

Figure 2. FTIR spectra of the adsorption of SO_2 on $Sn_{0.5}Ti_{0.5}O_2$.

MCM-41 Supported Homo- and Hetero-metallic Hydrogenation Catalysts: A Comparative Study

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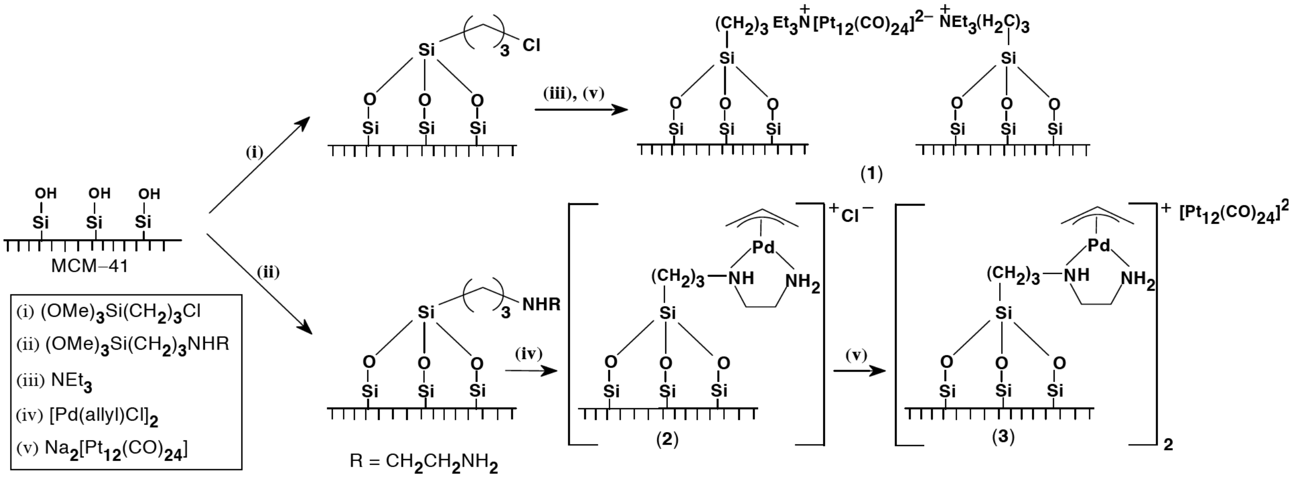
MCM-41 supported homo- (**1** and **2**) and hetero-metallic (**3**) heterogeneous catalysts have been developed *via* the functionalization of MCM-41 support using selective silane reagents, $(MeO)_3Si(CH_2)_3Cl$ and $(MeO)_3Si(CH_2)_3NH$-$CH_2CH_2NH_2$ followed by ion-pairing with $[Pt_{12}(CO)_{24}]^{2-}$ in **1**, covalent linkage with $[Pd(allyl)Cl]_2$ in **2** or covalent linkage with $[Pd(allyl)Cl]_2$ and subsequent ion pairing with $[Pt_{12}(CO)_{24}]^{2-}$ in **3** as shown in the figure. The materials have been characterized in each step using solid state spectral (^{13}C,^{29}Si-NMR, IR, XPS), microscopic (TEM/SEM/EDAX) and microanalytical (C,H,N) techniques.[1,2,3] A comparative study among the three catalysts (**1-3**) has been performed towards the catalytic hydrogenation of variety of unsaturated substrates such as methyl pyruvate, nitrobenzene, styrene, cyclohexanone, acetophenone and S–(+)–carvone. Upon hydrogenation of S–(+)–carvone platinum based catalyst (**1**) leads to the only product 2-methyl-5-isopropyl-cyclohexanone whereas palladium based catalyst (**2**) leads to moderate isomerized product 2-methyl-5-isopropyl-phenol along with aforesaid saturated cyclohexanone derivative. The heterometallic catalyst (**3**) gives result in betwen (**1**) and (**2**).



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Allyl Transition Metal Complexes as Important Precursors for Homogeneous and Heterogeneous Catalysis

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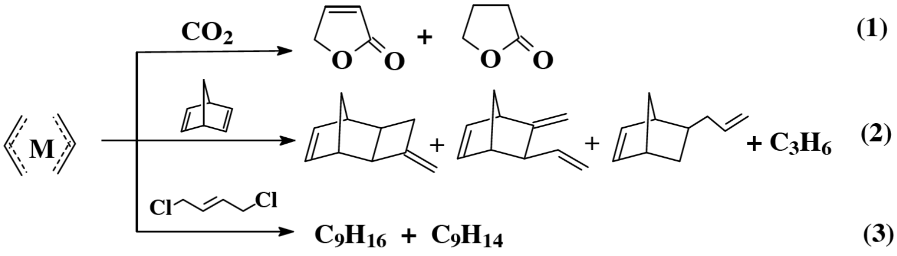
The report comprises results concerning unusual direction of transition metal allyl complexes, that appears to be the redox disproportionation of allyl ligands.[1,2,3]



1. M – *Ni, Pd*; 2. M – *Fe, Co, Ni, Rh, Pd, Pt*; 3. M – *Ni*

The share of disproportionation depends on the effective positive charge (from +0.4 up to +0.8) on metal and the substrate nature. The reaction is accompanied by β-hydride transfer, which can either proceed from a substrate, or from the allyl moiety. Possible mechanisms are considered. The disclosed factors determine the ratio of disproportionation and conventional directions of transformations of allyl complexes.

Phosphite nickel and phosphine palladium complexes show high catalytic activity and regio/stereoselectivity in nonconventional norbornadiene allylation in both homogeneous and heterogeneous catalysis conditions.[4] The ratio of stereoisomers and the number of catalytic cycles depends on the metal-ligands ratio.[5]

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Graphite Oxide: A Novel Host Material for Transition Metal Nanoparticles

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Graphite oxide (GO), an oxygen-rich carbonaceous layered material, is produced by the controlled oxidation of graphite. GO is a typical two-dimensional solid in bulk form, with strong covalent bonding within the layers. Weaker interlayer contact is made by hydrogen bonds between intercalated water molecules.[1] GO consists of intact graphitic regions interspersed with sp^3 hybridized carbons containing hydroxyl and epoxide groups and sp^2 hybridized carbons with carboxyl and carbonyl goups at the sheet edges. Accordingly, GO is a hydrophilic material, which may be readily dispersed in water to form stable colloidal suspensions.[2] As related to its swelling ability and cation exchange capacity,[3] GO is also regarded as a promising host material for the intercalation of transition metal nanoparticles.

In the present study, Pd nanoparticles were immobilized in GO for the first time. Low-loaded Pd-GO materials were synthetized in a micellar system, by using the cationic surfactant tetradecyltrimethylammonium bromide ($C_{14}TAB$) as a stabilizer.[4] In the first synthesis step, an aqueous solution of the precursor K_2PdCl_4 was added to a $C_{14}TAB$ solution under vigorous stirring. Reduction by $NaBH_4$ resulted in the formation of a stable Pd sol, consisting of monodispersed particles of 2-3 nm in diameter. On addition of the surfactant-stabilized Pd sol to a dilute aqueous suspension of GO, cation exchange took place, producing a hydrophobic GO organocomplex, whereas the reduced Pd particles were immobilized in the GO layers. The above procedure ensured the preparation of organophilic Pd-GO materials with different Pd contents. Structural characterization of the samples was performed by ICP-AES, XRD and TEM. It was established that a considerable proportion of the Pd particles was intercalated in the interlamellar region of GO and the presence of the cationic surfactant prevented particle aggregation. As related to their hydrophobic character, the Pd-GO samples were readily dispersed in organic solvents. The samples were tested as catalysts in the liquid-phase hydrogenations of internal alkynes under mild conditions (298 K, 10^5 Pa). The catalytic measurements were performed in an automated hydrogenation apparatus under vigorous stirring, by applying reactant:Pd ratios exceeding 5000. The hydrogenation rates and the turnover frequencies were determined for the transformations of 3-hexyne and 4-octyne, together with the product distributions obtained by capillary GC. For both reactions, pronounced hydrogenation rates and marked *cis*-alkene stereoselectivities ($>$ 94%) were observed, indicating that the Pd-GO samples were highly active and stereoselective catalysts.

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Immobilization of (1R,2S)-(-)-N-dodecyl-N-methylephedrinium Bromide and its Catalytic Application in the Enantioselective Alkylation of Benzaldehyde with Diethylzinc

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Owing to the possibility of easy recovery and reuse, the immobilization of chiral catalysts has gained in importance. Recently, many attempts have been made to immobilize chiral auxilieries.[1] However, this is not a trivial exercise and in some cases the enantiomeric excesses (ee%) obtained have been lower in the supported systems.[2] In the domain of carbon-carbon bond forming reactions, the homogeneous enantioselective alkylation of aldehydes with diethylzinc has been extensively studied by using (-)-ephedrin derivatives as catalysts[1,2]. The reaction of benzaldehyde with diethylzinc to give 1-phenylpropanol has been reported to occur slowly in the absence of catalyst to give a racemic product mixture. The immobilized chiral catalysts are therefore operating in a competititve situation, which makes it rather difficult to obtain enantiomeric excesses as high as those obtained in homogeneous systems[2].

The present study is concerned with the immobilization of a chiral cationic surfactant, (1R,2S)-(-)-N-dodecyl-N-methylephedrinium bromide (DMEB), to be applied as a heterogeneous catalyst for the alkylation of benzaldehyde with diethylzinc, in comparison with the original surfactant operating as a homogeneous catalyst under the same conditions. High-purity sodium montmorillonite (Na-M, CEC = 75 meq/g) was employed as a host material. Na-M was rendered organophilic with DMEB via ion-exchange at 313 K. The hydrophilic clay was suspended in an aqueous solution of DMEB and maintained at 313 K under stirring for 2 days. After organophilization, dodecylmethylephedrinium-montmorillonite (DME-M) was purified by Soxhlet extraction in 2-propanol for 48 h and freeze-dried from benzene. The organic cation exchange capacity, determined by a Q-1500 D derivatograph and a TOC-1200 analyzer, proved to be 0.63±0.3 meq/g. The basal spacings of DME-M, dispersed in various organic solvents were obtained from XRD patterns, determined by a Philips X-ray diffractometer. The extent of swelling was negligible in hexane, suggesting that this solvent cannot enter the interlamellar space of DME-M. In contrast, pronounced interlayer expansions were observed in ethanol, tetrahydrofurane and toluene, indicating an efficient wetting of the silicate surface and good solvation of the alkyl chains. DME-M was present as highly ordered lamella packages in the dispersion media, except for toluene, for which delamination occurred. The alkylation of benzaldehyde with diethylzinc was investigated in a batch reactor under an Ar atmosphere at 273 K and 10^5 Pa, by using the molar ratios benzaldehyde:diethylzinc:ephedrine = 1:3:0.05. The product mixture was quenched with 2 M HCl and extracted with dichlorometane. Product analysis was carried out by GC-MS, by using a Cyclodex B capillary column. At a reaction time of 24 h, the application of DMEB in a homogeneous reaction afforded a conversion of 42.8% and an ee(%) of 18.9 in favour of the R enantiomer. In the heterogeneous reaction, the immobilized surfactant DME-M afforded a higher conversion of 51.6%, but a lower ee(%) of 10.2. The application of DME-M also affected the product distribution by decreasing the selectivity of benzoic acid produced in the homogeneous reaction. An elevated reaction temperature of 283 K was found to have an increasing effect on the conversion, together with a decreasing effect on the ee(%) values for both catalysts.

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[2] P. Hodge, D.W.L. Sung, P.W. Stratford *J. Chem. Soc. Perkin Trans.* 1 (1999) 2335.

What is the Most Widely Used Industrial Homogeneous Catalyst?

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Cobalt acetate is the simplest representative of perhaps one of the most complex homogeneous catalysts. Cobalt carboxylates find extensive use in the oxidations of hydrocarbons, such as p-xylene to terephthalic acid or dimethyl terephthalate (the largest industrial use of homogeneous catalysts), or the oxidation of cyclohexane to cyclohexanol and cyclohexanone in the generation of adipic acid for nylon synthesis. Paradoxically, despite these extensive applications, the nature of simple cobalt(III) acetate is poorly understood. First reported as a solid in 1924, cobalt(III) acetate has never been structurally characterised as an unique material. We report the constitution and catalytic reactivity of the cobalt acetates. Dimers, trimers, tetramers, heptamers and octamers abound, characterised by beautiful structures, complex catalytic behaviour, and multiple oxidation states.

CO + NO Reaction Activity of SnO_2/CeO_2 Composite Oxide: Study of Real and Model Catalysts

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A new SnO_x/CeO_x catalysts were prepared by impregnation of nanosized CeO_2 particles with tin acetyl acetate dissolved in toluene. The catalysts were calcined in O_2 and then reduced in hydrogen. The catalyst showed high activity for NO reduction by CO relative to pure ceria and tin oxide. The temperature dependence of the reaction rate was measured in a micro flow reactor with mass spectrometer detection. The catalyst structure was investigated by high resolution transmission electron microscopy (HRTEM) and scanning TEM combined with energy dispersive spectroscopy (EDS). The TEM analysis revealed that tin oxide particles (2-10 nm) had grown on the ceria particles surface.

The high catalytic activity of the SnO_x/CeO_x catalysts might be explained by strong Ce-Sn interaction and Sn - Ce charge transfer that leads to weakening of cerium - oxygen bond and consequently to formation of oxygen deficient active sites on the ceria surface. This hypothesis is supported by the results of model studies performed on a well defined $Sn/CeO_2(111)/Cu(111)$ system.

The model system was prepared by growing a continuous $CeO_2(111)$ epitaxial film 1.5 nm thick (5 ML of CeO_2) on the Cu(111) substrate in oxygen atmosphere. The film structure corresponding to the (1.5 x 1.5) $CeO_2(111)/Cu(111)$ reconstruction was checked by low energy electron diffraction (LEED). Tin was deposited on the $CeO_2(111)$ surface by molecular beam deposition. The X-ray photoelectron spectroscopy (PES), vacuum ultra violet PES and Resonance PES studies of tin interaction with cerium oxide were performed at Material Science Beamline at the synchrotron Elettra in Trieste. The resonant photoelectron spectroscopy in the Ce 4d - 4f photoabsorption region showed resonance enhancement of the 4f state emission at the photoelectron energies Ep= 122 eV (resonant feature corresponding to Ce^{3+}) and 124.5 eV (resonant feature corresponding to Ce^{4+}).

The tin-cerium oxide interaction led to the $CeO_2 \rightarrow Ce_2O_3$ phase transition that was observed as a giant 4f resonance of the Ce^{3+} species. High resolution Sn 4d spectra taken at E_p= 115 eV (i.e. at "off resonance" energy) showed formation of SnO species. Al K line XPS (E_p = 1487 eV) of the Ce 3d core level showed that the $Ce^{4+} \rightarrow Ce^{3+}$ transition occurred not only on the surface but also in the ceria film depth. The tin induced $Ce^{4+} \rightarrow Ce^{3+}$ phase transition was observed even at low temperature below 140 K.

NO adsorption on cerium oxide at 250°C resulted in a small effect of NO dissociation and decrease of the resonant Ce^{3+} signal, i.e. to filling of the surface oxygen vacancies that were always present, to the limited extent, on the $CeO_2(111)$ film surface. The Ce_2O_3 phase obtained due to Sn deposition exhibited considerable increase of the dissociative NO adsorption, an obvious decrease of resonant Ce^{3+} signal and increase of the Ce^{4+} one. XPS showed an appearance of the N 1s intensity of the N^- species.

The observed CeO_2 - Ce_2O_3 phase transition and oxygen mobility is of high fundamental importance. Transition between these two stable ceria phases is an important step of catalytic reactions and processes based on "oxygen storage" properties of ceria. Metal-oxide interaction is one of the most important phenomena influencing adsorption and catalytic properties of metal-oxide systems. Strong interaction between a metal and a reducible oxide is a driving force determining properties of metal-oxide catalysts. Interaction of tin with cerium dioxide is a prototype of such systems.

CO Oxidation Over Palladium Doped Tin Oxide: Changes in Chemical Composition and Structure

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Palladium doped tin oxide powder exhibits interesting catalytic properties towards low temperature CO oxidation.

Pd(O)/SnO_2 powder catalysts were prepared by impregnating nanostructural tin oxide particles with palladium acetyl acetonate that was thermally decomposed in a mixture of Ar and O_2 and/or in 10% H_2 + 90% He atmosphere at different temperatures between 120 and 360°C. The catalysts obtained by this way were composed of Pd particles of average diameter below 5 nm supported by tin oxide powder support.

Chemical composition and structure of prepared samples was determined by X-ray photoelectron spectroscopy (XPS), scanning transmission electron microscopy (STEM), high resolution transmission electron spectroscopy (HRTEM), scanning TEM combined with energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD). CO oxidation on this system was performed in flow tube reactor using the mixture of Ar, O2 and CO. and in a flow micro-reactor where the catalyst was deposited on a silicon oxide chip by ensuring a very reliable catalyst temperature control.

The temperature dependent CO conversion curves showed a dependence of catalyst reactivity on treatment conditions, i.e. on Pd-Sn interface formation. The TEM measurements showed that the interface is formed by more or less extended Pd-Sn alloy region. XRD confirmed this observation by revealing Pd-Sn alloy features and traces of metallic tin. The observed behavior was explained by the effect of strong metal-substrate interaction that was entrained by the Pd-Sn interface formation. Strong metal-tin interaction resulting in lowering of CO desorption temperature was confirmed by model study of the Sn/Pd(110) system.

Significant lowering of CO oxidation temperature was observed in comparison with the pure SnO_2 powder.

Single Laser Broadband CARS Spectroscopic Imaging Platform with Integrated TPF and SHG Functions for Chemical Identification

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CARS is a nonlinear, multiphoton spectroscopic/imaging technique using molecular vibrations as a contrast mechanism. It relies on the resonance enhancement of the third order nonlinear susceptibility of a vibrational mode of a molecule and can provide similar vibrational information as a spontaneous Raman spectrum. Similar to other multiphoton techniques, CARS has gained tremendous momentum in recent years with principal advantages such as intrinsic optical sectioning capabilities, chemical specificity, and video-rate imaging. Other nonlinear imaging techniques such as two-photon fluorescence (TPF) and second harmonic generation (SHG) are also active areas of research.

While conventional CARS generates single-wavelength signal using two pico-second lasers, we use a single laser multiplex CARS which is able to generate a CARS spectrum with a spectral width >2500 cm^{-1} with the use of a 100 femtosecond laser and a highly nonlinear photonic crystal fibre (PCF) to generate a supercontiuum Stokes beam. Biochemical spectroscopic measurements from multiplex CARS in forward and backward scattering directions can be collected simultaneously. A scanning system allows spectroscopic imaging of the sample.

We have developed the CARS platform in order to combine other non-linear techniques such as two-photon fluorescence (TPF) and second harmonic generation (SHG). These techniques use an ultra-short pulse laser for nonlinear signal generation. Our multi-modal platform opens up the possibility of co-registering images generated from different modalities. The system can switch from CARS to TPF-SHG measurements of the same sample in a few seconds. The system is configured for TPF measurement in a backscattered configuration and SHG measurement in a forward direction using high numerical aperture microscope objectives. Beam expanders and relay optics are added to optimize the signal generation and collection efficiency for improved sensitivity.

In this work, we will give an overview of the platform configuration, technical issues related to instrumental design and the critical parameters for system optimization. The advantages and future improvements of a multi-modal platform geared towards biomimetic materials spectroscopy and imaging will also be discussed.

