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FINAL REPORT

ASSESSMENT OF RESEARCH NEEDS FOR ADVANCED HETEROGENEOUS CATALYSTS FOR ENERGY APPLICATIONS

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ABSTRACT

This report assesses the direction, technical content, and priority of research needs judged to provide the best chance of yielding new and improved heterogeneous catalysts for energy related applications over a period of 5-20 years. It addresses issues of energy conservation, alternate fuels and feedstocks, and the economics and applications that could alleviate pollution from energy processes.

Recommended goals are defined in three major, closely-linked research thrusts:

I. **CATALYTIC SCIENCE** — Establish a scientific knowledge of essential catalyst structure/performance relationships and work toward developing the ability to predict the catalytic capabilities of novel materials.

II. **ENVIRONMENTAL PROTECTION BY CATALYSIS** — Prevent pollution by developing economical processes that are free of pollutant formation. Diminish pollution by achieving higher selectivity in fuels and chemicals manufacture and by new and improved catalytic processes for the removal of pollutants.

III. **INDUSTRIAL CATALYTIC APPLICATIONS** — Develop energy-saving, environmentally benign processes for manufacture of liquid fuels and commodity chemicals based on domestic natural gas, biomass, and coal. Emphasize research on synthesis gas ($CO + H_2$) production and conversion, oxidation catalysis, new methods of hydrogen production, and the synthesis of novel materials for catalytic applications.

This study was conducted by an eleven-member panel of experts from industry and academia, including one each from Japan and Europe. Discussions were held with a wide variety of authorities, supplementing an intensive review of technical literature. Panel conclusions were assisted by critical peer reviews.

There is a high level of confidence that the research proposed can provide catalytic technology which will achieve major economic and environmental improvements in energy applications.

Volume I provides a comprehensive Executive Summary, including Research Recommendations. Volume II first presents an in-depth overview of the role of catalysis in future energy technology in chapter 1. Then current catalytic research is critically reviewed and research recommended in eight topic chapters: 2. Catalyst Preparation: Design and Synthesis; 3. Catalyst Characterization: Structure/Function; 4. Catalyst Performance Testing; 5. Reaction Kinetics/Reactor Design; 6. Catalysis for Industrial Chemicals; 7. Catalysis for Electrical Applications; 8. Catalysis for Control of Exhaust Emissions; and, 9. Catalysts for Liquid Transportation Fuels from Petroleum, Coal, Residual Oil, and Biomass.

EXPERT PANEL

This report has been prepared by a panel of experts who have evaluated the research needs for advanced heterogeneous catalysts for energy applications. The project has been conducted under a grant to Consultec Scientific, Inc., Knoxville, TN from the U.S. Department of Energy, Office of Energy Research. Dr. G. Alexander Mills served as the Principal Investigator. The following distinguished scientists served as members of the panel:

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Special thanks are expressed to the peer reviewers of the report who are listed below. Their comments and criticisms were invaluable in improving the quality and completeness of this report.

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EXECUTIVE SUMMARY

CATALYSTS IN ACTION

Catalysts are remarkable chemical tools, used to accelerate and direct chemical reactions. A catalyst can speed up a reaction, perhaps by a million fold, to produce selectively a desired product. Catalysts are the philosophers' stone of modern alchemists, not changing lead into gold, but rather changing cheap and abundant raw materials into fuels, plastics, and pharmaceuticals far more valuable than gold. The manufacture of energy fuels and chemicals by catalytic processes is of major economic and social consequence. Catalytic processes are responsible for about 75% of chemical and petroleum processing products by value and, in new technology, this proportion is over 90%. In the U.S., the annual $2 billion catalyst industry is responsible for manufacture of about $900 billion of products or 17% of our GNP. Productive employment is provided for about 2 million persons. Further, major health benefits are provided by pollution prevention technology, for example, via use of automotive catalytic converters.

Catalytic research over the past seventy years, particularly in the U.S., has created a wide array of catalytic refining processes for transforming crude petroleum to low-sulfur, high octane gasoline. Chemical reactions accomplished in catalytic hydrodesulfurization, cracking, reforming, and alkylation processes are being used on a massive scale worldwide. The dynamics of catalytic innovation is such that major progress is observed to occur in quantum jumps, fueled by a period of intensive research. According to the National Research Council 1992 report, *Catalysis Looks to the Future*, the use of zeolite catalysts, introduced in 1962, provided an amazing increase in the efficiency of converting crude oil to gasoline that has permitted a saving of more than 400 million barrels of oil a year, or more than $8 billion a year, and greatly benefiting the U.S. balance of payments by decreasing oil importation.

Catalysis is the dominant technology in the manufacture of chemicals used for products such as polymer-based plastics, fibers, and films found in every household. The catalytic manufacture of chemicals is highly energy-related. Advanced U.S. technology is critical not only for domestic consumption but also for improving the favorable international balance-of-trade for chemicals export. The chemical industry employs 1.2 million workers producing $140 billion worth of materials, including 30 petrochemicals worth over $60 billion. Of the 63 major chemical product innovations and 43 process innovations between 1930 and 1990, more than 60% of products and 90% of the processes were based on catalysis.