Reflection-absorption Infrared Spectroscopy Studies of the Stability and Reactivity of Alkylidynes on Pt(111) Single-crystal Surfaces in the Presence of Atmospheric Pressures of Hydrogen

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An understanding of how heterogeneous catalysis works requires a good knowledge of the structure and reactivity of the adsorbed overlayer that form on the catalyst's surface during reaction. It is well known that during catalytic processes involving mild reactions such as hydrocarbon hydrogenations, dehydrogenations, and isomerizations the surface of the catalyst is not pristine but it is covered with carbonaceous residues produced by fast hydrocarbon dehydrogenation at the start of the reaction instead. The level of participation of such residues in the mechanism of the catalytic process, in particular how they may affect or influence the nature of the products formed, is still not fully understood. In this study we have made use of reflection-absorption infrared spectroscopy (RAIRS) in conjunction with a high-pressure cell to look into the kinetics of the surface reactions of those carbonaceous residues. In particular, we have investigated how the stability and reactivity of alkylidyne species (ethylidyne, propylidyne, and butylidyne) adsorbed on a model Pt(111) single-crystal surface are affected by the presence of hydrogen or deuterium atmospheres at different temperatures. We have found that, in the presence of 200 torr of hydrogen, the alkylidyne species are stable at room temperature, but either hydrogenate and convert on the surface at temperatures above 330K. A normal kinetic isotope effect has also been observed in these systems, with higher temperatures needed for alkylidyne removal from the surface when deuterium is used instead of hydrogen. Work in progress is aimed to identify the intermediate species that form on the surface during hydrogenation reactions and participate in olefin conversion catalytic processes.

Acetone Transformation on PtSn/H[Al]ZSM5 Bifunctional Catalysts: Effect of the Density of Acidic Sites

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Among the different driving forces of contemporary catalysis research is the development of selective catalysts toward the production of specific products. More selective catalysts have been obtained by the adding of a second metal to catalysts and they have proven to often provide additional catalytic stability, selectivity and/or activity. For instance, we have shown that PtSn/H[Al]ZSM5 catalysts show significant improvements in selectivity towards the methyl isobutyl ketone (MIBK) synthesis from acetone. However, keeping in mind that in bifunctional catalysis the selectivity, activity and stability of the catalysts not only depends on the metal site but, in fact, is also affected by the balance between the acid (or basic) and the metal sites. In this way, the present study shows the effect of the density of acidic sites in the synthesis of MIBK from acetone when bifunctional and bimetallic catalysts of the PtSn type supported on H[Al]ZSM5 zeolites, with two different Si/Al ratios, are used. The catalysts that were synthesized and characterized were Pt/H[Al]ZSM5, PtSn/H[Al]ZSM5 (X_{Sn} ∼0.4), and Sn/H[Al]ZSM5 catalysts with Si/Al ratios of 15 and 37. Different characterization techniques were used here, namely, X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and toluene hydrogenation reactivity studies. Interesting correlations were found for the conversion and selectivity for the studied reaction. Also, based on XPS data, it was found that alloy formation between the two metals is dependent of the support acidity, where alloy formation between Pt and Sn seems to be favored on more acidic supports.

Catalytic Properties of Electrophilic Organozirconium Adsorbates on γ-Alumina. A DFT Study

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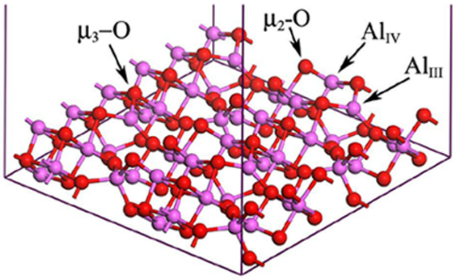
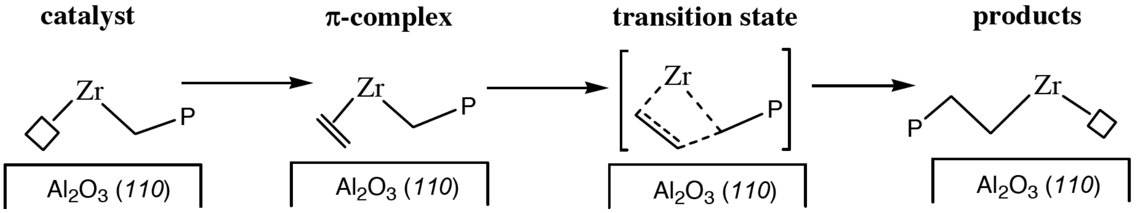
This contribution focuses on modeling of the catalytic properties of the organozirconium catalyst precursor $Cp'_2Zr(CH_3)_2$ chemisorbed on dehydroxylated γ-alumina (Al_2O_3) using density functional theory. The interactions of the catalytic cation species $Cp'_2Zr(CH_3)^+$ with the $Al_2O_3(110)$ surface are scrutinized. In particular, two oxygen sites on the surface namely, μ_2-O and μ_3-O - depending on the coordination with the aluminum atoms - are responsible for the interaction between the catalytic species and the surface. It is found that the interactions of catalyst with μ_2-O sites are stronger than with μ_3-O because of the greater coordinative power of the μ_2-O species respect with the μ_3-O species.

Next, the catalytic behavior of the system with respect to the ethylene polymerization processes is investigated on both oxygen sites, comparing the results with the homogeneous $Cp'_2Zr(CH_3)^+H_3CB(C_6F_5)_3^-$ molecular analogues.



In all cases, the polymerization process follows the Cossee mechanism that involves a two-step process: i) olefin coordination to a vacant catalytic site, and ii) alkyl migration of the σ-coordinated growing chain to the π-coordinated olefin. The energy profile associated with this process on μ_3-O surface sites evidences greater stabilization in terms of transition state and product structures than does the analogous process on the μ_2-O surface site. The observed trend in energy profile on passing from μ_3-O to μ_2-O surface sites is due to the greater interaction of the electrophilic catalytic cation species $Cp'_2Zr(CH_3)^+$ with the μ_2-O site versus the μ_3-O site. A close correlation is found between the ion pair interaction (molecular cation–surface anion in the heterogeneous case) and the kinetic and thermodynamic parameters for the ethylene polymerization process.



Theoretical Investigation of Proximity Effects in Binuclear Catalysts for Olefin Polymerization

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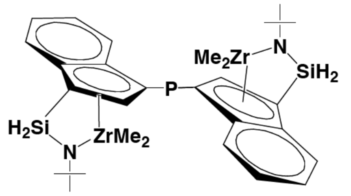
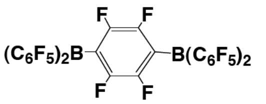
This contribution focuses on distinctive features associated with bimetallic constrained geometry catalysts (CGCs) and analyzes the proximity effects operative in (μ-CH_2-3,3){(η^5-indenyl)[1-H_2Si(tBuN)]($ZrMe_2$)}$_2$ (**Zr**$_2$)-mediated in ethylene polymerization processes using density functional theory. In particular, the configurational geometries of the precatalyst are discussed, and the ion pair formation/heterolytic dissociation processes accompanying reaction with the binuclear bisborane cocatalyst, 1,4-$(C_6F_5)_2BC_6F_4B(C_6F_5)_2$ (**BN**$_2$), have been scrutinized and compared with the analogous mononuclear case. It is found that on passing from mononuclear to binuclear CGCZr catalyst systems, the ion-pair dissociation energies increase due to stronger electrostatic interactions. Moreover, in the binuclear case, the interaction energies are sensitive to geometrical matching between the binuclear bisborane centers and the precatalyst methyl positions. The proximity effects between Zr centers are then analyzed with regard to polymerization processes. To better understand the specific contribution of the second metal center proximity to the distinctive features of the binuclear systems, the counteranion effects, to first approximation, have been neglected. The possible formation of agostic interactions between a vinyl-terminated oligoethylene chain coordinated to one Zr center with the second Zr center of the same catalyst molecule has been scrutinized for 1-octene. It is found that these agostic interactions are responsible of the unusual behavior of the bimetallic catalysts. In particular, the greater ethyl branching, experimentally found for bimetallic catalysts, appears to be associated with intramolecular olefin reinsertion processes, favored by the agostic interactions. Moreover, it is found that similar agostic interactions of the growing chain attached to one metal site with the other metal site of the same system, constrain the geometrical environment around the catalytic site, favoring chain propagation step instead of the termination and, in turn, favor increased polyolefin molecular weight (Mn) in the case of bimetallic catalysts, in agreement with experiment.

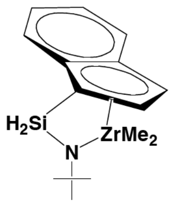


P = CH$_2$

Zr$_2$



BN$_2$



Zr$_1$

$B(C_6F_5)_3$

BN

A Comparative Study of the Bimetallic AuPt/A Zeolite Catalyst in the Single-stage and the Two-stage Reactor for the PROX Reaction

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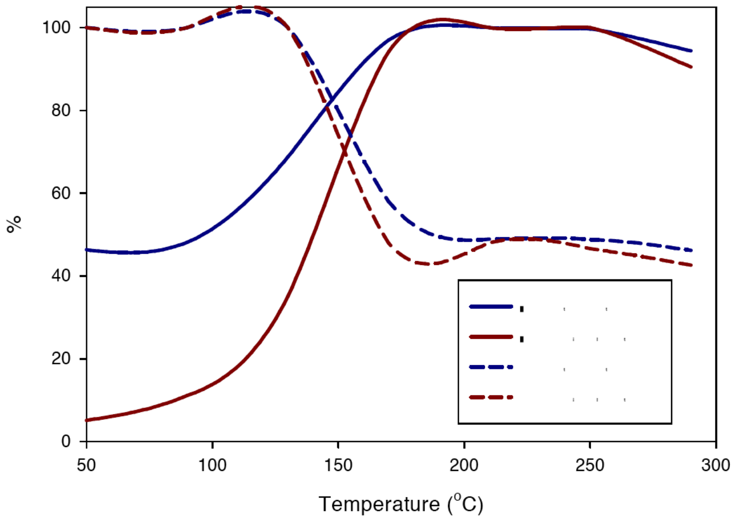
The catalytic performance of the bimetallic AuPt/A zeolite catalyst in the preferential oxidation of carbon monoxide in the hydrogen atmosphere was investigated. The overall reactant gas mixture contained CO (1%), O_2 (1%) and H_2 (40%) with the balance being He at a total flow rate of 50 ml/min. The AuPt/A zeolite catalyst in preliminary study was applied to the two-stage reactor and it was tested at an oxygen split ratio of 50:50. The results clearly showed that the two-stage process provides a wider range of the operating temperature that gives the CO conversion approach to 100% in the range of high temperatures (210-300°C). Moreover, the twostage reactor gives a better CO selectivity than that of the single-stage reactor to minimize H_2 loss. Interestingly, an essential requirement of the amount of oxygen that use in the preferential oxidation of CO for the two-stage reactor process was less than that of the single-stage reactor around 20%. Nevertheless, the optimization of temperature in the two-stage reactor was studied also. The first reactor was controlled at a constant temperature and the temperature in the second reactor was varied from 50°C to 300°C. The best performance of the process was achieved at 170°C for both reactors. This process exhibited a stable performance during 12 hrs of testing time. The in-depth studies will be investigated further.



Application of Simultaneous Redox Ability of TiO_2 in Synthesis of Carbon/Metal Nanocomposites

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TiO_2 photocatalysis has been widely employed in decomposition of organic compounds and in organic synthesis. In consideration of current interest in nanomaterial fabrication, potential of the TiO_2 photocatalysis in the nanostructured material preparation has started to draw attention. In this study, we report for the first time the fabrication of hollow carbon nanospheres encapsulating platinum nanoparticles (nPt@hC) using the redox ability of the TiO_2 photocatalysts[1].

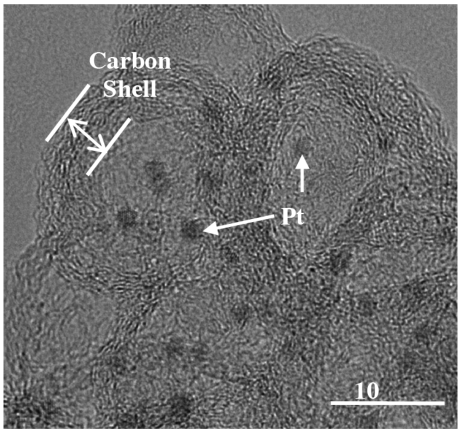

Figure 1. TEM image of nPt@hC

The concept of our methodology in this study is based on the ability of TiO_2 to induce simultaneous photodeposition of platinum and oxidative polymerization of phenol on the TiO_2 surface, i.e., photogenerated electrons and positive holes in TiO_2 were used for reduction of the Pt^{4+} precursor and oxidation of phenol, respectively. This resulted in Pt-loaded TiO_2 fully covered by phenolic polymer. By carbonizing this phenolic polymer at 973 K under vacuum condition and subsequently removal of TiO_2 through chemical etching, nPt@hC as shown in Figure 1 was obtained. From the N_2 adsorption-desorption measurement, the nPt@hC nanocomposites were found to possess high surface area of 1500 m^2 g^{-1} and contain microporosity inside the thin carbon layer. Owing to this developed microporous system and high surface area, this material appears to be a potential candidate in catalytic reactions. In fact, we have confirmed that the nPt@hC exhibited excellent activity in a series of olefin hydrogenation (Table 1).

Table 1. Liquid-phase hydrogenation of various olefins catalyzed by nPt@hC

	Hydrogenation Reaction		Conversion
	Substrate	Product	(%)
1	1-Hexene	Hexane	>99
2	2-Hexene	Hexane	>99
3	1-Decene	Decane	>99
4	1-Hexadecene	Hexadecane	>99
5	Cyclohexene	Cyclohexane	98
6	Phenyl-1-cyclohexene	Phenylcyclohexane	>99

All reactions were carried out with 0.1 μmol of catalyst (Pt) under H_2 (200 KPa in absolute pressure) at 348 K with stirring.

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Checking the Mechanism of the Asymmetric Isomerization of Allylamines to Enamines Catalyzed by Rhodium

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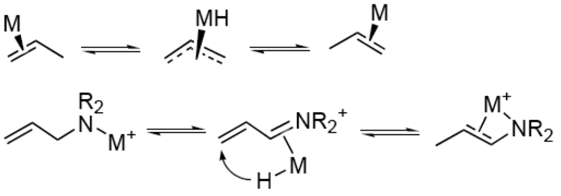
The enantioselective asymmetric isomerization of allylamines to enamines was achieved by Noyori using as catalyst cationic BINAP rhodium complexes.[1] The mechanism proposed for this reaction consists of the oxidative addition of the C-H bond to the metal starting with a κ^1-(N) coordinated allylamine (eq 2) followed by reductive elimination accompanied by allylic transposition.[2] This mechanism, named N-triggered to be distinguished from the classical π-allylic mechansim (eq 1), was supported by an ab initio molecular orbital study, which shows that the proposed intermediates were thermodynamically plausible.

(1)

(2)



Some recent experimental observation in related systems together with the improved theoretical methods and calculation facilities prompted us to revisit this mechanism.[3] In the present work, the allylamine isomerization reaction has been computationally studied considering the N-triggered mechanism as well as the classic allylic mechanism using the *cis*-$[Rh(PH_3)_2]^+$ complex to model $[Rh(BINAP)]^+$. The N-triggered mechanism shows a very high energy barrier for the hydrogen transfer step and also affords the wrong Z isomer of the enamine. Therefore, the results show that the most favourable mechanism is a slight modification of the traditional allylic one.

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[2] M. Yamakawa, R. Noyori *Organometallics* 11 (1992) 3167.

[3] A.C. Albéniz, P. Espinet, A. PérezMateo, A. Nova, G. Ujaque *Organometallics* 25 (2006) 1293.

Selective Hydrogenation of Toluene Using Ionic Liquidcoated Ru on C as Catalyst

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The hydrogenation of arenes is of major technical interest as a large range of industrial chemicals, such as dyes, pharmaceutical components and pesticides are hence accessible. Especially the partially hydrogenated cyclic alkenes are interesting products for further synthetic applications. Unfortunately, in technical hydrogenation processes completely hydrogenated products are predominantly obtained due to the stable nature of the aromatic feedstock leading to full hydrogenation once the hydrogenation process has started.

Our aim was to establish a reaction system that would allow the synthesis of cyclic alkenes from aromatic feedstock in good selectivity. For this purpose we prepared ionic liquid-coated Ru on charcoal catalysts and used the latter in the selective hydrogenation of toluene. Ionic liquids have the potential to stabilize thermodynamically instable reaction intermediates, in our case methylcyclohexenes.

Our poster presents the results of our kinetic investigations carried out in a batch slurry system. By varying the ionic liquid coating and reaction parameters (temperature and pressure) we were indeed able to identify influencing factors to improve methylcyclohexene selectivities. Scope and limitations of ionic liquid-coated, heterogeneous hydrogenation catalysts will be discussed.

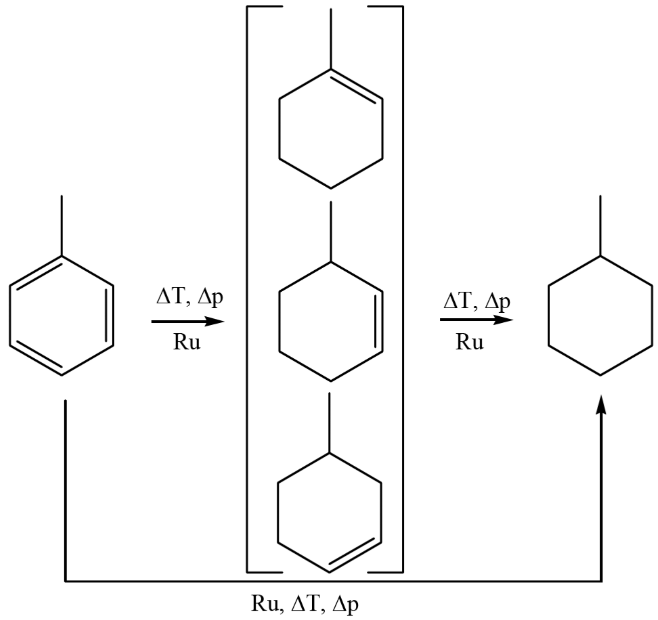

Figure 1. Reaction scheme of the hydrogenation of toluene.

Inertization of a Pyrophoric Heterogeneous Nickel-catalyst (Raney-Nickel) by Ionic Liquid Coating

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Raney-Nickel is an important heterogeneous catalyst for commercial hydrogenation processes, e.g. for fat hardening. However, an important disadvantage of commercial Raney-Nickel catalysts is their pyrophoric nature. The dry catalyst tends to ignite when contacted with oxygen[1]. This characteristic property makes the commercially available Raney-Nickel catalyst difficult to handle and requires special treatment prior to catalyst deposal.

In our poster contribution we present a methodology to coat commercial Raney-Nickel catalyst with a thin film of an ionic liquid thus obtaining a fully air and even oxygen stable catalyst system. The inert coated catalyst still shows good catalytic activity in hydrogenation reactions. In detail, we studied the hydrogenation of 2,3-dimethyl-1,3-butadiene (see Figure 1). For this reaction a comparison of the catalytic performance (activity and selectivity) of the IL-coated system vs. the pyrophoric standard Raney-Nickel will be presented.

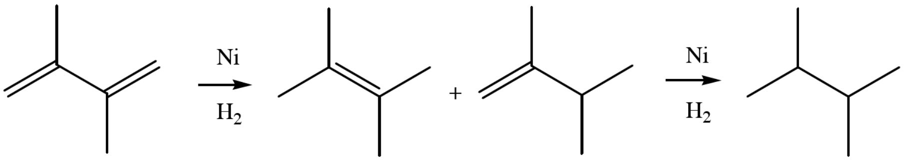

Figure 1. Hydrogenation of 2,3-dimethyl-1,3-butadiene

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Asymmetric Catalysis using Supported Ionic Liquid Phase (SILP) Materials

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Supported Ionic Liquid Phase (SILP) catalysts are novel materials consisting of an ionic liquid, metal catalyst and a porous support.[1] The support is covered with a thin film of ionic liquid and the homogeneous or heterogeneous catalyst is dissolved in this ionic liquid film.

The SILP-catalysis concept combines the advantages of homogeneous and heterogeneous catalysis. The ionic liquid stabilizes the homogeneous catalyst and enables easy product separation and catalyst recycling. For this novel and innovative technology continuous gasphase and slurry reactions are highly suited. Therefore SILP application is of interest to research and industry.

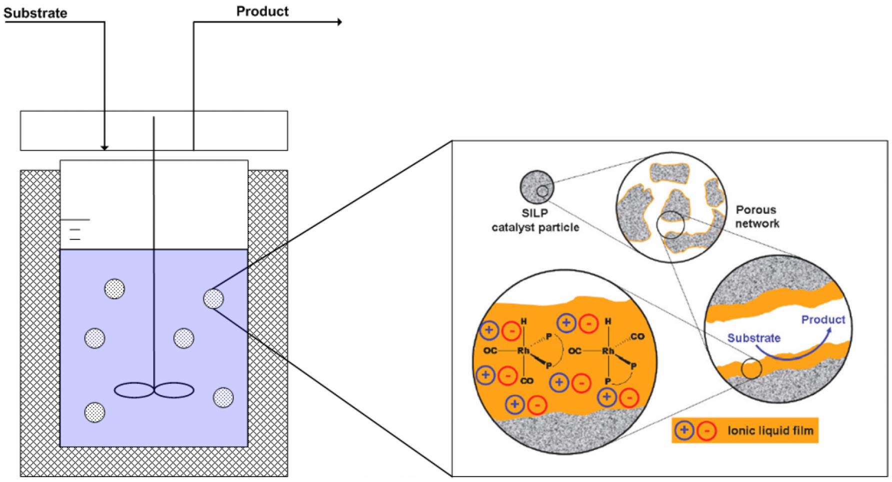

Figure 1. SILP catalyzed system (left) and schema of SILP-system (right)

At our institute we have applied the SILP concept very successfully in different important chemical reactions such as hydroformylation.[2,3] and methanol carbonylation[4] For the hydroformylation of propene long-term stabilities up to 800 h time on stream without loss in selectivity were obtained.

In this contribution we demonstrate the possibility to incorporate chiral transition metal complexes into SILP systems for asymmetric catalysis. Chiral compounds are of high interest for fine chemical and pharmaceutical industry. The supported transition metal complex enables the selective production of chiral compounds in continuous reactions.

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P-125

Synthesis and Characterization of Zeolite-Supported Metal Complex Catalysts

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Here we report the synthesis and characterization of nearly uniform zeolite-supported site-isolated iridium and ruthenium complexes with reactive ethylene ligands, starting from acetylacetonate complexes of the two metals, $Ir(C_2H_4)_2(acac)$ and $Ru(C_2H_4)_2(acac)_2$ (where acac is $C_5H_7O_2$).

$Ir(C_2H_4)_2(acac)$ was synthesized from $(NH_4)_3IrCl_6{\cdot}H_2O$ in a yield of about 45% and characterized by X-ray diffraction crystallography, IR, Raman, and NMR spectroscopies, and calculations at the level of density functional theory. $Ru(C_2H_4)_2(acac)_2$ was prepared according to the literature method. These complexes were chemisorbed on dealuminated (high-silica) zeolite Y (DAY) (Si/Al = 30 [atomic], 1 wt% Ir or Ru). The chemisorption of these compounds on the zeolite resulted in the formation of site-isolated iridium and ruthenium complexes, respectively, each incorporating reactive ethylene ligands. The structures of the resultant supported species and their treatment in He, CO, ethylene, and H_2 were investigated with IR and extended X-ray absorption fine structure (EXAFS) spectroscopies.

The IR spectra of the DAY zeolite-supported iridium complex show that $Ir(C_2H_4)_2(C_5H_7O_2)$ reacted readily with surface OH groups of the zeolite, leading to the removal of $C_5H_7O_2$ ligands and the formation of supported mononuclear iridium complexes, confirmed by the lack of Ir–Ir contributions in the EXAFS spectra. The EXAFS data show that each Ir atom was bonded to four carbon atoms at an average distance of 2.10 Å, consistent with the presence of two ethylene ligands per Ir atom and in agreement with the IR spectra indicating -bonded ethylene ligands. The EXAFS data indicate that each Ir atom was bonded to two oxygen atoms of the zeolite at a distance of 2.15 Å. Time-resolved EXAFS and IR spectroscopies indicate that treatment of the supported metal complex in CO led to the formation of $Ir(CO)_2$ complexes bonded to the zeolite. The sharpness of the ν_{CO} bands indicates a high degree of uniformity of these complexes on the support. The iridium ethylene complex on the crystalline zeolite support is inferred to be one of the most nearly uniform supported metal complex catalysts.

EXAFS data characterizing the zeolite-supported ruthenium complex catalyst indicate approximately four Ru–O bonds per complex (at a bonding distance of 2.05 Å) and a Ru–Al contribution, consistent with the IR data indicating bonding of the Ru complex at sites where the acidic OH groups had been present. No detectable Ru–Ru contributions were evident in the EXAFS spectrum, within error. The IR data indicate -bonded ethylene ligands, as in the iridium complex. The EXAFS data support this conclusion, showing a Ru–C contribution with a coordination number of nearly 4. We infer that the ruthenium complex was anchored tightly to the zeolite through Ru–O bonds and incorporated reactive ethylene ligands. The IR data suggest that only one of the acac ligands of $Ru(C_2H_4)_2(acac)_2$ had been replaced by oxygen atoms from zeolite upon chemisorption. Therefore, we infer that the ruthenium was coordinated to two ethylenes and one acac ligand and anchored to the zeolite by Ru–O bonds.

In summary, the data indicate that in both cases acac ligands can be easily replaced with oxygen atoms of the zeolite, and the resultant metal complexes are anchored tightly to the surface through metal–oxygen bonds with the ethylene ligands remaining intact.

Catalytic reaction experiments were conducted with a once-through flow reactor with a feed of C_2H_4 and H_2, each at a partial pressure of 40 mbar at atmospheric pressure and room temperature. The iridium complex catalyst produces ethane as only detectable product, with a TOF of 0.07 s^{-1}. The ruthenium complex gave a mixture of 1-butene, *trans*-2-butene, and *cis*-2-butene at room temperature, with a TOF = 0.11 s^{-1}.

Hot Electron Flow in Metal-Semiconductor Catalytic Nanodiodes: A New Tool of Heterogeneous Catalysis

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Atomic or molecular processes in metals can generate a pulses of hot electrons with kinetic energy of 1-3 eV, and mean free path of the range of ~10 nm. The electron flow is detected as a chemicurrent if the excess electron kinetic energy generated by the exothermic reaction is larger than the effective Schottky barrier formed at the metal-semiconductor interface. Detection of hot electron flows could allow us to understand the role of electronic energy dissipation and charge transport through the metal-semiconductor interface in exothermic metal catalyzed reactions. We fabricated Pt-TiO_2, Pd-TiO_2, Au-TiO_2 and Pt-GaN Schottky nanodiode that were constructed from metal catalyst film, high bandgap semiconductor layers, and Ohmic contact pads. The thickness of metal catalyst film used as the catalyst was 5 nm, less than the electron mean free path, resulting in the ballistic transport of hot electrons through the metal. The chemicurrent were measured during catalytic CO oxidation (at pressures of 100 Torr of O_2 and 40 Torr of CO at 373~523 K). The chemicurrent was well correlated with the turnover rate of catalytic reactions separately measured by gas chromatography. The results reveal that exothermic catalytic chemical reaction turnover is directly converted into continuous hot electron flux in the catalytic nanodiode. We found that the chemicurrent yield (number of hot electrons per product molecules) depends on the roughness of metal-semiconductor interface, the thickness of metal catalyst. Chemicurrent through the metal-semiconductor interface exhibits good current stability over 3 hours, and reversibility as changing the temperature under CO oxidation. The influence of the flow of hot charge carriers on the chemistry at the metal- semiconductor interface, and the turnover rate of the chemical reactions will be discussed.

Chemical Reactivity of Multinuclear Gallium Cations in Ga/ZSM-5 Zeolite

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Gallium exchanged ZSM-5 zeolites are known to be effective catalysts for promoting selective dehydrogenation and aromatization of light alkanes.[1] The modifying cations can be present in the zeolite in a variety of forms. Among others gallyl ions (GaO^+) have been proposed before to be responsible for the high catalytic activity of Ga/ZSM-5 zeolites in dehydrogenation of light alkanes.[2] Subsequently the enhanced activity of the selectively oxidized catalysts initially modified with univalent gallium cations has been ascribed to the conversion of the Ga^+ ions to GaO^+.[3] Most of the investigators suggest $Ga(H)(OH)^+$ to be one of the key-intermediates in the catalytic transformation of alkanes over gallyl ions. However, it was shown by Gonzales et al[4] that water desorption from such species and formation of Ga^+ ions is strongly favored over H_2 recombination and regeneration of the gallyl ions. Frash and van Santen[5] have shown that despite of a high reactivity of the gallyl ions for the initial C-H cleavage, the subsequent regeneration of the catalytic site is prohibited. This disagrees with the experimental observations[3] that on average 1000 molecules of propane can be converted per oxidized gallium site before being reduced to Ga^+.

This study presents a detailed picture on stability and reactivity of various oxidized gallium sites in the zeolite matrix. We found that isolated gallyl ions are very unstable and tend to form multinuclear cationic species. Activation of light alkanes over the thus formed cations can lead to formation of a wide variety of different gallium-oxide clusters. The mechanism of ethane dehydrogenation over these species was investigated; special attention was given to the mechanism and the energetics of regeneration and reduction of the active sites. It is concluded that formation of multinuclear gallium cations significantly facilitates the former process, whereas the energetics of reduction of the active site is affected by this factor to much lesser extent. The theoretical results obtained allow a good explanation of the recent experimental data and provide an insight in factors determining the reactivity of different gallium species stabilized in the zeolite matrix.

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Artificial Metalloenzymes: Modified Proteins as Tunable Transition Metal Catalysts

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The excellent chemo-, regio-, and stereoselectivity of enzymatic catalysis are rarely achieved by organometallic catalysis. Many important chemical reactions are catalyzed by transition metal complexes because enzymes for fundamental steps like carbonylation and alkene insertion are lacking.

To combine the properties of enzymatic catalysis with those of homogeneous catalysis, two members of the intracellular fatty acid-binding proteins (FABPs) family: Adipocyte Lipid Binding Protein (ALBP) and Δ98Δ Intestinal Fatty Acid Binding Protein (Δ98Δ IFABP) have been used for the construction of artificial metalloenzymes for enantioselective catalytic reactions. The final constructs contain phosphine ligands coordinated to Pd and Rh inside the protein cavity.

Both proteins exhibit a similar β-barrel fold. The entrance of the β-barrel in ALBP is largely blocked by a helix-turn-helix cap. In the Δ98Δ fragment of IFABP the cap is genetically removed, resulting in an easier access to the cavity. Both proteins were genetically optimized to contain a unique cysteine at a central position inside their hydrophobic binding pocket.

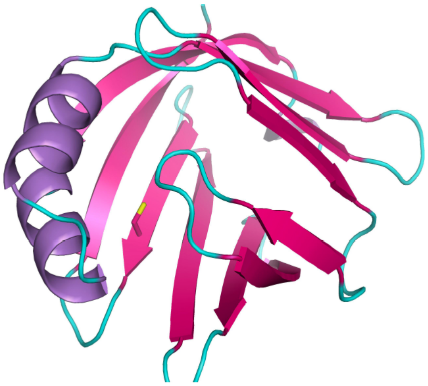


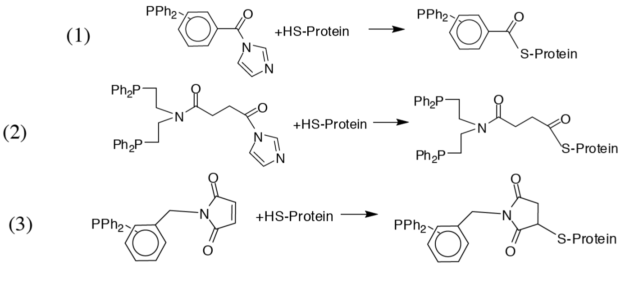
Figure 1 *Crystal structure of ALBP*
The cysteine in position 117 is highlighted

Figure 2 *Model structure of Δ98Δ IFAB based on the crystal structure of IFAB*
The new cysteine introduced in position 90 is highlighted

For coupling of phosphine-ligands to the proteins, two strategies were used:

- coupling of CDI activated phosphine containing carboxylic acids (2,3 and 4 diphenyl-phosphinobenzoic acid (1) and the carboxylic derivative of Whitesides ligand (2)) to the nucleophilic thiol group of the cysteine, resulting in a thioester linkage between ligand and protein;

- coupling of phenyl-maleimide phosphine derivatives (3) to the thiol group of the cysteine, resulting a thioether linkage between ligand and protein.



Pd and Rh phosphine-protein complexes were obtained both by coordinating Pd and Rh to the phosphine protein complexes and by coupling the preformed Pd and Rh coordinated phosphine complexes to the proteins. The systems formed were characterized by mass spectrometry, ^{31}P NMR and CD.

The new hybrid catalysts were tested for asymmetric allylic amination and hydrogenation reactions. The catalytic properties of the complexes will be optimized by modifying the ligand structure, by changing the position of the ligand inside the protein cavity (through changing the location of the cysteine) or by introducing subtle changes to the protein structure (through site directed mutagenesis).

Sterically Congested Cylcophane-based Late Transition Metal Olefin Polymerization Catalysts

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Our laboratory has recently prepared a new cyclic cyclophane-based α-diimine ligand for olefin polymerizations with nickel (II) and palladium (II). In contrast to Ni (II) polymerization with the established acyclic α-diimine catalysts, the robust cyclophane system maintains high activity and affords high molecular weight polyethylene at elevated temperatures.[1] In the polymerization of propylene, the cyclophane Ni (II) catalyst system affords living polymerization with lower polydispersities at higher temperature than the acyclic system and gives polypropylene of reduced branching due to different insertion and isomerization kinetics.[2] Furthermore, research in cyclophane-based Pd (II) catalysts has shown much higher incorporations of acrylate monomers than the acyclic Pd (II) catalysts, indicating reduced olefin monomer selectivity.[3] We attribute all these potentially useful properties to the uniquely crowded steric environment introduced by the cyclophane ligand. Further studies into substituent effects and the effects of structural variation to this cyclic ligand motif on polymerization are underway.

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[2] *Macromolecules* 38 (2005) 2544.
[3] manuscript submitted for review

Porphyrin and Schiff Base Complexes Immobilized in Polymeric Membranes as Catalysts for Aziridination and Cyclopropanation Reactions

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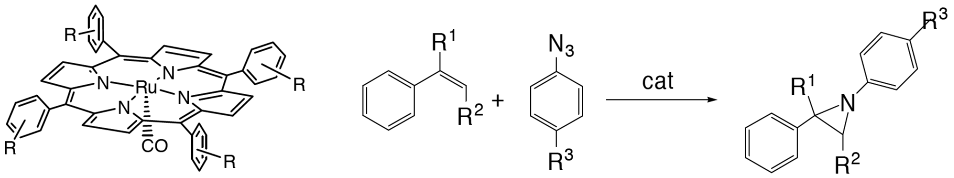
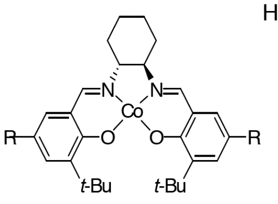
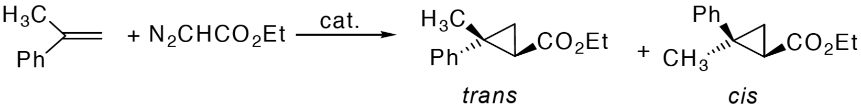
The entrapment of an homogeneous catalyst inside a polymeric membrane is one of the easiest ways to heterogenize it, since it does not require the modification of the ligand to introduce functional groups needed for covalent or ionic binding as with most other classes of supports. On the other side, leaching of the complex can become a major problem. We have recently investigated the use two classes of membrane-entrapped catalysts, respectively ruthenium porphyrin complexes for aziridination reactions of olefins by organic azides (Scheme 1) and cobalt salen-type Schiff base complexes for olefin cyclopropanation (Scheme 2). All membranes were thoroughly characterized by different physical and spectroscopic methods. Both leaching and recycling issues were carefully investigated.

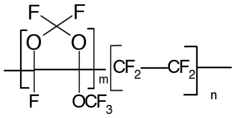


Scheme 1





Scheme 2



Hyflon AD60X

Several polymers (polydimethylsiloxane, polydifluoroethylene, polyethersulfone, polysulfone, Hyflon AD60X) and solvents were investigated. In many cases either complete leaching or inactivation of the catalyst by the polymer were observed, but good results could be obtained for both reactions by using Hyflon AD60X membranes. The main results are the following: 1) Whereas benzene has to be used as solvent for aziridination reactions in an homogeneous phase, the less toxic hexane can be employed with the membranes. 2) A small leaching was observed, but the amount of lost catalyst is much too low to account for the observed catalytic activity. The membranes without the complexes have no catalytic activity. 3) Up to three recycles were performed with a small decrease in rate and no loss in selectivity in favorable cases. 4) The regiochemistry (*cis/trans*) of the cyclopropanation reaction is influenced by the membrane. 5) A good dispersion of the catalyst was observed up to a ca. 7% w/w catalyst amount in both cases, but at higher loadings the catalysts formed aggregates and no increase in catalytic activity was observed. 6) Porous membranes show a better activity of dense ones, but leaching is also higher. 7) Fluorinated groups on the complexes help dispersion in Hyflon, but long fluorinated tails are not required and -CF$_3$ groups works well.

Metal Catalysts Supported on Chiral Organic-inorganic Solid Hybrids. Use as Catalysts in the Enantioselective Hydrogenation of Ethyl Piruvate

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It is well known that homogeneous catalysis has played an important role in the development of enantioselective reactions. More recently, the immobilization of chiral complexes as well as the use of modified metal supported catalysts have appear as alternatives for various hydrogenation reactions of α- or β-ketoesters and diketons. Different modifiers have been used as chiral inducer in metallic catalysts.[1] In order to get reusable catalysts it is highly desirable that the modifier remains chemically anchored on the support.

The aim of this work is to prepare and characterize metal supported catalysts in which the support is a chiral organic-inorganic hybrid. The support was synthesized by a hydrosylation reaction of of Divynilbenzene (DVB) and (-)-Cinchonidyne (CD) with 1,3,5,7-tetramethylcyclotetrasiloxane (TMCTS) using PtO_2 as catalyst.[2] The catalysts were prepared by impregnation of a colloidal dispersion[3] of ruthenium or platinum on the support. Catalysts having 1, 3 and 5 wt% of Ru and 3 wt% of Pt were prepared. The catalysts were characterized by N_2 adsorption-desorption at 77 K, TG, O_2-H_2 titration, TEM, XRD and XPS. The reaction was carried out in a stainlees steel batch reactor at 298 K and 40 bar of hydrogen using cyclohexane and acetic acid as solvents.

FTIR was used to followed the anchorage of CD to the support. TG studies demonstrated that the catalysts are thermally stable up temperatures close to 700 K. N_2 adsorption-desorption isotherms revealed that the support is essentially a mesoporous solid with a specific area of 35 m^2/g and the hysteresis loop suggests the presence of ink bottle type pores having a pore diameter close to 4.0 nm. No significant changes in the porosity neither in the specific area occurs upon the colloid deposition. Metal particle size obtained from TEM showed an increases from 2.8 to 4.8 nm as Ru loading increases whereas the 3 wt% Pt catalyst exhibits an average metal particle of 3.1 nm. In line with these results, XPS has shown that the Ru/Si atomic surface ratio increases from 0.031 to 0.074 from the catalyst with 1 to the one with 5 wt% of Ru suggesting an increases in the metal particle size. Binding energies of the Ru $3p_{3/2}$ or Pt $4f_{7/2}$ showed that the metal precursors were not fully reduced, being the reduction degree in the range 52 to 68% for Ru and 33% for Pt. Catalytic results showed that the activity increases with Ru loading being more active and enantioselective to the R- lactate when acetic acid was used as solvent. If Pt and Ru catalysts with the same metal loading are compared, significant differences in the catalytic behavior were observed. Thus, using cyclohexane as solvent, the conversion at 2h reached 100% for Pt compared to only 10% for the Ru catalyst, being the enantiomeric excess to R-lactate, 35 and 17% respectively.[4]

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[4] The authors thank CONICYT for financial support (Grant FONDECYT 1061001).