Pollution remediation and new catalytic processing technology designed to prevent pollution formation are rapidly becoming of enormous and in some instances of dominant importance. Major environmental benefits are provided by catalytic desulfurization of fuels, by manufacture of pollution-lowering oxygenate fuels, and by catalytic converters to reduce combustion emissions from automobiles. Catalytic converters, first introduced in the U.S. in 1974, have cut auto exhaust pollutants by 95% with important health benefits. Selective catalytic reduction is being used to reduce emissions of oxides of nitrogen from electrical generation plants in Europe and Japan.

The unusual concept of a chemical agent which can control the rate and selectivity of chemical reactions, without itself being consumed, has long captured the imagination of scientists and industrialists alike. Over a dozen Nobel prizes have been awarded for catalytic inventions, many of them energy-related. A catalyst may be thought of as a mountain guide, who joins a group of people (molecules) and directs them to a selected valley over a favorable mountain pass (low activation energy pathway) known to the guide, who returns unchanged to guide additional groups. The scientific knowledge of how this is accomplished has advanced greatly, particularly elucidation of the secrets of the structure of those rare, unique "active sites" in catalysts which typically have surface areas of several football fields per pound.

As pointed out by the National Academy of Science report *Opportunities in Chemistry,* an array of powerful instruments have now made it possible to "see" molecules as they react on catalytic surfaces. This capability and related knowledge of reaction mechanisms now provides great promise for preparation of rationally designed catalysts with purposeful high steric specificity and reactivity.

CATALYSTS FOR THE FUTURE

The main thrust of this report is the future, that is, new directions and concepts leading to catalytic discoveries for energy applications. Interwoven in the fabric of our future energy pattern are the warp threads of new energy needs and the interlacing research threads which create the technology to meet these needs. Fortunately, there are clear foreseeable needs: for synthetic energy fuels from abundant gas, coal, and biomass; for more efficient production of strategic chemicals; and for environmental control and pollution abatement. It is not our task to predict the future but to provide the technology to enable it to happen.

As the energy scenario continues to unfold, it will be recalled that world oil prices were $40/barrel in the 1970s and expected to increase, but now are about $20/barrel. Current low prices are expected to rise slowly. Natural gas is beginning to displace oil as the resource of choice in the near term, although coal remains the more abundant fossil resource. Almost 90% of U.S. fossil fuel reserves are coal.

The need for alternative or synthetic fuels has long been recognized. Instructive examples of alternative fuel manufacture and use can be observed in South Africa, Brazil, and New Zealand. The use of U.S. developed ZSM 5 zeolite catalyst to convert methanol, made from off-shore gas, to high octane gasoline now supplies one-third of New Zealand's total liquid fuel demand and is a key to increasing that country's energy self-sufficiency.

In the U.S., there is ongoing informative experience in manufacture and public acceptance of:

- Gasohol containing 10% ethanol made from biomass
- Gasoline blends containing MTBE (methyl tertiary butyl ether) and industrially reformulated gasoline containing oxygenates (ethers and alcohols)
- Test marketing of M-85 fuel which contains 85% methyl alcohol
- Testing of flexible fuel vehicles capable of operating on any gasoline-alcohol blend.

Technically, catalysts can be used to transform gas, biomass, or coal into synthetic fuels that can provide superior engine performance, both for transportation and for generation of electricity. At present, the main barrier to synthetic fuels is their higher cost relative to fuels from petroleum at today's price.

This report describes major opportunities to improve the economics of conversion of gas, biomass, and coal into low-pollution fuel, such as oxygenates or very clean hydrocarbon fuels by developing new catalysts and processes having higher energy efficiencies and lower investment costs (a key issue). The environmental benefits to be derived from utilizing these cleaner fuels further improves their economics.

The most influential recent societal action concerning energy is embodied in the 1990 Clean Air Act Amendments (CAAA). Since 1992, gasoline in 44 cities must contain 2.7% oxygen in winter months and by 1995 in certain cities must contain 2% oxygen all year. The electric utilities are most affected by reduction of SO_2 and NO_x required to meet acid rain concerns. The CAAA requires the reduction of SO_2 to half the 1980 levels and by the year 2000 requires a permanent reduction cap.

Many believe that of all possible options, new catalytic processes holds the greatest promise for increasing the efficiency and environmental benefits of energy related processes. The tempo of technical growth has quickened for high performance and highly functionalized materials - preeminent catalyst characteristics. With global competition on the rise, tapping the potential of advanced catalytic technology represents an opportunity to strengthen the market position of U.S. industries. However, in sharp contrast, in the past decade industrial catalytic research has greatly decreased, particularly research for synthetic fuels. The drastic reduction of oil prices led to the conclusion that synthetic fuel research is too long-term for industry.