Synthesis, Characterization and Catalytic Behavior of the Ir/Nb_2O_5/SiO_2 System in the Citronellal Hydrogenation

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Important properties of niobia such as acidity, thermal, the capability to generate the well known SMSI effect has been reported. The main approach for the use of mixed oxides containing niobium or niobia supported over other oxides such as silica is catalytic application is related to their redox properties as well as the Lewis acidity of the niobium species. Iridium supported catalysts have revealed as effective solids in the selective hydrogenation of α, β unsaturated towards the corresponding allylic alcohol, due to the preferential hydrogenation of the C=O bond compared to the C=C bond. This behaviour has been attributed to the presence of partially oxidised Ir species ($Ir^{\delta+}$) generated as consequence of SMSI effect.[1] The addition of cationic species provides an alternative procedure to induce polarization in the carbonyl bond. Isopulegol is an attractive product which may be obtained from citral or their partially hydrogenated products by reaction involved both metallic and acid sites. For this purpose the presence of Lewis acid sites has been claimed as active to obtain isopulegol.[2]

As support of catalysts Nb_2O_5 (Merck 99%) and SiO_2 (Aerosil silica Syloid-266-Grace Davidson) have been used. As mixed oxides a series of mixed Nb_2O_5-SiO_2 samples were by impregnation of silica with toluene solution of niobium ethoxide (Aldrich, reagent grade) followed by calcinations in air at 673 K. Four mixed oxides were prepared with different Nb loading (1.1 to 5.3 wt%). Later on the supports were impregnated with an aqueous solution of H_2IrCl_6 in appropriate amount to get catalysts with 1 wt% of Ir. After calcination at 673 K the solids were reduced at 473 or 773 K to produce Ir catalysts (LT or HT series). The catalysts were characterized by N_2 adsorption at 77 K, H_2 chemisorption at 298 K, surface acidity, XRD, FTIR, TEM and XPS. The citronellal hydrogenation was performed in a Batch Reactor at 363 K and 6.2 bar, and the reactant and products were evaluated by GC-MS. The characterization of the solids revealed that Ir is highly dispersed on the support and the mixed oxides exhibit highly dispersed niobium oxides species being only possible to detect niobia crystallites in the sample with highest Nb content. This occurs with a partial coverage of the support and consequently, decreases in the surface area. Suppression of H_2 chemisorption after HT treatment lead to a surface decoration of Ir crystals by partially reduced Nb_2O_{5-x} species. The mixed oxides present a significant amount of acid sites as TPD of NH_3 has shown. Catalytic results indicate that the presence of niobia in Ir catalysts is necessary to induce selectivity towards isopulegol due to their higher surface acidity and the presence of metallic sites. Conversely, Ir/SiO_2 catalyst, which possesses lower surface acidity, produces mainly the hydrogenation of the C=O bond to get citronellol. However, no significant differences were observed in terms of catalytic activity in the LT or HT series.[3]

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Catalytic Properties of MgO (111) Nano-Sheets

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MgO has a typical rocksalt structure and possesses a high melting point and high ionic character. Although the stoichiometry and crystallinity change little, the morphology can vary in shape, particle size and surface structure. The MgO(100) facet is unambiguously the most stable due to its low surface energy, therefore, it is normally a product after cleavage and is unaminously the surface demonstrated by current wet chemical preparations. Numerous studies have demonstrated that the shape and size of crystalline MgO is highly influential on the adsorption properties and the configuration of surface species formed during chemical adsorption. Furthermore, nanoscale MgO has been reported to be extremely effective for the destructive adsorption of numerous environmental toxins and several chemical warfare agents (VX, sarin, mustard gas).[1] However, the (111) surface consists of alternating polar monolayers of oxygen anions and magnesium cations and thus, a strong electrostatic field perpendicular to the (111) surface is created.[2] Such a surface has provided a prototype for the study of surface structure and surface reactions, which drew great attention for both experimental and theoretical studies.[3,4] These studies imply the importance of size and shape control in MgO synthesis for its applications, as it is not only the surface area that matters, but also the surface chemistry. Recently, we reported an efficient wet chemical method to synthesize MgO nano-sheets possessing the (111) lattice plane as the main surface and the catalytic properties thereof.[5] In situ spectroscopy of the chemistry occurring at such a surface provides the opportunity for molecular level insights that allows direct comparison with homogeneous systems.

MgO(111) nano-sheets can be prepared through a facile self-assembly process following a thermal treatment. The MgO(111) nano-sheets possessing the exposed (111) plane as a main surface have a thickness typically between 3 and 5 nm. Study by in-situ DRIFT spectroscopy of MgO(111) nano-sheets suggests that hydroxyl groups, oxygen vacancies and surface oxygen anions exist on the surface and the (111) surface may be stabilized by hydroxyl groups. DRIFTS and TPD studies of CO2 adsorption reveals that there are large amounts of medium strength basic sites which can be attributed to high concentrations of surface O^{2-} Lewis base species. DRIFTS and TPRS studies of methanol also reveals that, in contrast to the commercial MgO, MgO(111) nano-sheets are highly reactive and strongly basic. Methanol can be readily decomposed and the surface C=O species formed can be oxidized quickly at low temperature by the high concentration of oxygen anions on the surface of MgO(111) nano-sheets, which demonstrates that the MgO(111) nano-sheets have potential application in fuel cells and methanol based alternative energy technologies. Additionally, MgO(111) nano-sheets also demonstrate ultrahigh activity for the base catalyzed Claisen-Schmidt condensation thus providing a superior heterogeneous alternative to the conventional reagents such as $AlCl_3$, $POCl_3$ and BF_3. The structure and function relationships have also been investigated by in-situ DRIFTS studies of adsorption and reaction of benzaldehyde and acetophenone and the reaction intermediates observed.

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Platinum and Palladium Nanoparticle Synthesis for Catalysis Applications

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Nanoparticles of metals such as Pt and Pd have been employed to investigate the roles of surface area to volume and specific crystal faces in the catalysis of simple reactions.[1] We have synthesized crystalline Pt and Pd nanoparticles using surfactant-directed assembly, and without agents typically used to direct crystal growth (i.e., PVP or alkylammonium bromide salts).[2,3] We are exploring how the individual surfactants used contribute to the formation of octahedral, spherical and hollow particles (Figure 1). Tailoring the shapes of these particles may enable us to maximize catalytic activity and efficiency. We have encapsulated these Pt nanocrystals in cobalt oxide shells;[4] controlling the thickness and defectiveness of the CoO shell allows for tuning the access of molecules to the catalytically active Pt surface.

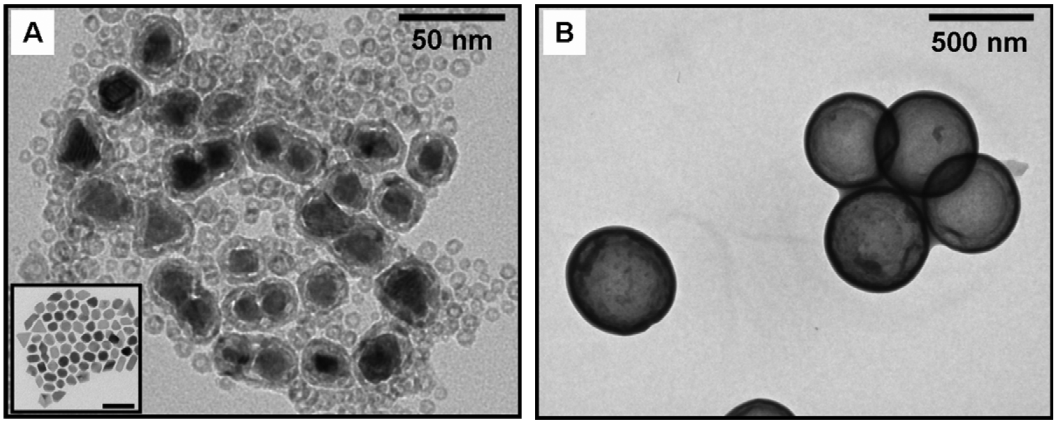

Figure 1. (A) Transmission electron micrograph (TEM) image of Pt nanoparticles encapsulated within CoO shells. Hollow CoO nanoparticles are also present. Inset: Pt nanoparticles for CoO deposition synthesized using surfactant-directed assembly (scale bar = 20 nm). (B) TEM image of hollow Pd nanoparticles.

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The Influence of Surface Modification on Olefin Epoxidation with Aqueous H_2O_2 over Tantala-Silica Materials

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The thermolytic molecular precursor (TMP) method was used to introduce site-isolated Ta(V) centers onto the surface of mesoporous SBA15. The resulting surface Si-OH and Ta-OH sites of the TaSBA15 catalysts were modified with a series of (N,N-dimethylamino) trialkylsilanes, $RMe_2Si(NMe_2)$ (where R = Me, ^{n}Bu, and ^{n}Oc).

Compared to the unmodified catalyst, the surface modified catalysts are more active and exhibit excellent selectivity for epoxide formation (>98% after 2 h) in the oxidation of cyclohexene using aqueous H_2O_2 as the oxidant. The modified catalysts exhibit an increased lifetime, and retain excellent epoxide selectivity (>95%) after 6 h of reaction time. Diffuse reflectance UV-visible (DRUV-vis) and Fourier transform (FT) Raman spectroscopies were used to probe the local structure of the Ta(V) site. Mechanistic studies revealed that the trialkylsiloxy-capped Ta site is essential to maintain high epoxide selectivity over extended reaction times.

Biocatalysis Studies Utilizing HLADH and Monooxygenase Enzymes with Biomimetic NAD$^+$ Models and [Cp*Rh(bpy)H]$^+$ for Co-factor Regeneration: Molecular Recognition, Chiral Alcohol Synthesis, and Regioselective Hydroxylation of Aromatic and Aliphatic Substrates

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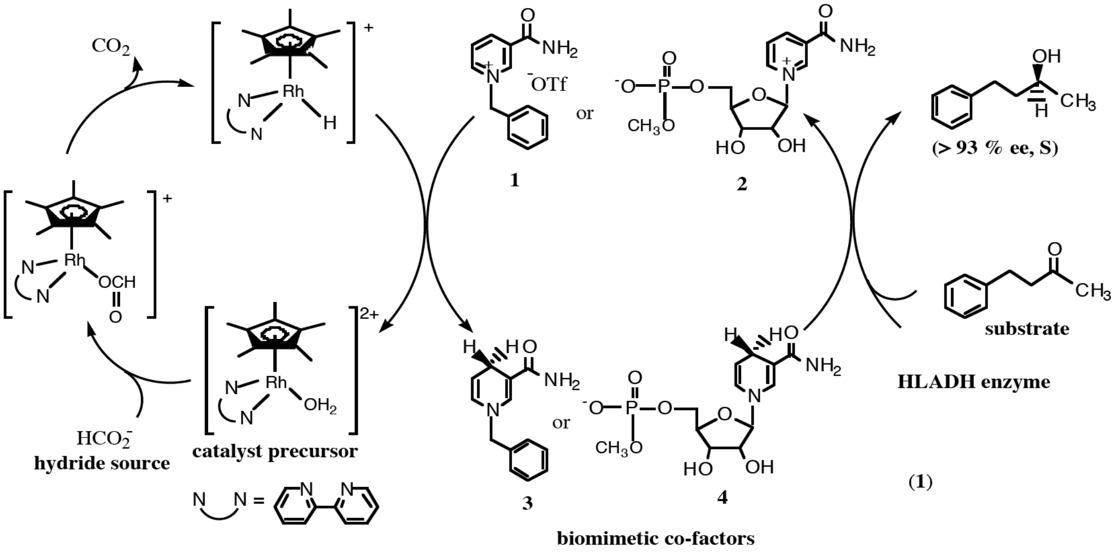
Biocatalysis studies utilizing redox enzymes with biomimetic NAD$^+$/NADH cofactors, and a organo-rhodium hydride for cofactor regeneration, represents a new paradigm for chiral synthesis, and regioselective hydroxylation. Thus, the chiral synthesis of alcohols from their prochiral ketones, and regioselective hydroxylation of aromatic and aliphatic substrates, via two novel catalysis approaches, will be presented, including a cofactor regeneration procedure with *in situ* generated [Cp*Rh(bpy)H]$^+$ and NAD$^+$ models, 1-benzylnicotinamide triflate, **1**, and β-nicotinamide-5'-ribose methyl phosphate, **2**. Importantly, their in situ formed, biomimetic 1,4-dihydro analogs, **3** and **4**, are indeed recognized by the enzymes, horse liver alcohol dehydrogenase (HLADH) and several monoxygenases (P450 cam and HbpA), at their respective binding sites, for catalyzed, highly enantioselective reductions, and regioselective hydroxylations, respectively (eq 1).



These biocatalysis results clearly show that redox enzymes will allow biomimics of NAD$^+$/NADH, **1**,**2**/**3**,4, to transfer hydrogen atoms or their electrons to either substrates or to components (other dependent cofactors such as FAD or electron shuttles) that produce chiral alcohols, or afford regioselective oxidation products. This novel approach could provide economic incentives to the biocatalysis industrial community for the synthesis of important drugs, or other biologically active compounds of interest.[1]

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[1] We thank DOE for financial support.

Oxidation of Toluene to Benzoic Acid Catalyzed by Platinum Supported on Zirconia in the Liquid Phase – Solvent Free Conditions

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Toluene oxidation over platinum supported on zirconia using molecular oxygen as oxidant under solvent free conditions at temperature range 363-393K, in a batch reactor. The effects of different parameter (agitation effect, partial pressure effect and time profile) were studied. The catalyst was easily separated by simple filtration and reused. The selectivity of the catalyst was found to be $> 99\%$. Kinetic analysis was performed by fitting experimental data to Eley -Rideal, Mars- van Krevelen and Langmuir – Hinshelwood mechanisms.

In situ GISAXS and GIXS Evidences for Au/TiO_2(110) Restructuring During CO Oxidation

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Gold clusters of nanometer size are known to act as catalysts of the oxidation of CO.[1] The catalytic activity of these particles has been shown to strongly depend on the size of their size by near field microscopy.[2]

The present work reports on an attempt to study in situ gold clusters of 1 to 5 nm deposited on TiO_2(110) by Grazing Incidence X-ray Scattering (GIXS, large angles) and Grazing Incidence Small Angle X-ray Scattering (GISAXS). It was performed thanks to a new setup which allows to elaborate model catalyst in UHV environment and then to follow them during catalytic reaction by x-ray measurements on beam-line BM 32 at ESRF (Grenoble).[3]

The CO oxidation reaction was run for oxygen pressure of 2000 Pa and CO pressure from 10 to 100 Pa, respectively at 300 and 500K. It was analyzed via a controlled leak towards a mass spectrometer. By recording GIXS diffraction patterns and GISAXS images, the average size of the particles could be correlated with the Au-Au distance within the particles. Further, these parameters could be associated to the reactivity of the particles. The oxygen alone had no visible effect on the GISAXS images of the gold particles. Instead, the presence of either a partial pressure of CO or a reactive mixture of CO + O_2 resulted in a change in the morphology that could be analyzed by GISAXS and GIXS. The capability of the set up to simultaneously analyse the crystallography, the size and the reactivity of supported gold particles is demonstrated. The values determined herein are discussed with respect to the measurements already performed by near-field microscopy.

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Synergistic Immobilized Catalyst

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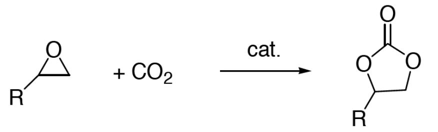
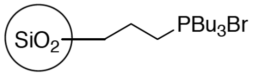
Development of immobilized molecular catalysts, which have merits of both heterogeneous catalysts (ease of catalyst separation) and homogeneous catalysts (high activity and selectivity), has been a dream for synthetic chemists.[1] We have developed a very active recyclable catalyst for the cyclic carbonates synthesis from carbon dioxide, by immobilizing phosphonium salts on silica. Cyclic carbonates are useful as intermediates for polycarbonate through dimethyl carbonate and diphenyl carbonate, electrolytes for Li ion batteries, polar solvents, fuel additives, and so on.

Note that the separate use of silica or phosphonium salt alone resulted in very low catalytic activities (see the Table shown below). On the other hand, the combination of phosphonium salts and silica dramatically enhanced the catalytic performance. Indeed, the immobilized catalyst on silica afforded nearly quantitative yields. In other words, a large synergistic effect was observed between acidic part (silica surface) and basic part (phosphonium salt).

The reaction could be carried out not only as a batch process but also by using a flow reactor. Compared with current industrial processes, the present procedure allows easier catalyst separation and higher reaction rate.[2]



Catalyst	Yield (%)	
	97	⇨ Heterogeneous
PBu_4Br	4	⇨ Homogeneous
	0	

Conditions: 100 °C, 10 MPa, 1 h, batch reactor.

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Exceptional Activity of Nanostructured Pt-Catalysts for Partial and Total Oxidation

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The design of catalysts at the nanoscale offers novel opportunities to meet the technological needs for sustainable industrial development. However, the low thermal stability of nanoparticles constitutes a significant hurdle towards using these materials in realistic catalytic applications.

We previously demonstrated the successful synthesis of sinter-resistant nanocomposite materials which combine the high reactivity of nanosized noble metal particles with the excellent high-temperature stability of hexa-aluminates. In this contribution, we report on an investigation of nanostructured Pt-BHA catalysts in the catalytic partial oxidation of methane (CPOM) to synthesis gas at high-temperature (T= 1000-1300 K) conditions and the low temperature (T= 250-340 K) oxidation of CO to CO_2. CPOM is of great industrial importance in the production of syngas and hydrogen from fossil and renewable methane resources and constitutes a stringent test for the stability of these materials at extreme reaction conditions. CO oxidation is a key reaction in any fuel processing scheme (from total oxidation of hydrocarbon fuels to preferential oxidation of CO in H_2 streams) and serves as a simple reaction to allow for fundamental studies of size effects in these nanometer sized catalysts.

We find that the materials are exceptionally robust, withstanding high-temperature conditions over extended periods of time, and highly active, allowing for reduction of the Pt content by up to two orders of magnitude in comparison to conventional catalysts. Similarly, we find in low-temperature CO oxidation that the apparent activation energy over the nanocomposite Pt catalyst is reduced by as much as a factor of four in comparison to a conventional alumina supported Pt catalyst.

Experimental results and the great potential of these carrier materials for clean energy applications will be discussed in detail in the presentation.