REPORT FINDINGS

Several noteworthy findings emerged in compiling this report:

- *It is expected that scientific advances will enable the rational design of catalysts tailored for highly selective and energy efficient operation.*
- *There are great opportunities for energy and economic savings by novel kinetic and engineering applications. One example could be integration of catalysis and separation by fabrication and utilization of catalyst/membrane combinations.*
- *Recent research has uncovered promising new opportunities for clean hydrocarbon and oxygenate fuels from natural gas, biomass, and coal, and for co-production of electricity and liquid fuels.*
- *The application of catalysis can bring both environmental and efficiency benefits to fuel combustion technology.*
- *There is a growing need for cheaper manufacture of hydrogen required for production of clean fuels and chemicals.*
- *Carbon dioxide remediation by catalysis may become of future concern.*
- *In large part because of increased environmental concerns, research recommendations presented here do not assign high priority to direct coal liquefaction in contrast to the 1989 Coal Liquefaction Research Needs Assessment Report DOE/ER-0400. It is recognized that with improved catalysts direct coal liquefaction could be successful for manufacture of liquid fuels from coal.*

SUMMARY OF RESEARCH RECOMMENDATIONS

Overview:

The pace of catalytic research has quickened as new scientific and engineering tools have revealed a greater understanding of how catalysts perform and have generated new ideas for synthesis and applications of new, more selective catalysts.

Research recommendations are based not only on potential economic and environmental benefits, but also on an in-depth evaluation of the recent technical advances described in this report, on research suggestions and opinions of experts consulted during the course of this study, and on the judgment of the panel about the likelihood of success.

Recommended goals are defined within three major research thrusts:

I. **CATALYTIC SCIENCE** — Establish a scientific knowledge of essential catalyst chemical structure/catalytic performance relationships and work toward developing the ability to predict the catalytic capabilities of emerging new materials.

II. **ENVIRONMENTAL PROTECTION BY CATALYSIS** — Prevent pollution by developing economical processes that are free of pollutant formation. Diminish pollution by achieving higher selectivity in fuels and chemicals manufacture and by catalytic processes for the removal of pollutants.

III. **INDUSTRIAL CATALYTIC APPLICATIONS** — Develop energy-saving, environmentally-benign processes for manufacture of liquid fuels and commodity chemicals based on domestic natural gas, biomass, and coal. Emphasize research on synthesis gas ($CO + H_2$) production and conversion, oxidation catalysis, new methods of hydrogen production, and the synthesis of novel materials for catalytic applications.

These thrusts are regarded as elements of a single program, essentially linked as indicated below.

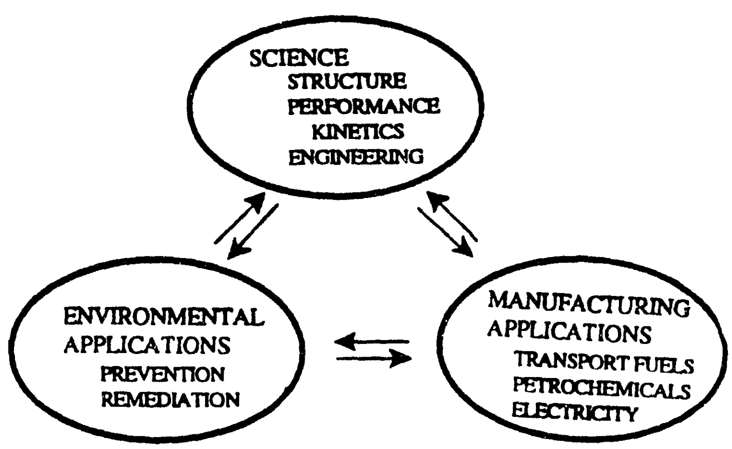

Figure 1. Interactive Research Linkages

Manufacturing and environmental applications depend critically on science contributions. More energy efficient manufacturing can lessen pollutant formation. Feedback from applications findings can assist, sometimes unexpectedly, in scientific advances.

There is a high level of confidence that the recommended research can provide catalytic technology which will achieve major improvements in energy applications.

A reasonable and expected goal is improvements in economics of clean fuel manufacture by 10% to 30%, see Chapter 9 (important in moving toward energy independence) and the development of new technology for pollution reduction by 90% or more.

The following discussion summarizes the panel's analysis of research motivations and its research needs recommendations. More detailed discussions of research status and new concepts are presented in appropriate report chapters.

I. SCIENCE OF CATALYSIS

Research Motivations

The goal is to provide the design basis for highly specific catalysts. Of particular interest are catalysts for synthesis gas reactions, for oxidation reactions, for NO_x abatement, and for highly active and environmentally harmless solid acid and base catalysts.

Catalyst Characterization - Structure/Chemical Functionality

- Identify catalytic sites and understand their interactions with promoters and supports, particularly in the steady-state of catalytic reactions in the presence of reactants and products under the conditions of pressure and temperature of commercial reactors.

- Develop new photon-based, surface science spectroscopies applicable to surfaces at high coverage under dynamic reaction conditions and develop probes that can determine surface catalyst structures under actual reaction conditions, a regime that is as yet largely inaccessible to present spectroscopic techniques.