Reactivity of Silica Supported Hafnium Tris-neopentyl with Dihydrogen: Formation and Characterization of Silica Surface Hafnium Hydrides and Alkylhydride and Their Role in Catalysis of Alkanes Transformation

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Surface organometallic chemistry represents an approach to the preparation of well-defined single sites for catalysis, the possibility of observing some elementary reaction steps and the development of a fundamental basis for the synthesis of tailor-made catalysts. Silica supported metal hydrides are an important class of new catalysts for alkane metathesis, methane-olysis of alkanes, Ziegler-Natta depolymerization, alkane hydrogenolysis etc. Understanding their mechanism of formation and ageing is crucial. In the work presented here, the reaction of the well-defined silica surface organometallic complex $[(\equiv SiO)Hf(CH_2tBu)_3]$, **1**, (($\equiv$SiO) = silica surface ligand) with dihydrogen has been performed at different temperatures (θ). At $\theta \leq 100°C$, there is formation of a stable hafnium neopentyl dihydride $[(\equiv SiO)Hf(CH_2tBu)(H)_2]$, **2**. For $100 \leq \theta \leq 200°C$, **2** affords, via a succession of β-methyl-transfer and subsequent hydrogenolysis of the resulting Hf-alkyl bonds, the formation of $[(\equiv SiO)_2Hf(H)_2]$, **3**, and $[(\equiv SiO)_3SiH]$ with evolution of methane (C_1) and ethane (C_2). For $150 \leq \theta \leq 300°C$, **3** is totally converted into $[(\equiv SiO)_3Hf(H)]$, **4**, and $[(\equiv SiO)_2Si(H)_2]$. For $\theta \geq 300°C$, $[(\equiv SiO)_3Hf(H)]$, **4**, is transformed into $[(\equiv SiO)_4Hf]$, **5**, and $[(\equiv SiO)_2Si(H)_2]$ into $[(\equiv SiO)_3SiH]$. At this temperature, $[(\equiv SiO)_3SiH]$ is the only hydride remaining on the surface. All these species have been fully characterized and their structure identified by elemental analysis, Infra-Red, ^1H Solid State NMR, ^1H DQ solid state NMR and EXAFS spectroscopies. The results elucidate a complete mechanism of surface organometallic chemistry by which one observes the stepwise transformation of a hafnium tris-neopentyl, to hafnium neopentyl-hydrides, hafnium mono and bis hydrides, silicon bis-hydride with the ultimate formation of surface silicate of $Hf^{(IV)}$ and silicon mono-hydride, the only hydride stable at very high temperature. It is suggested that the formation of these surface silicon hydrides is responsible for the ageing of such catalysts in any reaction involving dihydrogen in particular in the hydrogenolysis of paraffins and polyolefins.

Studies on the Structural Characterization of Fe-MFI

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ZSM-5s 3-D pore structure of straight and sinusoidal channels allows for selectivity of products and structural stability. Transition metal loading into the zeolite pores has been extensively studied, producing results that indicate that iron loaded zeolite exhibits a strong ability to convert methanol to gasoline, even in the presence of water.

In this study, differing Si/Al ratios, varying iron loadings and various iron-loading procedures were carried out on H-MFI to begin characterization of the iron-oxygen bonds within the zeolite pore. UV Raman spectroscopy at excitations of 225 nm, 244 nm and 287 nm were utilized to character the iron-oxygen bonds within the pores and to take an in depth look at structural differences between loading techniques. Chemical vapor deposition (CVD) technique and incipient wetness impregnation (IWI) were compared, keeping other variables steady. Differences in the spectra, especially in the 700 $\text{cm}^{-1} - 800\ \text{cm}^{-1}$ region were noticeable and give beginning support to the theory of an ironperoxo bond within the zeolite pore.

Washing studies were also performed on CVD samples to help determine the influence of water on the geometry of the iron-oxygen bond. Samples were either washed with DI water or unwashed and calcined in either O_2 or O_2/H_2O. Differences in intensities and band placement show that washing is influential in the iron structure but that the different calcinations made little difference.

ICP was performed on CVD prepared samples to test for reproducibility of the CVD loading technique and to investigate a correlation between the Si/Al ratio and iron loaded on the sample. Preliminary results show that the Si/Al ratio has an affect on how much iron is loaded into the sample and that overloading iron onto the zeolite does occur and occurs only on samples that were unwashed.

Catalytic Reactions in Micellar Media: a Sustainable Methodology for Catalyst Recycling

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Commodities as well as fine chemicals are high value industrial productions which in the latest years are experiencing profound transformations in order to better match typical production standards like economy and efficiency with the latest emerging international requirements concerning eco-compatibility and protection of the environment. Among the many components involved in a chemical transformation, organic solvents are used in the large amounts and their volatility, flammability and toxicity often pose the need for their replacement. A real alternative solvent characterized by the best eco-compatibility is water, in fact its use in the development of new processes is experiencing a sort of renaissance witnessed by several review articles.[1] Mimicking nature, reactions performed in water can exploit unique features, in primis hydrophobic effect and polarity that in many cases allowed higher regio, diastero and enantioselectivity compared to common organic solvents.[2] A plethora of organic transformations have been extended in water solvent, spanning from reduction, oxidation and C-C coupling reactions.

Far less studied is the use of water/surfactants under micellar conditions that provides a viable solution to circumvent the need for water soluble catalysts, to avoid tedious chemical functionalization of ligands and offers many advantages,[3] among which catalyst recycling is one of the most important ones.

In the present contribution, examples of metal catalyzed reactions in micellar media are reported, paying particular attention to selectivity issues, catalysts lifetime and recycle. Special focus is given to oxidation reactions with Pt(II) complexes like enantioselective sulfoxidation and epoxidation where the soft Lewis acidity of the metal is not compromised by the aqueous media allowing activation of hydrogen peroxide as environmentally friendly oxidant. Higher enantioselectivities compared to the reactions performed in common organic solvents and the use of easily prepared chiral catalysts clearly speaks for the eco-efficiency of such methodologies.

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Ultrasound Assisted Synthesis of Bimetallic Sulfides for HDS

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The use of unsupported catalysts, which could be used either dispersed on a heavy feedstock,[1] or in the preparation of bulk metal catalyst for a conventional process, is considered to be a promising way to improve HDS/HDT process efficiency.[2]

The use of ultrasonic irradiation has proven to be an effective way for the synthesis Mo sulfide nanoparticles.[3,4,5,6] However, in spite of the well known promotion of Mo by Ni or Co leading to more active hydrotreating catalysts, there are not many reports in the literature on the preparation of NiMo or CoMo nanometric sulfides. In a previous work[7] FeMo and NiMo nanometric bimetallic sulfides were prepared from thermal decomposition of emulsions, and its activity tested in thiophene HDS.

In the present work, ultrasound assisted synthesis of bulk Ni, Co, Mo, NiMo and CoMo sulfides, was studied. Catalysts were prepared according to previously reported methods.[6,8] Solids thus obtained were characterized by X Ray Diffraction (XRD), Chemical Analysis, Surface Area determinations (BET), Dynamic Light Scattering (DLS) and its activity benzothiophene hydrodesulfurization (HDS) was also evaluated.

X ray diffraction showed that the solids are poorly crystallized. Also, particle sizes were in the range of 50-100 nm as evidenced by DLS measurements. It was found that NiMo and CoMo catalyst are more active than the monometallic ones. It is proposed that the high activity for bimetallic solids is due to the precipitation of a mixed sulfide in nanometric size particles.

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Thermal chemistry of Diiodomethane on V(100) Single-crystal Surfaces

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The thermal chemistry of methylene diiodide on clean and oxygen-predosed V(100) surfaces have been studied under ultrahigh vacuum (UHV) conditions by temperature-programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS), and deuterium labeling experiments. On the clean surface the thermal activation was found to start from 140 K and to lead to the formation of a mixture of CH_2(ad) and CH_2I(ad) adsorbed species, the latter of which then undergoes hydrogenation into methyl iodide and desorbs at ~280 K. The surface CH_2 groups were found to follow a complex reaction mechanism that includes hydrogenation into methane, dehydrogenation to carbon and hydrogen, coupling to ethylene, and chain propagation to propylene. The transformation into methane dominates at low coverages, while ethylene production becomes comparable at high coverages. The propylene production, on the other hand, shows up in two desorption peaks, and is maximized at intermediate CH_2(ad) coverages. Results from additional experiments using CH_2CHI, C_2H_4, and C_2H_5I suggest that the propylene is mostly likely produced by a complex mechanism via the formation of C_2H_3(ad) groups as the intermediates. This mechanism is unique, differing from what has been reported on other transition metals, and implies the potential dehydrogenation of methylene to methylidyne, the coupling of methylene and methylidyne to form this vinyl intermediate, and the further coupling of vinyl and methylene and hydrogenation to propene. The effect of pre-adsorption of oxygen was also briefly surveyed. It was found that the co-adsorbed oxygen does not add to the CH_2(ad) groups, but only exerts a stabilizing effect on CH_2I_2 to higher temperatures.

Stereoselective Hydrogenation of Aromatic Compounds over Supported Metal Catalysts in Supercritical Carbon Dioxide Solvent

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Hydrogenation reactions over supported metal catalysts in organic solvents have wide range application in pharmaceutical and fine chemical processes; however, an energy intensive one or more distillations are mandatory for separation of products from solvents. Also due to the toxic and hazardous nature of organic solvents, their elimination in the organic transformation is highly desirable. Hydrogenation over supported metal catalysts in supercritical carbon dioxide solvent has several advantages such as 1) higher solubility of hydrogen in supercritical carbon dioxide, leading to higher reaction rates and controlling the product selectivity; 2) easy separation of products and catalysts; and 3) maintaining clean active sites on solid surfaces by washing with supercritical carbon dioxide solvent.

We applied the catalytic system in supercritical carbon dioxide solvent to the hydrogenation of aromatic compounds.[1] Hydrogenation of naphthalene was examined over various transition metal (rhodium, ruthenium, palladium, and platinum) catalysts supported on charcoal in supercritical carbon dioxide solvent at low temperature. Among these, a charcoal-supported rhodium catalyst was found to be the most active, while a charcoal-supported ruthenium catalyst was found to give the highest *cis*-decahydronaphthalene (*cis*-decalin) selectivity. Also, it was found that the selectivities to *cis*-decalin over the charcoal-supported metal catalysts was higher in supercritical carbon dioxide than organic solvents. The stereoselective hydrogenation of tert-butylphenols to corresponding *tert*-butylcyclohexanols was also studied and high selectivities to cis forms of *tert*-butylcyclohexanols were obtained over a charcoal-supported rhodium catalyst in supercritical carbon dioxide solvent. In this paper, we discuss the hydrogenation mechanism based on their reaction profiles and enhancement of high corresponding cis-forms in supercritical carbon dioxide.

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Pd and Au Catalysts Supported on Nanocrystalline Mixed Oxides Prepared by Sol Gel Method

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Noble metals supported on single nanocrystalline oxides are characterized by unique adsorptive and catalytic properties. As en example gold supported on nanocrystalline ceria manifests high catalytic activity.[1,2] The present work is devoted to the study of palladium and gold catalysts supported on complex nanocrystalline Al-Zr-O and Al-Ce-Zr-O mixed oxides.

Mixed oxides have been prepared by sol gel technique. This method has many advantages and it is suitable particular for the preparation of multicomponent catalysts with homogeneous distribution of finely dispersed components.[3] Organometallic compounds were used as precursors of metal oxides. The content of ZrO_2 oxide in the system Al-Zr-O was varied within range 0- 40 wt%. The contribution of mixed oxides $Ce_xZr_{1-x}O_2$ in the system Al-Ce-Zr-O does not exceed 10 wt%, while value x was changed in sequence: 0, 0.25, 0.33, 0.5, 0.67, 0.75, 1. The size of oxide crystals was in nano level. The increase of Zr content in Al-Zr-O system results in the changes of specific surface area of samples and the formation of different structural aluminum states according to Nuclear Magnetic Resonance data (NMR). Redox properties of prepared mixed oxides probed by temperature programmed reduction with hydrogen and CO (TPR) depend on the Ce/Zr ratio. The hydrogen/CO uptake was the highest at Ce/Zr ratio at about 1.

Palladium was deposited by wet impregnation of solid Al-Zr-O and Al-Ce-Zr-O mixed oxides with palladium chloride solution, while gold was supported via adsorption of water soluble $Au(NH_3)_4(NO_3)_3$ complex on solid Al-Ce-Zr-O mixed oxides. The Pd and Au content in final catalysts was 0.3 and 3.0 wt%, respectively. After thermal treatments catalysts were tested by XRD, TEM, TPR, NMR, and temperature programmed desorption of CO and NO (TPD). Catalytic activity of samples was measured in micro flow reactor in CO oxidation and NO reduction. It was shown that the catalysts prepared with nanocrystalline mixed oxides are more active then those prepared with single nanocrystalline ceria only.

In summary, the data demonstrate that both cationic and metallic gold and palladium are present in the catalysts prepared with nanocrystalline supports including ceria. The nanocrystalline ceria species stabilized in alumina matrix and particular those disordered by partial replacement of Ce atoms with Zr ones seem to be able to supply reactive oxygen and effective electron donation to the gold and palladium active species for the oxidation of CO and reduction of NO.

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Study of α- and β-pinenes Hydroisomerisation Over Heterogeneous Ru/C Catalyst: Effect of Reaction Conditions and Catalyst Modification on Products Distribution

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Natural monoterpenes, α- and β-pinenes, are of great interest as cheap industrial sources for production of valuable fragrances for pharmaceutical and cosmetic application. The high commercial demand of β-pinene exceeds amounts obtained from natural turpentine oil. At present a synthetic preparation of β-pinene by catalytic isomerization of much more abundant α-pinene can be the most perspective way.[1] α-Pinene to β-pinene isomerisation was observed to carry out during α-pinene hydrogenation over VIII group metals supported on carbon materials in the course of multistep linalool synthesis from raw α-pinene (Fig. 1).[2]

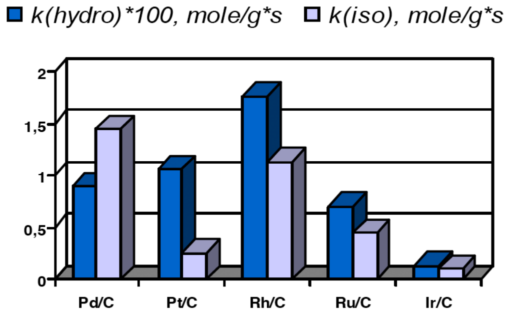

Fig. 1. Hydrogenation and isomerisation during α-pinene hydrogenation over VIII metals group

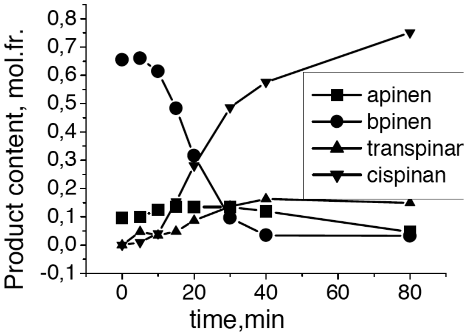

Fig. 2. Liquid phase isomerisation of α- and β-pinenes over Ru/C in n-octane, PH_2 = 5,5 bar, T = 60°C

Molecules of α- and β-pinenes contain various reaction centres, such as C=C double bond in six-member ring, three types of allylic hydrogen atoms and cyclobutane ring. The proper catalyst and reaction conditions determine the pathways of monoterpene functionalities transformation. The present work is devoted to study the competitive migration and saturation of C=C double bond in α- and β-pinene six-member rings over Ru/C in order to find optimal reaction conditions for preferential β-pinene synthesis.

Experiments on isomerisation of α- and β-pinenes solution (10% mol. in n-octane) were carried out in autoclave and up-flowing glass reactor at PH_2=1-5,5 bar, T=60-200°C over catalyst 1.5% Ru/C mass. Initial mixtures of α- and β-pinenes were isolated from raw turpentine oil by vacuum rectification. Reaction products were identified by method GC/MS on VG-7070, using a capillary quartz column 30 m×0.2 mm (Silicone SE-30) and were analyzed in reaction mixture by GLC method on a capillary quartz column 50 m×0.5 mm (Carbowax-20).

According to GLC analysis the different products were formed in a course of hydroisomerisation versus reaction conditions and catalyst modification (Fig. 2). Samples of Ru/C were modified by relevant salt additives to accelerate the isomerization rate[3,4] however hydrogenation reaction rate increased in the same time. To find out the effect of the solvent three types of solvents have been chosen: nonpolar aprotic – n-octane, n-hexane, polar aprotic – DMFA, benzene, polar protic – ethanol, i-butanol. It was found that the isomerization rate increases in n-octane and decreases coming from n-octane to the n-hexane. The effects of solvent, temperature and hydrogen pressure as well as catalyst modification on competitive migration and saturation of C=C double bond in six-member cycle of pinenes during hydroisomerisation reaction were discussed.

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Zeolite Encapsulated Cu (II) Complexes of Pyridoxal Based Ligands as Catalyst for the Oxidation of Styrene, Cyclohexene and Methyl Phenyl Sulfide

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Interaction of Cu(II) exchanged zeolite-Y with the Schiff base derived from Pyridoxal hydrochloride with 1,2 diamminoethane (H_2Pydx-en) and 1,3 diamminopropane (H_2pydx-1,3-pn) in refluxing methanol leads to the formation of corresponding complexes, abbreviated here in as [Cu(pydx-en)]-Y (**1**) and [Cu(pydx-1,3-pn)]-Y (**2**) in the super cages of the zeolite-Y. Spectroscopic studies (IR, electronic and EPR), elemental analysis (CHNS), thermal analysis, AAS, magnetic susceptibility, scanning electron micrographs (SEM), NMR (ligands), and X-ray diffraction patterns have been used to **characterise** these complexes. **Structural Studies** for neat complexs suggest that zeolite-Y can accommodate these complexes in the nano-cavity without any strain. These encapsulated complexes **catalyse the oxidation** by H_2O_2 (also by TBHP), of Styrene, cyclohexene and thioanisole efficiently. Under the optimised conditions, the oxidation of styrene catalysed by **1** and **2** gave 23.61% and 27.98% conversion, respectively, where styrene oxide, benzaldehyde, benzoic acid, and phenylacetaldehyde being the major products. Oxidation of cyclohexene catalysed by these complexes gave cyclohexeneoxide, 2-cyclohexene-1-ol, cyclohexane-1,2-diol and 2-cyclohexene-1-one as major products. A maximum of 90.07% conversion of cyclohexene with **1** and 79.32% with **2** was obtained under optimized conditions. Similarly, a maximum of 68.42% conversion of methyl phenyl sulfide with **1** and 80.99% with **2** was observed where the selectivity of major product methyl phenyl sulfoxide was found to be ca. 60%. Test for **recycle ability** and **heterogeneity** of the reactions (results supports the nature of study carried out) and **possible reaction pathway** (titration with H_2O_2) of the catalysts were also carried out.

All these results suggest the high catalytic potential of the copper(II) complexes studied here.

Olefin Metathesis Mechanistic Considerations Through DFT Calculations

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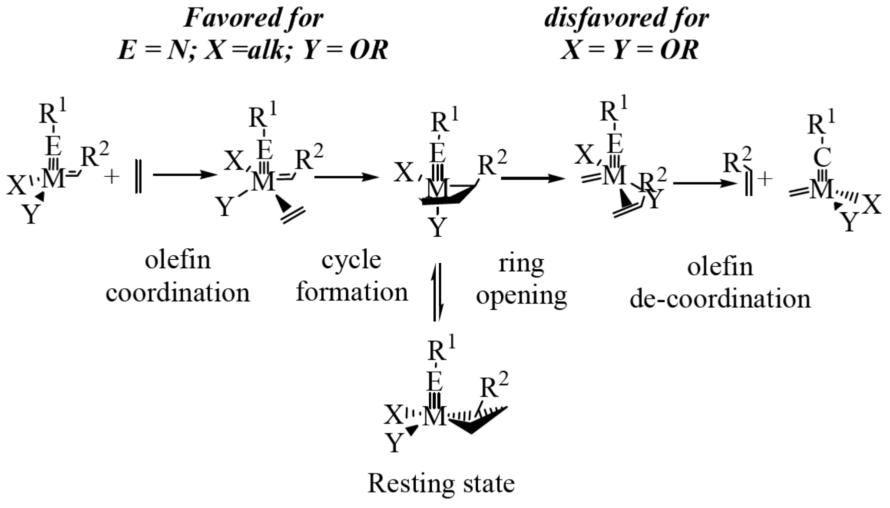
Olefin metathesis has become a key process to build carbon-carbon bonds. Since the Chauvin olefin metathesis mechanism,[1] the synthesis of well-defined metallocarbene complexes based on d^0 (Mo, W or Re)[2] or d^4 (Ru)[3] transition metals have been developed. The efficiency of d^0 Schrock type catalysts, $M(\equiv ER^1)(=CHR^2)(X)(Y)$ (M = Mo and W; E = N; M = Re, E = C) largely depends on the nature of both the metal and the spectator ligands. For instance, for a given X and Y pair, the catalytic efficiency normally decreases from Mo/W to Re and for a given metal, the catalytic efficiency normally increases with the presence of electronegative X and Y ligands (OR). However, very recently a new generation of silica grafted $(R^3O)M(\equiv ER^1)(=CHtBu)(CH_2tBu)$ complexes (M = Mo and W; E = N; M = Re, E = C), which are unsymmetrical (X = CH_2tBu and Y = OR^3), have been synthesized and their efficiency in olefin metathesis is usually higher than the analogous symmetrical bisalkoxy complexes: $M(ER^1)(=CHtBu)(OR)_2$.[4]

DFT calculations have been used to explore the reaction mechanism[5] and to determine those combinations of metal and ligands that favor the catalytic activity of d^0 Schrock type olefin metathesis catalysts. Moreover, several proposed decomposition pathways are also analyzed and the factors that lead to longer catalyst life times are discussed.