Structure/Performance Relationships

- Establish fundamental knowledge, at the molecular level, of the relationship between catalytic performance and catalyst structure — particularly with insight into the dynamic operations of actual working catalysts.

Catalyst Design/Predictive Science
▸ Use modern materials science techniques to design and synthesize highly structured catalysts having more accurately defined sites, which have high activity and specificity. Investigate particularly catalysts which have a) uniform sites, b) kinetically isolated sites, c) synergistically coupled multifunctionality and, d) emerging novel materials. ▸ Design and fabricate new materials capable of both catalysis and separation. This requires a combination of the sciences of inorganic, organometallic, and computational chemistry together with chemical reaction engineering, surface analysis, and material science.

Engineering Science
▸ Conduct micro and non-linear kinetic studies to transfer information into computer models of advanced reaction sequences and to describe reactions of multicomponent mixtures. Model complex reaction networks in complex reactor systems. ▸ Develop advanced models of fluid mechanics and catalytic reactors, particularly for trickle bed and monolithic reactors.

II. CATALYSTS FOR CONTROL OF EXHAUST EMISSIONS

Research Motivations

There is a need to develop new science and technology for catalytic abatement of the formation of pollutants: CO, NO_x, SO_x, VOCs (volatile organic compounds), and ozone, in energy conversion processes.

Research Needs

Chemistry
▸ Establish an understanding of the chemistry of pollutant formation and remediation. ▸ Develop catalytic sensors for pollutants measurements.

Remediation

- Develop catalytic technology that abates ozone pollution
  - by removing NO_x and VOCs which are responsible for ozone formation.
- Decrease NO_x pollution
  - by developing catalysts which catalytically decompose it to nitrogen and oxygen at practical rates.
  - by providing improved selective reduction of NO_x, particularly by methane, for application with more efficient, lean-burn engines.

Prevention

- Seek more energy efficient processes - a basic method of decreasing pollution formation as well as achieving energy conservation.
- Decrease NO_x formation by developing technology which prevents NO_x formation
  - Catalytic combustion at lower temperatures where NO_x formation does not occur
  - Explore the application of catalysis in engines capable of removing NO_x under lean-burn conditions with the objective of increasing fuel efficiency and environmental protection.
- Seek catalytic chemistry and processes which lessen CO_2 emissions
  - by segregation and utilization of CO_2
  - by utilization of biomass.
- Improve catalysts and processes for the manufacture of low pollution fuels.
- Improve catalytic processes used in petroleum refining and petrochemicals manufacture to reduce pollution. Catalysts which themselves are not environmentally hazardous during disposal are desired.

III. INDUSTRIAL CATALYTIC APPLICATIONS

Research Motivations

The main barrier to production of liquid synthetic fuels from coal, biomass, or gas is their cost relative to that of gasoline made from petroleum at present day prices. There is a major opportunity to improve the economics of conversion of gas, biomass, and coal into low-pollution fuels, oxygenates, or very clean hydrocarbon fuels by developing new catalysts and processes having higher energy efficiencies and lower plant investment costs (a key issue). Also, economics are improved when environmental benefits are taken into consideration. An added benefit is that these fuels can offer superior engine performance for transportation and for generation of electricity.

Coproduction of electricity and fuels also presents possible economic advantages. Processes for manufacture of energy-intensive chemicals which operate at higher energy efficiency are a prime research target.

Recommendations stress favorable opportunities for advances in catalytic processes that involve synthesis of fuels and chemicals via incorporation of CO (synthesis gas catalysis) and, also, those involving catalytic oxidations.

Research Needs - Performance Maintenance; Process Scale-up

- Loss of activity and selectivity during catalytic operation is a universal, serious problem. Research is needed to identify the chemistry of deactivation and to develop reliable accelerated-aging testing techniques.

- Establish accurate correlations between laboratory and commercial-sized reactors to enable accurate scale-up and to obviate pilot plant experimentation.

Research Needs — Transportation Fuels

- Design more selective catalysts and processes for the manufacture of:
  - fuel oxygenates — methanol, isobutanol, ethers.
  - very clean hydrocarbon fuels that contain a minimum of sulfur, nitrogen, and aromatics.

Specific research progress and opportunities are discussed in the detailed report. A modest improvement in a near-commercial process could serve the important function of crossing the threshold in making it commercially viable.

- Design improved catalysts for energy processing based on zeolites, metal sulfides, and metals, as well as new catalytic materials such as carbides and solid acids.

- Take the lead in developing technology for catalyzed combustion systems, engines, and turbines aimed at higher energy efficiency and reduced pollution.

Research Needs - Transportation Fuels (continued)

- Develop catalyzed hardware — that is, catalysts bonded to heat-transfer surfaces for improved heat management.
- Seek new catalysts for non-conventional reactor systems including slurry operation and membrane techniques.
- Conduct exploratory research for efficient direct partial oxidation of methane to syngas and by oxidative coupling to liquid fuels or liquid fuels precursors.
- Investigate catalysts and process systems for integral gasification/synthesis — simultaneous production of syngas from carbonaceous materials, by catalytic reaction with steam, combined with catalytic synthesis of fuels, such as methane or methanol.
- Conduct research on catalysts and processes for converting biomass to liquid transportation fuels. Build on methane and CO chemistry being developed for other purposes and on technology for gasification of coal.
- Seek new catalysts and processes for utilization of CO_2.

Research Needs — Chemicals

- Provide catalysts that promote the selective oxidation of hydrocarbons, especially alkanes, with air or oxygen. Highest priority is recommended for the synthesis, characterization, and catalytic evaluation of catalysts for the selective oxidation of hydrocarbons. In particular, greater understanding is required of the catalytic functions that lead to activation of molecular oxygen and of hydrocarbons.
- Pursue exploratory catalytic research for CO chemistry, particularly for heterogeneous catalysts, that promote reactions of carbon monoxide, especially the relatively undeveloped oxidative carboxylation reactions.
- Investigate new catalytic approaches for the production of hydrogen without coproduction of CO_2.

Research Needs — Generation of Electricity

- Investigate coproduction of fuels and electricity by integrated gasification/combined cycle, developing improved catalysts and process integration for the synthesis of methanol, ethers, hydrogen, or ammonia. Needed are catalysts that are less sensitive to H_2S or COS impurities in syngas and catalysts that can operate at lower than usual temperatures and pressures.
- Develop an endothermic process for production of a fuel gas from methanol/ethers that, by utilizing waste heat, increases fuel heating value.
- Seek processes for CO_2 segregation and catalytic conversion to useful fuels.
- Carry out research on gasification of biomass, alone or with coal, to prepare a clean fuel for generation of electricity.

SUMMARY OF REPORT CHAPTERS 1 — 9

Chapter 1. CATALYSIS OVERVIEW

The main thrust of this study is the future, that is, new directions leading to new discoveries for higher efficiency in development of advanced heterogeneous catalyst technology.

The catalyst market in the U.S. is $1.9 billion. The value of fuels and chemicals derived from catalysis in 1990 was $891 billion or 17% of the GNP. Employment in the petroleum industry was 750,000. In the last decade, catalysis has also become a key factor for the protection of the environment. Here, part of the challenge is to reduce pollutants emitted, and another is to help produce friendlier fuels and chemicals.

The amazingly wide range of chemical transformations in petroleum refining is based mainly on two types of catalytic transformations: hydro-dehydrogenation and acidic hydrocarbon catalysis. The first type controls the distribution of hydrogen among hydrocarbon products while the second type, the acid catalyst, controls the carbon number and boiling range, the skeletal structure as well as the types of hydrocarbons produced. Today's advanced catalysts combine these two catalytic functions with highly specific catalyst structure features, called shape selectivity, which control the size and other chemical features of molecules produced.

Catalysis is an interdisciplinary science and technology. The catalytic reactions take place in the solid-gas or solid-liquid interface. Therefore, the study of catalytic phenomena involves the solid matrix, the surface of solids, gas and surface diffusion, reaction kinetics, and process engineering. At present, heterogeneous catalysis is rapidly moving from a mainly experimentdriven endeavor to a more scientific discipline of enormous potential. It is envisioned that progress in catalyst characterization and theoretical modeling should facilitate an operative linkage between catalyst conception → synthesis → characterization → testing → modeling. This should provide an effective feedback and improve the efficiency in developing advanced catalysis. To be on the leading edge of this development, to improve the predictive power of the knowledge base in heterogeneous catalysis would be an important advantage.

Major challenges for new and more flexible catalysis technology come from new and changing feedstocks, markets, and environmental considerations. The increasing trend toward heavier feedstocks poses great challenges.

Natural gas plays a pivotal role as an energy source. There is the need to expand the role of methane as feedstock for motor fuels. At present there is no industrial technology available for the direct conversion of methane in a single step to quality motor fuels. Efficient processes for the conversion of unsaturated hydrocarbons to oxygenates and liquid hydrocarbons are well developed, but this is not the case for paraffins.

At present, indirect liquefaction of coal and biomass deserves higher attention because of the flexibility it provides for choice of fuel, because hydrocarbon or oxygenated fuels can be produced, and because very clean fuels can be produced. But syngas production is expensive, particularly because of the high cost of plant equipment.

An important objective is to increase chemical efficiency in catalytic processes used for production of chemical feedstocks. This is critical in order to maintain leadership worldwide, and is strategically important in the U.S.'s positive trade balance in chemicals.

Great advances have been made in catalysis in the energy industry. However, new approaches to advanced catalysis will be necessary to meet future environmental and energy supply challenges.

In the last four decades the largest impact on heterogeneous catalysis has been the introduction of new catalytic materials, particularly zeolites and dual function catalysts. Highly selective, uniform catalytic sites combined with shape selectivity offer new opportunities for the direct conversion of saturated hydrocarbons to oxygenates and liquid hydrocarbons. There is encouragement that the use of enzyme-like catalytic molecules encapsulated in solids, such as zeolites, could lead to new catalysts capable of very high activity and selectivity performance.