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Structural Characterization of Hybrid Molecular - Metallic Sites $Rh^{(I)}$-$Pd^{(0)}$ with Synergistic Effect in the Hydrogenation of Arenes

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In the context of bifunctional selective catalysis, we are investigating hybrid systems contain ing both highly dispersed supported metal nanoparticles and molecular heterogenized complexes tethered to the same support surface.

The combination on the same support of a grafted molecular rhodium complex (Rh(sulphos(COD)) and palladium nanoparticles, resulting in an amplification of reaction rates of arenes hydrogenation, was demonstrated in previous works.[1,2] Such effect was ascribed to the formation, under H_2 atmosphere, of $Rh^{I}(\mu\text{-}H)_xPd^0$ sites between grafted complex and palladium nanoparticles, resulting in an highly active catalyst. Here we will report about a new system based on (CF_3SO_3)-$[Rh(dppp)(COD)]^+$ grafted on Pd^0/SiO_2 as shown in Figure 1.[3] This hybrid catalyst is much more active than the previously described Rh(sulphos(COD) system. It has been found that the catalytic conversion is very high even at very low Rh loadings, then it remains almost constant up to 1 wt% metal loading (Fig. 2). A linear increase of activity vs H_2 pressure and a first to zero order transition vs. substrate concentration were found.

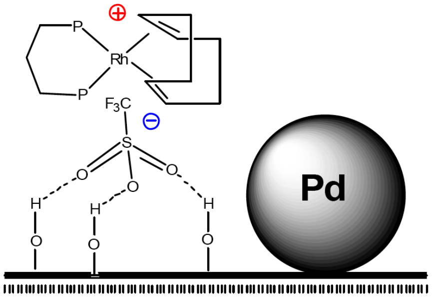

Fig.1 Scheme of Rh(dppp)(COD)-Pd/SiO_2 catalyst

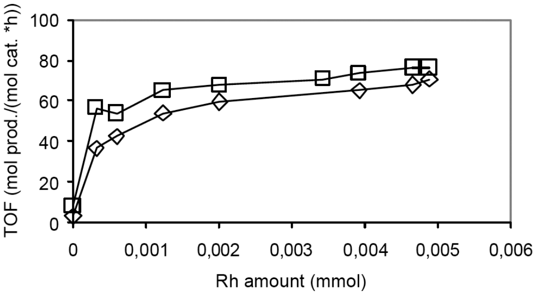

Fig.2 TOF(Pd) vs Rh amount, for benzene (squares) and toluene (diamonds) hydrogenation.

An extensive characterization of the hybrid catalysts has been performed using a variety of solid-state techniques (EXAFS, IR/DRIFT, HRTEM). In particular, EXAFS data at the Rh and Pd K-edge have been recorded before and after the deposition of the RhI complex on the silica surface, in either presence or absence of the preformed Pd metal particles, after each activation treatment and under quasi-in-situ hydrogenation catalysis. The Rh-edge spectra showed the molecular complex to be tethered intact to the support surface also in presence of the preformed Pd metal particles. The activation in hydrogen removed the cod ligand leading to the formation of contiguous Rh-Pd sites. Moreover, air exposure of both fresh and post catalysis samples resulted in a remarkable increase in the catalytic activity. Such effect was deeply investigated by means of EXAFS and CO-probe molecule-DRIFTS spectroscopies suggesting that the passivation operated in air at room temperature does not affect the Rh complex stability, yet it modifies the Pd nano-particles surface so favouring somehow the RhI single site proximity to metal Pd particles. As a result, the formation of more active and stable surface species would form.

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Palladium-containing Nanocatalysts Based on Ultrathin Polyelectrolyte Layers: Synthesis and Catalytic Properties

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Nanocatalysts, i.e., the catalysts containing metal nanoparticles (NPs) are of great interest due to their unique properties, which allow highly active catalysts with low amounts of noble metals. To control catalytic properties, one should control size and morphology of the NPs and their surface modification. This control can be provided by formation of NPs in ultrathin layers of some synthetic and natural polymers. When these layers are formed on traditional supports such as alumina or silica, the advantages both of homogenenous and heterogeneous catalysts are combined.

Polyelectrolytes (PEs) are known to form mono- or multilayers on the surface of charged support. When a monolayer of a cationic PE is deposited on the negatively charged alumina, the former is poorly adsorbed thus jeopardizing the stability of the nanocatalyst synthesized due to washing-off of the PE during the reaction, which leads to the loss of the catalytic activity. The use of cross-linking agent may decrease the uptake capacity of the polymer.

However, when positively charged alumina (native) is covered with the negatively charged PE [for example, poly(sodium-4-styrenesulfonate), PSS], the subsequent adsorption of a cationic PE allows much stronger adsorption of this bilayer on alumina. Such a method is known as the layer-by-layer deposition, which involves alternate polyanion and polycation adsorption. We expected that due to the upper chitosan layer this bilayer may interact with metal compounds and control NP formation.

This study is devoted to investigation of catalytic properties of Pd NPs formed in ultrathin layers of a cationic (at low pH) biopolymer: chitosan. Chitosan, which is obtained by deacetilation of chitin, is one of the most abundant polyaminosaccharides in nature. This determines its low cost. The presence of amino groups explains its affinity for metal ions. Chitosan can coordinate with metal species due to the nitrogen lone pair. Transmission electron microscopy (TEM) study of the model catalysts demonstrated the formation of Pd NPs whose diameters are in the range 2.0-2.8 nm.

The catalytic properties of these catalysts were tested in selective hydrogenation of dehydrolinalool (3,7-dimethyloctaen-6-yne-1-ol-3, DHL) to linalool (3,7-dimethyloctadiene-1,6-ol-3, LN). LN is a fragrance and an intermediate in the syntheses of vitamins A, E and K, β-carotene, geraniol, citral and exhibits antimicrobial activity. The catalytic properties were found to depend on the amounts of PSS and chitosan deposited on alumina, determining the nanoparticle coverage and formation of catalytic centers either before hydrogenation or in situ: the latter occurred when chitosan coverage was insufficient. . The best selectivity observed with these catalysts was 96% at 100% conversion.

Based on kinetic studies and physicochemical characteristics of the catalysts the hypothesis on the hydrogenation reaction mechanism was proposed.

High stability, low cost and exceptionally high catalytic activity, makes these catalysts promising candidates for industrial catalytic applications.[1]

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[1] This work has been supported by Sixth framework programme (no. 506621-1) and by NATO Science for Peace Programme (SfP 981438).

Resin Based Chiral Phosphorous Ligands: Useful Synthetic Intermediates in the Formation of Ligand Libraries and Immobilised Catalysts

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In the last decade chiral monodentate phosphite and phosphoramidite ligands have found wide applications in asymmetric catalysis. Not only are they readily accessible, inexpensive and highly diverse, in several transition metal catalysed reactions these ligands proved superior with respect to activity and enantioselectivity. The fast generation of chemical libraries offered by solid-phase organic synthesis (SPOS) is highly efficient, as workup and purification can be achieved by simple washing and filtration. Additionally the site-isolation of the reactants on the support can prevent the formation of by-products. In general work-up and purification is a mayor problem in preparation of these ligand types, which can be avoided by SPOS. We therefore developed a solid-phase based route to phosphites, using resin bound phosphoramidites as the key intermediate (Figure 1).

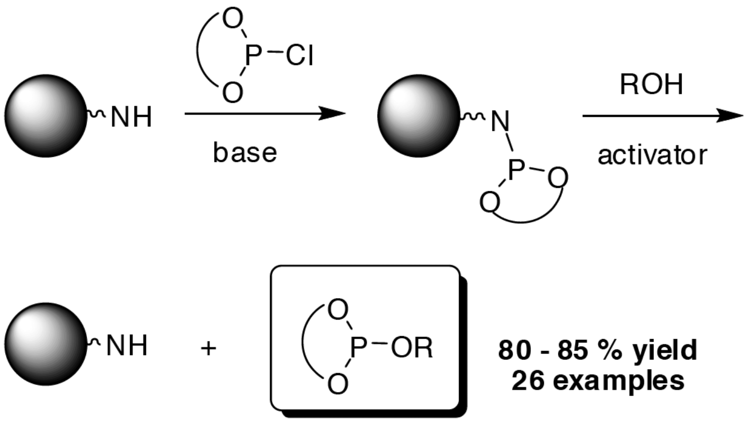

Figure 1. Resin bound phosphoramidite as intermediate in the synthesis of chiral phosphites.

Reaction of a chlorophosphite with an amino-functionalised support yields a resin bound phosphoramidite. Subsequent reaction with an alcohol in the presence of a suitable activator provides the desired phosphite. Using this route a variety of monodentate chiral and achiral phosphite ligands were prepared in good yields.

The resin bound phosphoramidites were tested as ligands, as they combine the good swelling properties of the polystyrene support with easy separation from the reaction mixture. The family of immobilised ligands was extended with phosphites and phosphoramidites bound to various polymeric-supports. In the rhodium catalyzed hydrogenation of alkenes and the palladium catalysed allylic alkylation they showed moderate to good enantioselectivities and activities. Comparing the performance of the resin bound and homogeneous counterparts allowed us to determine the influence of immobilisation on activity and selectivity.

Comparison of Catalytic Activity of Monomeric Metalloporphyrins, Their μ-oxo Analogues and Supported Complexes in Oxidation of Cyclooctane

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Metalloporphyrins play an important role in both biocatalytic and catalytic oxidation. They are able to activate dioxygen and oxidize many organic compounds.[1] However, the major drawback that prevents practical application of metalloporphyrins in large-scale processes is their fast deactivation by dimerization or self-oxidation. Recently much attention has been focused on the catalytic oxidation of cycloalkanes with macrocycle compounds.[2]

The oxidation of cycloalkanes to alcohols and ketones by dioxygen is an important process from both the academic and the industrial point of view; it is used to obtain valuable intermediates. Thus, we performed a compared study of the catalytic properties of simple metallopophyrins MTPFPP (where M = Fe or Mn) with 20 fluorous in phenyl rings and their μ-oxo analogues and metallocomplexes supported on silica, montmorillonite K-10, and polystyrene in oxidation of cyclooctane.

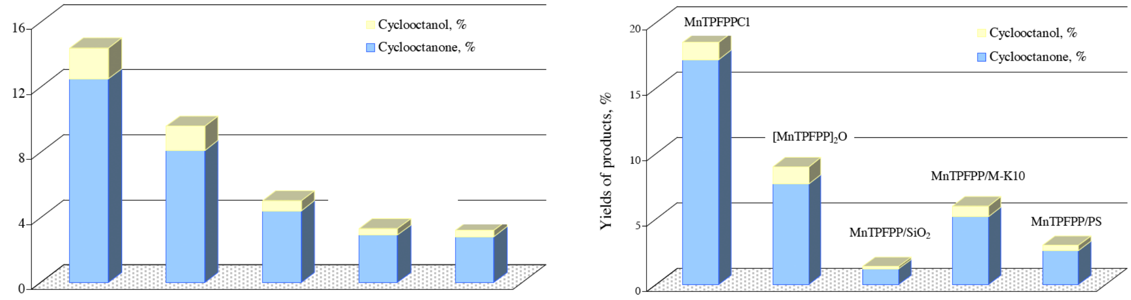

Figure 1. Catalytic activity of investigated catalysts.

Catalytic activity of the monomeric iron and manganese porphyrins, their μ-oxo analogues and supported metalloporphyrins is presented in Fig. 1. The catalytic oxidation of cyclooctane was carried at the temperature of 120°C and under the air pressure of 10 atm. Cyclooctanone and cyclooctanol were the major products of this reaction. Our study showed that monomeric metalloporphyrins as well as their μ-oxo analogues are active in the oxidation of cyclooctane with dioxygen and the formation of μ-oxo complexes could be the reason of the partial deactivation of metalloporphyrins. However, all the investigated supported catalysts showed lower catalytic activity in comparison with homogeneous systems due to the more restricted access of the cyclooctane to the metal center in metalloporphyrins. Heterogenization of metallocomplexes allows the catalyst to be recovered and reused practically without change in the catalytic activity and shifts the selectivity towards the desired product. The mechanism of the investigated reaction is proposed.

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Reaction Dynamics of Pt-Nanoparticles/C Cathode in Fuel Cell Studied by In-Situ Time-Resolved XAFS

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Environment-friendly PEM fuel cell systems can be used in both fuel-cell automobiles and energy systems to address the serious environmental and energy problems faced in our modern society. Power-on/off processes take huge energy transfer leading to deactivation of Pt/C fuel cell catalysts. Stability of Pt metal nanoparticles during the power-on/off processes is one of the major problems at cathode and it is required to overcome this problem for fuelcell automobiles that require the continual repetition of the on/off processes with rapid changes in cell voltages to alter the cars speed. We have investigated the reaction dynamics of the electrochemical reactions in rapid voltage-controlled processes on a Pt/C cathode catalyst by means of novel in-situ time-resolved time-gating QXAFS (1 s time resolution) and DXAFS (4 ms time resolution) for the first time under the operating conditions and found surface reaction dynamics at the cathode including 8 elementary steps and significant time lags among the electrochemical reactions, structural changes, and electronic changes of Pt cathode nanocatalysts.

The analysis of XANES, EXAFS and electrochemical data revealed the valence of Pt nanoparticles, the coordination numbers and distances of Pt-O and Pt-Pt, and electron transfer in the fuel cell, respectively, for both power-on/off processes. Such structural parameters about Pt-nanoparticle catalysts cannot be obtained by other spectroscopic methods, and we succeeded in measuring both the structural and electronic kinetics at Pt/C cathode under the working conditions for the first time. A hysteresis loop was found for the structural changes at Pt/C cathode as shown in Fig.1(right). It should be noted that there is significant time lag between four processes (two electron transfers, Pt-O bond formation/dissociation, and Pt charging/dischargning) on the cathode surface.[1]

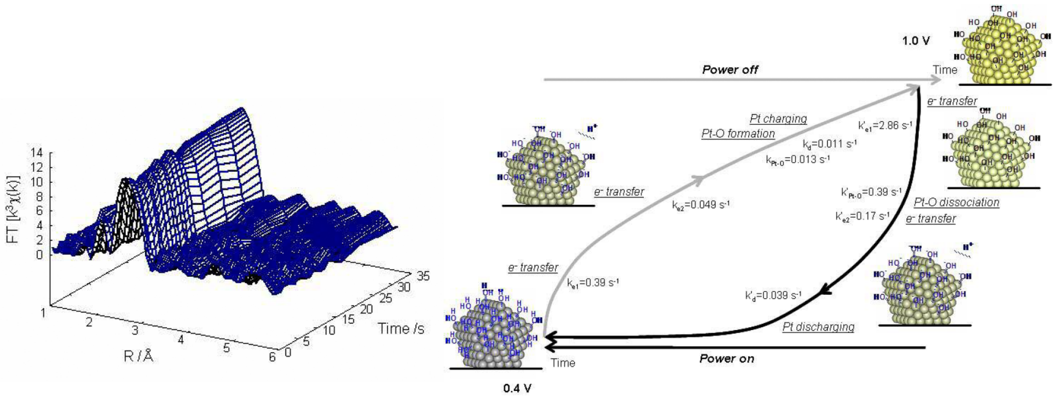

Figure 1. (left) A series of Fourier transforms of Pt L_3-edge time-gating QXAFS for voltage-stepping profess from 0.4 V to 1.0 V. (right) Reaction mechanism of Pt/C cathode surface between 0.4-1.0 V.

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Promotional Effect of Te in Vanadium Phosphate Catalysts for Partial Oxidation of *n*-butane to Maleic Anhydride

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The worldwide production of maleic anhydride (MA) from *n*-butane over vanadium phosphate (VPO) catalyst has been almost completely replaced the process based on benzene due to lower environmental impact and cost.[1] It should be noted that better economics from *n*-butane can be realized by improving the catalytic performance of VPO catalyst. To achieve this goal, a great number of promoters have been applied in the preparation of VPO catalyst. Most of the research papers and patents on doped VPO catalyst were focused on the improvement of the activity and selectivity.[2,3] However, little is known about the effects of the promoters, such as the structure-activity relationship and reactivity of the oxygen species.

In this study, Te doped VPO catalysts (VPDTe) were prepared via $VOPO_4{\cdot}2H_2O$ phase after calcinating the Te doped precursor, $VOHPO_4{\cdot}0.5H_2O$ at 733 K in a flowing of *n*-butane/air mixture for 18 h. Interestingly VPDTe leads to the increment of butane conversion to 80% compared to only 47% for the undoped catalytst. However, for Te doped VPD precursor which mechanotreated for 1 h in ethanol using high energy planetary miller only gave 50% of n-butane conversion. The surface reactivity and reducibility of the catalysts were investigated by temperature programmed reduction in H2/ Ar (5% H2 in Ar). TPR profiles show that all catalysts gave two reduction peaks. The first lower temperature peak was assigned to the removal of oxygen species from V^{5+}, whereas, the latter reduction peak due to the removal of oxygen species associated with V^{4+}. An addition of 1% Te to vanadium phosphate markedly lowered the reduction activation energies of both peaks. The amount of oxygen species removed from the peak associated with V^{4+} phase for VPDTe was significantly higher than the other catalysts. This active oxygen species has shown to be responsible for the activation of hydrocarbon.[4] The present study demonstrates that Te effectively promoted the catalytic activity of n-butane oxidation to maleic anhydride by induced higher removal and lower activation energy of oxygen species associated with V^{4+} phase which responsible for the catalytic activity.

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Chromium (III) and Vanadium (IV) Complexes Immobilized on Silica Gel as Catalysts for Oxidation of Cyclohexene

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Oxidation of olefins is of interest due to the formation of products with a range of different functional groups. These products are very important starting materials for synthesizing fine chemicals.[1]

Different approaches have been utilized to synthesize new heterogeneous systems included amongst which are inorganic-organic hybrids.[2]

Herein we report on catalysts based on salicylidimine chromium (III) and vanadium (IV) complexes bound to silica gel surfaces via a propyl silane spacer (Fig. 1). Homogeneous analogues of the immobilized complexes were prepared and characterized by various analytical techniques including X-ray structural analysis (Fig. 2). A comparison of these analytical results with those obtained for the heterogeneous systems indicate that the latter have the same coordination environment around the metal. Two different approaches were employed for the immobilization of these complexes. The immobilized catalysts were characterized by various physico-chemical techniques.