The ultimate purpose of gaining detailed knowledge about catalytic sites and reaction intermediates is to make catalysis a predictive science, and thereby achieve a higher level of efficiency in development of new advanced processes.

In the discipline of catalysis, most important is the continuously evolving focus towards more quantitative scientific understanding, leading to a point when theory can play a role as a more predictive tool in an operational linkage between the conceptual planning of catalysis synthesis and operation.

Chapter 2. CATALYST PREPARATION: DESIGN AND SYNTHESIS

The desire for new energy efficient and low-cost, zero-waste solutions to chemical process technologies is fueling the drive for new research in catalysis science and technology. The science of catalysis has overtaken the technology of catalysis, and future advances in technology are as likely to result from first principles application as they are from pure empiricism and discovery.

This trend brings with it the need for catalysis preparation to become a science in its own right, thus it is appropriate to consider catalysis materials preparation as a problem in supramolecular synthesis. In this way catalysts can be viewed as nano-scale reactors with specifiable structures and functions.

As catalysis synthesis becomes more controlled and scientific, hence predictable and reproducible, it is natural to consider the problem to be one of materials design at the nano-scale. Along with this view comes the need for modeling in order to guide design, to streamline experimentation, and to accelerate innovation. Computation at all levels will be required to bring *ab initio* design to its full fruition in catalysis.

Surface and materials science have provided valuable new tools for the analysis of catalytic steps and for the characterization of interfacial systems. With the advances that have been made in the fabrication of nano-scale devices with materials synthesis techniques, the field is poised to make major strides in bringing these new approaches into catalysis. In this way surface and materials methodologies can provide new routes to the synthesis of advanced structures and more complex model systems.

More specifically, it is recommended that over the next twenty years research thrusts be aimed at new concepts and effects in catalysis, especially:

- Combined catalysis and separation
- Shape selectivity and molecular recognition
- Site isolation
- Multifunctionality
- New solid acids and bases
- Numeric and heuristic computing for design

These topics are at the forefront of current catalytic science and technology and hold the promise for major advancements in the next decade.

Beyond these topics, integration of the enabling sciences of inorganic and organometallic chemistries, chemical reaction engineering and computation, and materials and surface science must be fully implemented into the science of heterogeneous catalysis.

Chapter 3. CATALYST CHARACTERIZATION: STRUCTURE/FUNCTION

The interpretation of the function of a heterogeneous catalyst in terms of structure implies characterization on an atomic scale, that is, the complete description of the catalytic sites involved in a given reaction. This chapter reviews some ways in which catalytic sites are characterized, using chemical and physical methods as background to formulate future needs. The dynamic nature of catalysts in action suggests the need to develop various time-resolved surface spectroscopies. This, and other attributes of desired surface spectroscopies are described. A brief statement of the current state of theoretical characterization of catalysts is given. This leads to the following ten recommendations:

- There is a need to identify sites more precisely, both in the catalyst as prepared and in the steady-state of the catalytic reaction, *i.e.*, in the presence of reactants and products under conditions of temperature and pressure in the catalytic reaction of interest.

- As active sites often comprise more than one atom, the design of optimum catalysts requires a detailed knowledge of the ensemble size and of the chemical interaction of these atoms with their environment, including supports, promoters, chemical anchors, and catalyst poisons.

- Complete characterization of catalyst sites (and description of catalyst preparation) should include the complete chemistry of catalyst preparation.

- Whatever techniques we contemplate, making these techniques applicable under reaction conditions and developing time resolution will be important and will pose essential challenges which should be given our continued attention.

- Characterization of catalyst sites should always involve complementary physical (spectroscopic) and chemical (chemisorption and/or catalytic kinetics) techniques of characterization and use as wide a combination of physical characterization techniques on the same catalyst as may be practical.

- New theoretical approaches, which are atomically based and can treat site dynamics that accompany adsorption and catalytic turnover, need to be developed.

- The community needs to agree on standard analysis programs, methods for assessing uncertainty, and minimum standards for experimental data that are analyzed and published, *e.g.*, for X-ray absorption spectroscopy.

- New photon-based surface science spectroscopies are needed that can be applied to surfaces at high coverage and under reaction conditions. Needs include surface science improvements that will make application to nonmetals routine.

- We need new and improved element specific spectroscopies that can determine local surface structure in high area catalytic materials. As a specific example, we seek improved line shape and data analysis for solid state NMR are needed along with continued improvements in field strength and dynamic probes.

- Needed also are new surface analysis techniques that provide both symmetry/morphological and chemical composition.

Chapter 4. CATALYST PERFORMANCE TESTING

Performance testing of catalysts can be divided into three areas: 1) mechanical characteristics of catalysts such as crushing strength, disintegration in liquids, *etc.*; 2) physical characteristics of catalysts which relate to performance such as surface areas, pore size, pore volume, *etc.*; 3) simulation of commercial performance in laboratory reactors to determine activity, selectivity, and catalyst deactivation.

While this chapter discusses primarily items 1 and 3 above, all three areas need research and development to improve predictions of commercial catalyst performance and to reduce the time lag currently inherent in testing for catalyst life. The chapter emphasizes the importance of the appropriate choice of a test reactor and points out the difficulties of scaling up from a laboratory to a commercial size reactor. Differences caused by flow modes, radial and longitudinal gradients of concentration and of temperature both within and between catalyst particles need study to predict behavior from a laboratory reactor to a commercial reactor. Freedom from transport disguises is an essential criterion for effective catalyst testing in small reactors. Heat transfer coefficients cannot be reproduced in laboratory scale reactors.

Catalyst aging is difficult to determine on a small scale except by operation over long periods of time. Simulated aging tests have been devised for specific applications, but even these are of limited use. Development of meaningful aging tests would greatly reduce time and cost of commercializing new catalysts.

Chemical characterization of catalysts by model reactions can throw much light on catalytic mechanisms and permit deductions on the performance of catalysts. This type of testing has not been favored recently, but can be very meaningful and should be further developed.

While spectrographic and surface science techniques to determine the structural and chemical properties of catalyst surfaces have led to a better understanding of catalysts and their performance, they are limited because of the need to extrapolate from the conditions of the spectroscopic study to the conditions of temperature, pressure, and the presence of reactants and products in the catalytic reaction. If reliable information were available, deductions to catalyst performance should be possible and would also lead to the ability to design catalysts for specific reactions.

Recommendations

- Research on correlations between laboratory and commercial size reactors to enable faster scaleup time and possibly avoid pilot plant construction.
- Research on accelerated catalyst aging techniques to reduce performance testing time.
- Research on surface properties and diffusional characteristics of catalysts at operating conditions and in the presence of reactants and products to permit reductions to rapid scaleup.
- New analytical techniques will have to be developed to ensure performance testing to meet increasingly sever specifications.

Chapter 5. REACTION KINETICS/REACTOR DESIGN

Reaction kinetics is an important tool for industry. It provides the basis for reactor design, and it may contribute to the understanding of reaction mechanisms, and thereby spark ideas to formulate new catalysts and to explore new reaction paths. Kinetic and reaction engineering was developed almost to perfection 25 years ago, but applied kinetics was still based on a simplified empirical approach.

The input from surface science to kinetics has made it meaningful to establish a more complex reaction sequence and to solve the steady state rate equation with modern computer techniques. Micro-kinetic analysis combines spectroscopic, kinetic, and surface chemistry data to provide a basis for new catalytic cycles and new catalyst systems to be studied. It requires a multi-disciplinary effort, breaking the barriers between catalyst research groups and highly specialized surface scientists.

Reaction engineering faces a new challenge dictated by environmental requirements currently affecting the process industry, which in turn is pushing for higher conversion and better selectivities to minimize losses and the release of pollutants. By combining catalysis with separation it is possible to push the chemical equilibrium by removing one of the products. As an example, membrane catalysis has the potential to significantly improve important reactions, such as steam reforming of methane, and dehydrogenation for olefins and styrene.

There is a need for better modeling of complex reactors (trickle bed for hydrocracking, catalytic combustion, *etc.*). This requires application of fluid mechanics to catalytic reactors, and a better understanding of coupled thermal and catalytic reactions.

It is important that reactor studies and innovative flowsheet analysis is included in the planning of fundamental studies of new processes in order to better identify constraints and opportunities for breakthroughs. Again, this calls for collaboration across conventional barriers. The continuous two-way interaction between science and engineering is essential for industrial progress.

Summary of Research Needs

Reaction Kinetics

- Micro-kinetic studies
  - Further development of methods to transfer information from a variety of techniques into computer models of advanced reaction sequences
  - Encouragement of "consolidated micro-kinetic synthesis", including the work of highly specialized groups

Reactor Design

- Separation catalysts
  - Materials development: stable Pd-membranes, ceramic membranes, zeolite membranes
  - New reactor concepts: low temperature steam reforming, dehydrogenation of alkanes and ethyl benzene
- Catalyzed hardware
  - Better temperature control
- Modeling
  - Fluid mechanics and catalytic reactors
  - Simultaneous gas phase and catalytic reactors
  - Complex reaction networks in complex reactor systems
- Construction materials
  - Metal dusting corrosion in CO-rich gases
- Improved flowsheet analysis

Chapter 6. CATALYSIS FOR INDUSTRIAL CHEMICALS

The chemical industry, even excluding petroleum refining, is one of the largest industries in the U.S. with annual sales of about $140 billion. It employs about 1.2 million workers, mostly with high skill levels. The largest component, based on catalytic processes, is the production of commodity chemicals and polymer intermediates. Of the 22 largest-scale organic chemicals ($37 billion annual sales), 19 are made primarily by catalytic processes based on petroleum and natural gas.