The catalysts were tested in the liquid phase oxidation of cyclohexene using H_2O_2 as an oxidant under various conditions. These heterogeneous systems were compared with homogeneous analogues in terms of activity and selectivity. The former showed similar, or better percentage conversion and selectivity. The effects of the nature of the solvent, temperature, reaction time, and substrate:oxidant molar ratios on the reactivity of the catalysts were evaluated. The catalytic activity of supported catalysts was found to be less active under nitrogen atmosphere. Oxygen was found to be an effective co-oxidant in reactions carried out under ambient or oxygen atmosphere. High conversions were obtained using THF and acetonitrile as solvent, while low conversions were obtained using benzene and 1,2-dichloroethane. It was also found that the selectivity towards cyclohexenoxide decreased with time due to instability of the epoxide, which undergoes ring-opening reaction.

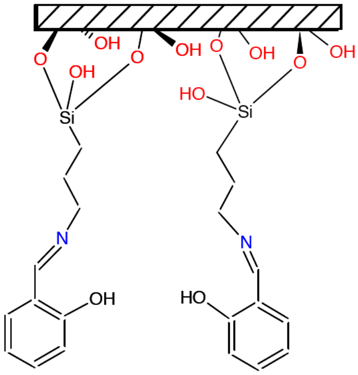

Fig.1 Structure of the immobilized ligand

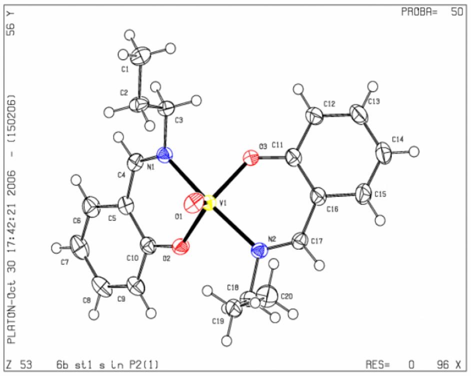

Fig 2. The molecular structure of V(IV) complex

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The Effect of Solvent and Counterions in Gold Catalyzed Functionalization of Alkenes

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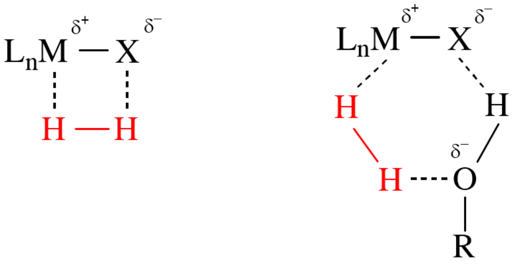
The use of gold complexes as homogeneous catalysts has been undervalued during the past years. Recent reports, however, are changing the preconceived idea that gold is chemically inert.[1] In the present work, the reaction mechanism of alkene hydrogenation catalyzed by an Au(III)-Shift base complex, and the reaction mechanism of hydroamination of alkenes catalyzed by an Au(I)-PR_3 complex are analyzed by means of theoretical (DFT) methods.

The hydrogenation mechanism study shows that the hydrogen molecule is activated in two different ways by the gold(III) catalyst. The initial step corresponds to a H_2 heterolytic activation to form a gold-hydride intermediate, without previous coordination of the H_2 molecule. In this process (the reaction controlling step), theoretical calculations suggested and experiments corroborate that the solvent is playing a critical role (Figure). Once the gold-hydride intermediate, the real catalytic species, is formed, then starts the proper hydrogenation catalytic cycle; in here, the H_2 activation is preceded throught its coordination to the metal centre.[2]

The mechanistic study on the hydroamination reaction by a gold(I) complex shows that the reaction proceeds without the coordination of the amine to the catalyst. A novel reaction mechanism for the proton transfer from the amine to the olefin is proposed: it implies a tautomerization process. In addition, the ligand (triflate) liberated during the process is shown to play a critical role catalyzing the proton-transfer step acting as a proton shuttle.[3]

These results can give some hints for the mechanistic description of other gold homogeneous catalyzed reactions. In addition, they illustrate that other species (as the solvent or liberated ligands during the process) usually considered as spectators during the reaction mechanisms are critical for the reaction to proceed.



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Carbon Dioxide Hydrogenation for Methanol Synthesis: From High Pressure Catalysis to Experimental and Theoretical Modeling

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Carbon dioxide activation mechanisms for low temperature partial hydrogenation to methanol are of key importance for both homo- and heterogeneous catalytic conversion and synthesis reactions. We present here a complete model study in which a combination of ultra-high vacuum (UHV) experiments and density functional theory (DFT) calculations identifies the reaction steps for adsorption, activation and stepwise hydrogenation of the CO_2 molecule on a nickel surface. The pressure gap is considered and effects of the use of an atomic hydrogen beam under UHV conditions are presented. The stable reaction intermediates are detected by means of core level x-ray photoelectron spectroscopy and high-resolution electron energy loss spectroscopy, while the thermal stability of the chemical species involved in the reaction is studied by means of temperature programmed experiments. The results are discussed with reference to stability, electronic and vibrational properties of the involved molecules, and in terms of hydrogenation energies.

AuPt Nanoparticles in Amine Functionalized MCM-41: Catalytic Evaluation in Hydrogenation Reactions

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The deposition of catalytically active nanoparticles on support materials with high dispersion is an important and effective strategy for the design of catalysts. Ordered Mesoporous materials with their intrinsically high surface areas are excellently suited for this purpose. Nano-sized Au-Pt nanoparticles (Au-Pt-bi-MNPs) have been synthesized by the simultaneous reduction of $HAuCl_4$ and $HPtCl_6$ by $NaBH_4$ inside the channels of amine functionalized Si-MCM-41 (NH_2-Si-MCM-41) at ambient conditions. These materials were characterized using chemical analysis, UV-vis, XPS, XRD, FT-IR, surface area and TEM analysis.The size of these alloyed nanoparticles (bi-MNPs) were found in the range of 2-4 nm. These nanoparticles were evaluated to study their catalytic activities towards hydrogenation of aromatic nitro compounds. The catalytic activity of the Au-Pt bi-MNPs was found to be superior to monometallic Au nanoparticles.[1,2,3]

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Selective Ethylene Oligomerisation

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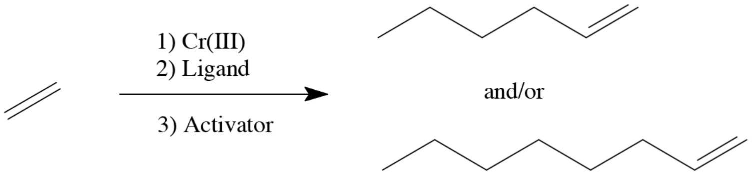
The selective oligomerisation of ethylene to targeted linear alpha olefins (LAOs) such as 1-hexene and 1-octene is a research area of increasing academic and industrial relevance due to the high demand for these LAOs for use as comonomers in the production of linear low density polyethylene (LLDPE). The selective trimerisation of ethylene to 1-hexene is a well established technology[1] and an analogous technology for the selective tetramerisation of ethylene to 1-octene, using an aluminoxane activated, Cr-diphosphine catalyst system has been reported by Sasol Technology (Pty) Ltd.[2] This presentation will summarise some of the selective oligomerisation catalyst development work carried out at Sasol Technology (Pty) Ltd. in recent years, highlighting results of a number of ligand structure-activity/selectivity studies.[3]



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Asymmetric Catalysis with Functionalised N-heterocyclic Carbene Ligands and Their Immobilisation on Silica

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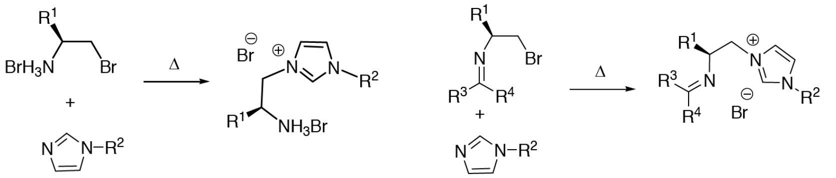
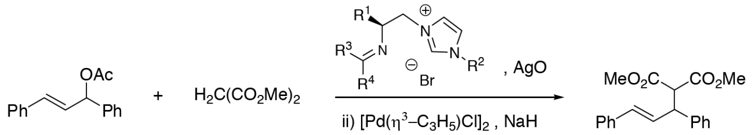
N-heterocyclic carbenes (NHCs) have been widely used as ligands in homogeneous catalysis,[1] particularly in cross-coupling reactions. However, their use in asymmetric catalysis and immobilising catalysts on supports is less well developed compared to that of nitrogen and phosphorus based ligands. Excellent enantioselectivities have been reported for a number of reactions using NHCs as ligands,[2] such as hydrogenation, olefin metathesis and allylic alkylation and there have been a number of reports of using tethered NHCs in developing immobilised palladium catalysts for cross-coupling reactions.[3] In this work we report the synthesis and evaluation of chiral iminoalkyl and aminoalkyl imidazol-2-ylidene ligands and preliminary work on tethering these ligands to silica supports.

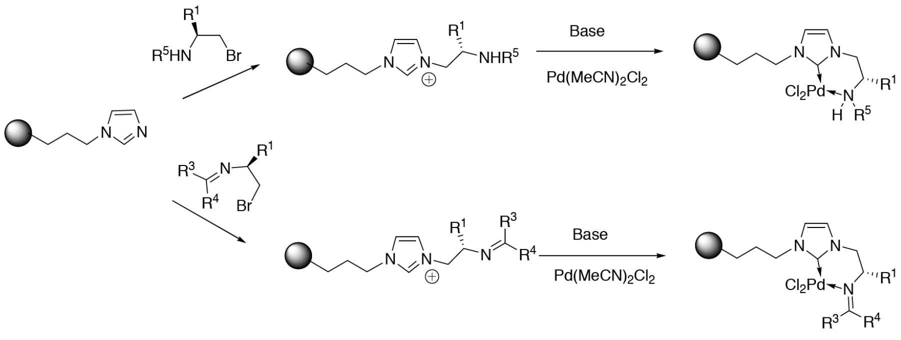
Chiral aminoalkyl bromides and iminoalkyl bromides, derived from amino acids, have been successfully coupled with a range of *N*-substituted imidazoles to give chiral imidazolium salts. Deprotonation of the imidazolium salts generates the NHC ligand.



Chiral iminoalkyl imidazol-2-ylidene ligands have been successfully applied to palladiumcatalysed allylic alkylation, with ees up to 55% being observed. Chiral amidoalkyl imidazol-2-ylidene ligands, have displayed promising enantioselectivities for asymmetric copper-catalysed conjugate addition reactions.



In recent work we have sought to couple chiral aminoalkyl bromides and iminoalkyl bromides to silica-tethered alkyl imidazoles to generate chiral imidazolium salts. Deprotonation and coordination to palladium generates immobilised palladium-NHC catalysts. These will be tested for a range of cross-coupling reactions.



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Heterogenised Heteropoly Acid Catalysts for Clean Chemical Syntheses

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Numerous industrial chemical syntheses proceed through the use of stoichiometric quantities of homogeneous acids, bases or salts which generate large volumes of often hazardous aqueous waste. The development of alternative cleaner technologies, in particular solid acid catalysts, is an area of significant academic and industrial importance.[1] In contrast to liquid acids, which possess well-defined acid properties, solid acids may contain a variety of active sites that are categorised by their Brønsted and/or Lewis acidity and their strength and numbers of these sites, thus new solid acid materials require detailed characterisation to determine the nature of the active site.

Heteropolyacids[2] are polyoxometalate clusters whose application in organic transformations has attracted much interest since they possess high Brønsted acid strengths (approaching the superacidic region) and are active in both vapour and liquid phase chemistries. Of these, phosphotungstic acid, $H_3PW_{12}O_{40}$ (HPW) exhibits the highest stability and strongest acidity; however it also has a high solubility in polar media and an inherently low surface area. There is much interest in the heterogenisation of HPWs using either porous supports or via the formation of insoluble alkali exchanged salts ($M_xH_{(3-x)}PW_{12}O_{40}$).[3] Here we investigate the active sites within Cs^+ exchanged HPW and silica-supported HPW, and reveal how their catalytic performance in both polar and non-polar chemistries can be regulated.

X-ray analysis of highly dispersed HPW/SiO_2 catalysts reveals the existence of two distinct tungsten chemical environments,[4] corresponding to tungstate either directly coordinated to the silica, or in a bulk-like environment (Figure 1). HPW clusters spread across the silica surface to form a close-packed monolayer at low loadings prior to the formation of crystalline, bulk HPW multilayers. Non-polar chemistry (α-pinene rearrangement) occurs preferentially over monolayer HPW clusters, in contrast to methanol condensation wherein reaction was favoured within the pseudo liquid phase of the bulk-like HPW multilayers. Insoluble $Cs_xH_{(3-x)}PW_{12}O_{40}$ have also been explored in esterification and transesterification reactions for biodiesel synthesis. Here we find that while HPW exhibits high activity in both reactions its high solubility the reaction media is undesirable. However, compositions with $\sim$ 2.3 Cs^+ per Keggin (Figure 2) exhibit excellent activity in both reactions and are readily recovered. The consequences of this for a heterogeneous biodiesel process will be discussed.

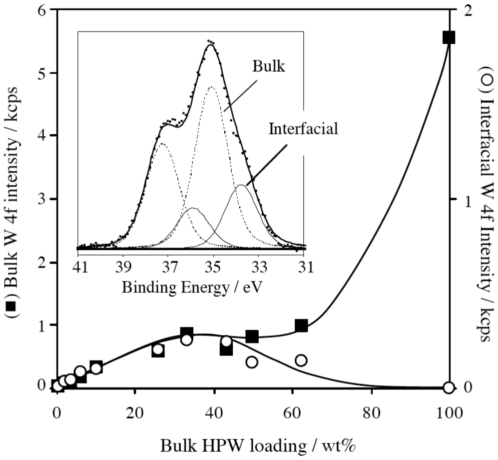

Figure 1: Evolution of surface tungstate chemical environment with HPW loading. ***Inset*** - W 4f XP spectra of HPW/SiO_2.

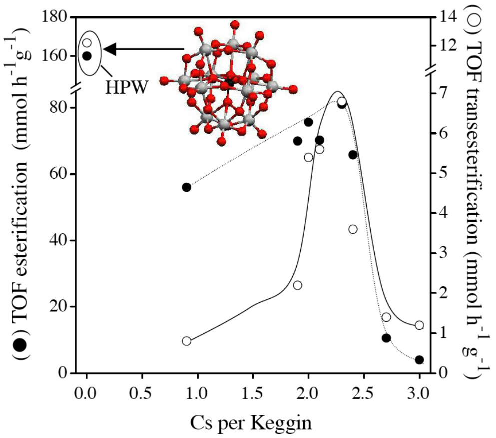

Figure 2: TOF of $Cs_xH_{(3-x)}PW_{12}O_{40}$ in fatty acid esterification and triglyceride transesterification

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Ethylbenzene Dehydrogenase – Biocatalytic Synthesis of Alkylaromatic and Alkylheterocyclic Alcohols

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Mononuclear molybdenum enzymes constitute a fairly large class of biocatalysts that contain the molybdenum cofactor in their active centers, which consists of one Mo atom linked to one or two molybdopterins. These enzymes are classified into three major families on the basis of structural differences and the mode of binding of the Mo cofactor, namely the xanthine oxidase family, the sulphite oxidase family and the DMSO reductase family.[1]

The recently discovered molybdoenzyme ethylbenzene dehydrogenase (EBDH) belongs to the DMSO reductase family[2,3,4]. It catalyses the oxygen-independent, stereospecific hydroxylation of ethylbenzene to (S)-1-phenylethanol, the first known example of direct anaerobic oxidation of a non-activated hydrocarbon (Figure 1).

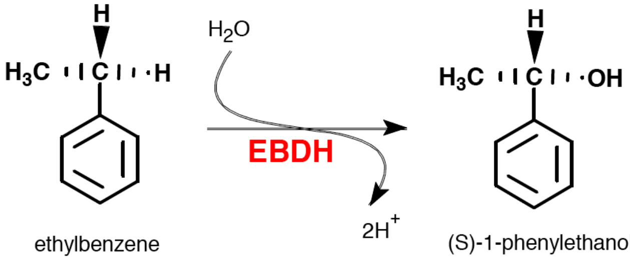

Figure 1. Anaerobic oxidation of ethylbenzene to (S)-1-phenylethanol by EBDH

This enzymatic system promises potential applications in chemical and pharmaceutical industries due to a fact that: i) pure enantiomers of alcohols are of a high value as building blocks for physiologically active compounds and ii) EBDH reacts with a relatively wide spectrum of alkyl substituted aromatic and heterocyclic compounds.

In our research the reactivity of EBDH was explored with different alkylaromatic and alkylheterocyclic compounds, which led to identification of 20 substrates and 9 inhibitors. Reaction products were identified as secondary alcohols by chromatographic analysis and MS experiments. The reactivity was analyzed by means of both simple linear quantitative structure activity relationships (QSAR) and complex non-linear artificial neural network models.[5] These analyses provided insight into the reaction mechanism. Moreover, based on recently obtained X-ray structure[6] of the enzyme, an ab initio modeling of ethylbenzene activation was performed leading to further understanding of the catalytic system. The presentation will provide the latest developments on EBDH reaction mechanism and its biochemical and physicochemical characterization.[7]

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Enantioselective Reductive Amination – Comparison of Homogeneous and Heterogeneous Catalytic Systems

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Introduction. Chiral amines are important products for fine chemistry and pharmacy. The most established industrial production method includes the heterogeneously catalyzed reductive amination leading first to a mixture of racemic amines and the consecutive racemate resolution either by crystallization or enzyme catalysis. However, this technology leads only to 50% of yield of the desired enantiomer. An alternative simple and cost effective process would be the direct enantioselective reductive amination of ketones. Especially, the formation of primary amines using ammonia as nitrogen source would be of interest:

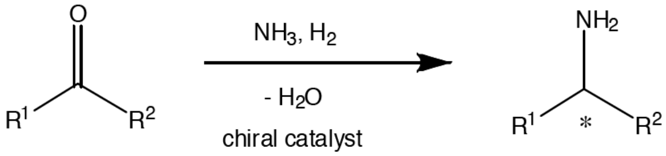

Figure 1. R^1, R^2 = Alkyl, Aryl

Even though the reaction looks very simple, it is still a challenge to perform the direct enantioselective reductive amination with ammonia. In the contribution, the design of proper catalytic systems will be introduced. Rh and Ru complexes with different chiral ligands as well as heterogeneous Pt catalysts chiral modified by optical active amino acid-derivatives have been investigated in the conversion of alkyl-phenyl-ketones.

Results. Remarkable ee values (>40%) as well as high selectivity to amines (99%) were found over chiral modified Pt/carbon and Pt/Al_2O_3 catalysts. In the catalyst screening, the emphasis was put on chiral amino-acid modifiers. A detailed analysis of the relationship between modifier structure, catalyst properties and enantioselectivity will be presented.

Homogeneously catalyzed direct reductive amination of acetophenone with ammonia could be performed only in methanol solution. Disappointing low chiral induction of 19% ee were found in broad screening of different chiral catalysts. In addition low selectivity towards amine was generally observed. However, successful enantioselective homogenous catalytic reductive amination was possible via transfer hydrogenation using ammonia formiate as hydrogen transfer agent. Hereby, ee values up to 95% and amine yields above 90% were achieved for a large variety of alkyl-phenyl-ketones.

Conclusion / Perspective. The application of homogeneous and heterogeneous catalytic systems discloses new complementary technologies for production of chiral amines. Chiral modification of solid catalysts with amino-acid-derivatives appears to be a promising concept for future development of enantioselective heterogeneous catalysts.

Glycerol as Alternative Green Reaction Medium

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Solvents are used daily in numerous industrial processes as reaction medium, in separation procedures and as diluters. As reaction medium, solvent are employed to bring reactants and/or catalysts together and to deliver heat and momentum. In addition, the solvent may also affect activity and selectivity. The choice of the solvent, i.e. its chemical, physical and biological nature, also plays a key role from environmental, economic, safety, handling, and products isolation points of views.

Water is the first solvent of choice regarding the above considerations, yet the negligible solubility of many organic and organo-metallic compounds in water limits its applications. On contrary, using organic, petroleum-based, solvents that allow dissolving a large variety of solids, liquids, and gases is usually accompanied with air, water, and land contamination. Various green reaction medium such as fluorous phases, ionic liquids and supercritical fluids have been reported as recyclable environmentally benign reaction medium in the past decade. However, their tedious and hazardous production, their high price, and technical problems, still limit their practical use. Glycerol, which is a non-toxic, biodegradable and recyclable liquid manufactured from renewable sources has a high potential to serve as green solvent for organic syntheses. It has also promising physical and chemical properties. Glycerol, as other polar organic solvents, allows the dissolution of inorganic salts, acids, and bases, as well as enzymes and transition metal complexes, but it also dissolves organic compounds that are poorly miscible in water. Different hydrophobic solvents immiscible in glycerol allow removing the products by simple extraction. Distillation of products is also feasible.

Our study is focused on exploring the scope and limitations of glycerol as alternative green reaction medium. We study its possible use as such in a variety of ways. Several noncatalytic and catalytic reactions, using homogeneous and heterogeneous chemo- and biocatalysts, were successfully performed in glycerol. High products yields and selectivities were achieved. The unique physico-chemical nature of glycerol enables easy separation of the product together with catalyst recycling. These properties can also be translated into other processes which require non-aqueous polar solvents such as non-aqueous emulsions and electrolytes as well as applications in microwave promoted synthesis.

Effect of Alkali Leaching on the Surface Structure of Ni_3Al Intermetallics Catalyst

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In Ni-Al system there are four stable intemetallic compounds, $NiAl_3$, Ni_2Al_3, NiAl and Ni_3Al. Among them a mixture of $NiAl_3$ and Ni_2Al_3 (Ni-50 wt% Al) is used as a precursor alloy for Raney nickel catalysts. For NiAl and Ni_3Al, very limited studies have been carried out on the catalytic properties. Ni3Al has been known as promising high-temperature structural materials because of its excellent high temperature strength and corrosion/oxidation resistance and thus many studies have been focused on the mechanical properties and the microstructures.[1,2,3] Recently, we found that Ni_3Al is highly promising as a catalyst for hydrogen production from methanol.[4,5,6] Our previous work indicated that the alkali leaching can improve the catalytic properties of Ni_3Al significantly. However, the mechanism of the effect of alkali leaching on the catalytic properties of Ni_3Al has yet to be studied in detail.

In the present study, the effect of alkali leaching on the surface structure of Ni_3Al single-phase intermetallic compound was investigated by means of X-ray diffraction, surface area analysis, electron microscopy, X-ray photoelectron spectroscopy, and temperature programmed reduction. Al atoms dissolved in the alkali solution, resulting in the formation of fine Ni particles on the surface. The selective dissolution of Al occurred only on the outer surface, thus the inside of the specimen powder retained the Ni_3Al structure, and a Ni supported by Ni_3Al structure can be obtained. This Ni/Ni_3Al structure contributed to the high activity and selectivity for hydrogen genernation from methanol.

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Structural Requirements of Supported Ruthenium Nanoparticles for Lignin gasification in Supercritical Water

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The gasification processes from waste biomass plays a key role in the upcoming sustainable society. Utilization of lignin is an important issue; however, the conversion of lignin to those gases requires very high temperature of more than 1073 K. Therefore, the development of catalytic technique for lignin gasification at low-temperature is desired. Supercritical water gasification over supported metal catalysts is a powerful technique to reduce the reaction temperature. We have reported that supported ruthenium catalysts are effective for the gasification of lignin in supercritical water around 673 K.[1] We demonstrated that catalytic gasification proceeded in supercritical water through two steps: (i) decomposition of lignin to low-molecular weight compounds and (ii) gasification of the low-molecular weight compounds over ruthenium metal particles. We also reported that charcoal- or titania-supported ruthenium catalysts showed higher gasification activity and stability than alumina- and silica-supported ones.

In this paper we report preparation, characterization and gasification activities of several charcoal-supported ruthenium catalysts. We discuss the effects of the ruthenium precursors and ruthenium metal particle size on the gasification.

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Preparation of $BaSO_4$ Coated $Fe/Cu/Al_2O_3$ Composites Granule for Sulfuric Acid Decomposition to Hydrogen Production

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Many separation and reaction processes in industrial applications require the use of the granules-composite. However, the granules prepared by the conventional methods, i.e. tumble growth, tabletting and extrusion, suffer from some drawbaks such as poor mechanical strength and low attrition resistance.

The iodine-sulfur (IS) cycle consist of the following reactions: (1) decomposition of H_2SO_4 to SO_2 and H_2O, (2) decomposition of HI to H_2 and I_2, (3) production of HI and H_2SO_4 through reaction of I_2 with SO_2 and H_2O. Metal oxides are considered as active catalysts for the sulfuric acid decomposition in temperature range of 600-950°C. Noble metals are reliably as highly active catalysts for decomposition reaction, but non-noble catalysts should be developed from the economic point of view.

The catalysts should be insulated in Al_2O_3 matrix to disperse and stabilize the active component. To overcome the problem of poor mechanical strength and attrition resistance, catalysts granules have be prepared by combination of the Yoldas sol-gel process and the oildrop method. Furthermore, a coating of the granules with meso-structured barium sulfate could prevent the active component of the catalyst from the corrosive environment of the sulfuric acid.

In our work, the optimum composition of granules based on Cu/Fe alumina has been identified in the SO_3 reaction. In this presentation, we will prepare the granule type of catalyst coated by $BaSO_4$ for the direct decomposition of H_2SO_4 to produce hydrogen in IS cycle. The granule will be coated carefully by spray pyrolysis combined with fluidized system. The catalytic performance of the catalyst will be investigated by both SO_3 and H_2SO_4 decomposition.

Figure 1. $Cu/Fe/Al_2O_3$ granular particles of ~ 1 mm in diameter.

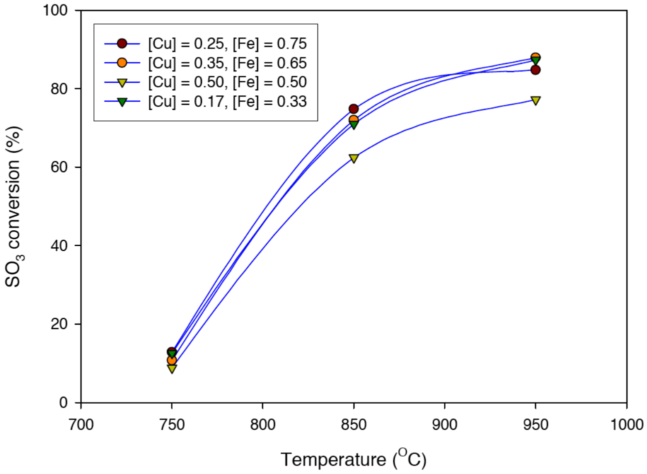

Figure 2. $Cu/Fe/Al_2O_3$ granular particles of 1 mm in diameter.

Designing Pt/CeO_2-Al_2O_3 Nanocatalysts: Synthesis, Characterization and Catalytic Properties in the Steam Reforming of Methane

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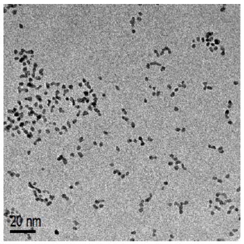
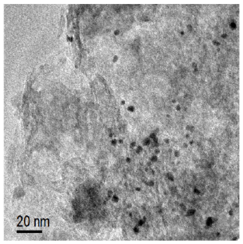
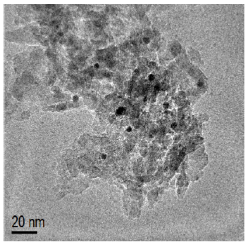
The partial oxidation of methane (POM) produces synthesis gas with H_2/CO ratio of 2:1, desirable for the synthesis of hydrocarbons. A two-step mechanism has been proposed for the POM, consisting of exothermic total oxidation of CH_4, producing CO_2 and H_2O followed by the reforming of the un-reacted CH_4 with the steam and CO_2 produced by the first reaction.[1] Here, we describe a new simple method to prepare nanocatalysts, formed by Pt nanoparticles (Pt-NPs) supported on Al_2O_3 and CeO_2-Al_2O_3. The catalysts were submitted to steam reforming of CH_4 at low temperature to clarify the effect of support on the catalytic activity. Pt-NPs of ∼3 nm were synthesized by colloidal methods,[2] to achieve a highly homogeneous size distribution, and they were encapsulated in mesoporous Al_2O_3 and CeO_2-Al_2O_3 prepared by sol-gel method. The solution of the Pt-NPs where added during the sol-gel synthesis of the supports to produce the Pt /Al_2O_3 and Pt /CeO_2-Al_2O_3 nanocatalysts. The figure below shows the transmission electron microscopy (TEM) images of the colloidal Pt-NPs, the Pt/Al_2O_3 nanocatalyst, after calcination at 773K in synthetic air, and after POM reaction at 1073 K for 24h. It can be seen that the Pt-NPs are well-dispersed on the support and there was no significant modification of the NPs size and/or agglomeration, due to the calcination and the POM reaction. Similar results were found for the Pt-NPs/CeO_2-Al_2O_3 nanocatalyst. Fourier transform infrared spectroscopy (FTIR) of CO adsorbed reflected the narrow size dispersion of the Pt-NPs and suggests that the Pt presents similar electron density, in both Pt /Al_2O_3 and Pt/CeO_2-Al_2O_3 catalysts. However, the Pt-NPs/CeO_2-Al_2O_3 presented a strong suppression of the bridgebonded CO adsorption, suggesting that Pt surface is modified by the geometric effect of CeO_x, which overlays the Pt-NPs. Concerning the CH_4 turnover rate in the steam reforming, the results for the Pt/CeO_2-Al_2O_3 catalysts was around two orders of magnitude higher than the results for the of Pt/Al_2O_3 catalyst, despite the same NPs size. In fact, experiments of dehydrogenation of cycle hexane showed that the number of available Pt sites is just slight higher in the Pt-NPs/Al_2O_3 catalyst. These results suggest that the activity depends on the support, in agreement with previous work on Pd/[CeO_2-Al_2O_3 catalysts obtained by impregnation.[3] The high activity for Ce-containing catalysts is assigned to the higher accessibility of the Pt site to CH4, due to the removal of $C^\star$ species on Pt surface by the mechanism of oxygen transfer from the ceria support. The use of colloidal NPs to produce a controlled set of nanocatalyst and the detail characterization was to clear show the important role of the Ce-species to improve the catalytic activity.



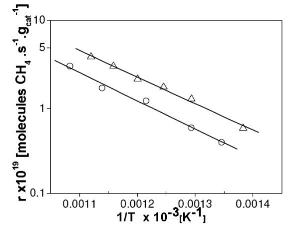
Colloidal Pt-NPs



Pt/Al_2O_3 nanocatalyst, before the reaction



Pt/Al_2O_3 nanocatalyst, after the POM reaction



Arrhenius plots for CH_4 steam reforming on Pt/Al_2O_3 (o) and Pt/12CeO_2-Al_2O_3 (Δ) catalysts

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Using Ni-colloidal Nanoparticles as Hydrogenation Catalysts: Relevant Aspects to be Considered

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The performance of heterogeneous catalysts containing supported metallic nanoparticles depends on the optimization of several aspects, such as size, shape and structure of these active nanoparticles, as well as on the interaction between these metallic nanoparticles and supports and on the textural properties of the supports. In the last years, the fast advance of the synthetic methods to produce nanoparticles combined with highly advanced techniques for characterization at nanoscale have significantly contribute to tailoring unique rational materials and new technologies. In heterogeneous catalysis, colloidal methods enabled the possibility of synthesizing metallic particles with tunable average size and very narrow size distribution, with shape and surface chemistry control, allowing a more comprehensive understanding of the catalytic aspects of these features. However, the interaction between metallic nanoparticles and support surfaces has also a central role in the catalytic properties. In this context, the aim of the present work is to use Ni-nanoparticles supported by impregnation on activated charcoal and sol-gel silica, which have different textural properties, addressing some relevant aspects such as the modification of the textural properties of the support and the availability of the active metallic sites. Ni-colloidal nanoparticles were synthesized by reduction of $Ni(OAc)_2$ with 1,2-dodecanediol in the presence of oleic acid (ligand) and trioctylphosphine in hot organic solvent. The different supports have been impregnated with the same colloidal solution, producing a set of supported Ni-catalysts. Fig. 1 shows the transmission electron microscopy (TEM) images of unsupported and supported Nicolloidal nanoparticles in activated charcoal (5 wt% Ni/C). Unsupported Ni-nanoparticles showed a narrow size distribution and mean size of 7.8 nm. These Ni-nanoparticles could be well dispersed on the external surface of the different supports and did not change the Ni-nanoparticle distribution. N_2 adsorption-desorption isotherms at 77 K showed that the impregnation of the nanoparticles on activated charcoal decreases its surface area and its total pore volume. Due to their size, the Ni nanoparticles are mainly on the external surface fo the supports, blocking part of the pores and drecreasing the surface area down to 50% in pure micropore supports, such as silica produce in acidic conditions. Part of ligand excess remained in impregnation suspension may have also block the micropores. In fact, oleic acid (ligand) has the pivotal role of controlling the Ni-nanoparticles growing during the colloidal synthesis and also stabilizing the dispersion of formed Ni-nanoparticles during the impregnation; however, for catalysis this also means blocking the active metallic sites. Preliminary thermal treatments of supported Ni-catalysts under H_2 were successful to expose the metallic surfaces, as determined by H_2 chemisorption. At the moment, we are optimizing these thermal treatments to maximize the catalytic activity in the hydrogenation of cyclohexene and we are analyzing their effects in the surface chemistry of supported Ni-catalyst by X-ray photoelectron spectroscopy (XPS).

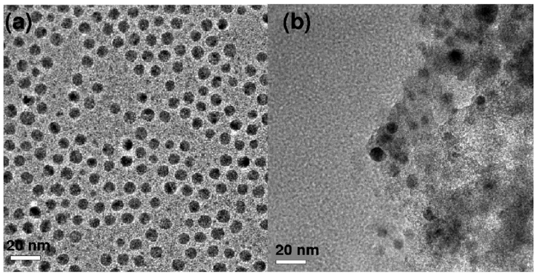

Figure 1. TEM image of (a) unsupported Ni-nanoparticles and (b) supported 5 wt% Ni/C catalyst.

Langmuir-BlodgettMonolayer Formation and Catalytic Properties of Size-tunable Monodisperse Rhodium Nanocrystals of (111) Orientation Synthesized by One-step Polyol Method

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Size-tunable monodisperse Rh nanocrystals can offer unique properties in many heterogeneous catalytic reactions (such as hydrogenation, hydroformylation, and hydrocarbonylation) of both scientific and technological interests. Herein, we report on Langmuir-Blodgett monolayer formation, catalytic properties of size-tunable monodisperse rhodium nanocrystals of (111) orientation synthesized by a one-step polyol method. The nanocrystals have polygonal 2-D projections, dominated by hexagons, pentagons and triangles with catalytically active (111) surface structures (>65% in yield). Among the polygons, multiple {111} twinned particles (hexagons and pentagons) favored by thermodynamics have a large population (>45%). With a Langmuir-Blodgett trough, monolayer films of the size-tunable Rh polygons have been deposited on silicon wafers. These monolayers can serve as good model heterogeneous catalysts for exploring the size-function relationship and metal-support interface structures in many organic reactions.

Thermal Characterization of Glucose Oxidase Purified and Overproduced from *Aspergillus niger* BCG-4

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An intracellular glucose oxidase (GOD) was isolated from the mycelium extract of a gamma rays mutated strain of *Aspergillus niger* BCG-4. The enzyme was purified to a yield of 55.91% and 344.23 fold purification with specific activity of 5139.06 U mg^{-1} through ammonium sulfate precipitation, anion exchange and gel filtration chromatography, respectively. The enzyme showed high affinity for D-glucose, with a K_m value of 25 mM, V_{max} 125 U mL^{-1}, K_{cat} 3676.47 and specificity constant showed to be 147.05 with a molecular weight of 131 kDa. The enzyme exhibited optimum catalytic activity at pH 5. Temperature optimum for glucose oxidase catalyzed D-glucose oxidation was 40°C.The enzyme showed a high thermostability having a half-life 32.5 min, enthalpy of denaturation 1.2027 kJ mol^{-1} and free energy of denaturation 78.62 kJ mol^{-1}. These characteristics suggest the use of glucose oxidase from mutant *Aspergillus niger* BCG-4 as a valuable analytical tool and in the design of biosensors for clinical, biochemical and diagnostic assays.

Ti(IV) and V(V) – AmineTri(Phenolate) Complexes as Lewis Acid Catalysts

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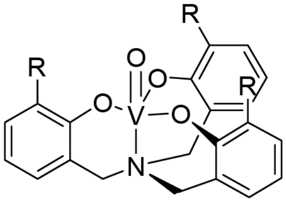
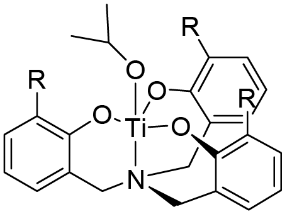
In the last years C_3 symmetric aminetri(phenolate) ligands have attracted much attention due to their ability to form thermodynamically stable complexes with a wide variety of transition metals and main group elements.[1] However, only a few reports dealing with catalytic activity, mainly in the field of polymerization, have appeared[1c,e]. More recently we have developed a new synthetic methodology toward the synthesis of amine tri(phenolate) ligands via reductive amination reaction.[2,3]

Here we will demonstrate that Ti(IV) and V(V) complexes are efficient Lewis acid catalysts. Oxidation reactions can be carried out using both CumOOH and aqueous hydrogen peroxide as terminal oxidants, with catalyst loadings down to 0.1% and excellent yields.

^{1}H NMR and ESI-MS studies toward the identification of the catalytically active specie have been carried out. Complexes **1a-c** efficiently catalyze oxidation reactions at room temperature. Reactions were performed with aqueous hydrogen peroxide as oxidant which adds value to the methodology from the environmental viewpoint.





Studies toward the immobilization of these catalysts on membrane supports are due on course.

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Fine Tuning of Activity and Selectivity of Immobilized Rh-complexes in Asymmetric Hydrogenations

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An increasing demand has recently developed towards the selective synthesis in production of fine chemicals, due to environmental and economical aspects. Among these processes selective hydrogenations, especially asymmetric hydrogenations, have become more and more important. Soluble complexes are widely used for the above purpose with excellent activity and selectivity.[1] However, the lack of recovering and recycling limits the practical application of these catalysts. The heterogenization of these complexes could be a solution to overcome the above mentioned problems.[2]

The Rh complex of a chiral diphosphane ligand, the [Rh(NBD)(2R,4R)-BDPP]ClO_4 was successfully applied in the hydrogenation of (Z)-methyl(α-acetamidocinnamate) with excellent activity and selectivity. Differently substituted derivatives of this complex were prepared and the substituents gave different basicity of the complex. The effects of substituents was studied on the rate and selectivity of the hydrogenation of C=C double bond. Full potential of this remarkable catalytic system can be used if the above catalysts will be heterogenized.

An efficient heterogenization method, has recently been introduced by Augustine and coworkers to get enantioselective, recyclable catalysts.[3] We have applied this method, with a slight modification to immobilize the different Rh complexes.

In order to evaluate the performance of our heterogenized samples, we have studied the hydrogenations of C=C and C=O double bond in homogeneous and in heterogeneous conditions. The obtained results clearly show that the heterogenized catalysts had about the same activity and enantioselectivity as the homogeneous ones. The effect of substituents was also studied and an increasing activity and selectivity was observed as a function of basicity. At the same time our heterogenized samples had all the advantages what we can expect from a heterogeneous system, namely the good performance, easy separation and the possibility to recycle, without any significant loss of catalytic properties.

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Index

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