In a survey of the best opportunities to conserve energy and fossil feedstocks, the greatest potential appears to lie in two areas:

- Improved catalytic technology to oxidize hydrocarbons, particularly alkanes, to functional organic chemicals such as olefins, alcohols, and carboxylic acids. Improvements in yields in these reactions translate into major savings in feedstocks and in fuel for process energy. These advantages, in turn, lead to environmental benefits such as reduced emissions of CO_2 (a "greenhouse gas") and organic by-products that can pollute the air or water. There is great opportunity for innovation in oxidative processes to introduce fluorine or amine functions into hydrocarbon molecules (*e.g.*, $CH_4 + HF + O_2 \rightarrow$ vinyl fluoride). The goal would be the elimination of organochlorine intermediates, which are potential depleters of stratospheric ozone as well as precursors of environmental toxins.

  Development of heterogeneous catalysts for processes based on synthesis gas (CO/H_2); a versatile intermediate available from abundant or renewable feedstocks such as coal, biomass, and current feedstocks. Most current CO-based chemistry, aside from methanol production, utilizes soluble catalysts. Heterogeneous catalysts would offer advantages, both in process efficiency (easy separation of products from catalysts) and in potential new process technology, for making major organic chemicals, such as ethylene glycol, vinyl acetate, and methyl methacrylate from synthesis gas. In addition, there is a major opportunity for innovative processes based on oxidative reactions of CO to produce chemicals such as alkyl carbonates, oxalates, and acrylates.

  The survey also examined potential energy savings by reducing the severity of reaction conditions for major catalytic processes. Reduced fuel consumption also would reduce CO_2 emissions. In surveying possible energy and feedstock savings for manufacture of the top nine polymers (annual sales $25 billion), the greatest potential seems to lie in improved processes for the manufacture of monomers. Many of these improvements employ the two approaches outlined above.

Based on the above findings, support of catalyst research is recommended in two major areas:

- **Selective oxidation of hydrocarbons, especially alkanes, with air or oxygen. We recommend that highest priority be given to the synthesis, characterization, and catalytic evaluation of catalysts for the selective oxidation of hydrocarbons. In particular, greater understanding is required of the catalytic functions that lead to activation of molecular oxygen and of hydrocarbons.** The goal is selective conversion of paraffins to specific products, such as olefins, alcohols, or carboxylic acids. For example, catalysts would be sought for selective oxidation of methane to methanol or formaldehyde, and of isobutane to *tertiary*-butyl alcohol, isobutylene, or methacrylic acid. In order to achieve the desired selective catalysts, we need much greater understanding as to how metal oxides function in oxidative catalysis. Much is to be learned from oxidative processes catalyzed by enzymes and by soluble catalysts.

- **Heterogeneous catalysis of CO chemistry. Exploration of heterogeneous catalysts for reaction of carbon monoxide is needed, especially the relatively undeveloped oxidative carboxylation reactions.** Most current processes use soluble catalysts, but heterogeneous catalysts open the way to new syngas-based processes and offer improvements in process efficiency. Research in this area can build on new developments for hydrocarbon oxidations, both in palladium-based soluble catalysts and in metal oxide-based catalysts.

Chapter 7. CATALYSIS FOR ELECTRICITY APPLICATIONS

About one-third of our carbonaceous energy fuels — coal, gas, petroleum, and biomass — is consumed in the generation of electricity, during which about two-thirds of their heating values are lost. New environmental regulations, based on the 1990 Clean Air Act Amendments, are causing profound technological and economic changes. By the year 2000, annual SO_2 emissions must be greatly reduced and placed under a permanent emissions cap. The costs of acid rain control are estimated to approach $7 billion annually once fully implemented in the year 2000.

Research objectives are to achieve pollution abatement, higher energy efficiency, and economy in electricity generation.

There is a growing interest in the manufacture of a clean fuel gas from coal, biomass, and petroleum residua for the generation of electricity, using Integral Gasification Combined Cycle systems. The IGCC system has important environmental and energy efficiency advantages, and several demonstration plants are being tested, cofunded by DOE and industry.

It is proposed that it could be advantageous to develop an IGCC plant to manufacture purified $CO + H_2$, which would utilize part of the fuel gas to generate electricity and part to synthesize chemicals like methanol, ammonia, or hydrogen.

In the synthesis reaction, there are several opportunities to incorporate improved technologies — slurry catalysis, once-through synthesis, coproduction of methanol and dimethyl ether.

There is a long-range target of improving the gasification of solid fuels to synthesis gas by low-temperature catalytic gasification, possibly integrated with fuel synthesis (methane or methanol).

Also, recent results on direct synthesis gas production by direct partial combustion of methane have been encouraging.

There is an opportunity for improved energy efficiency in the catalytic Chemically Recuperated Gas Turbine system.

There is concern that the increasing presence of CO_2 in the atmosphere will increase the "greenhouse effect". Technology for the segregation and conversion of CO_2 to fuels is known - for example, catalytic reaction of CO_2 with hydrogen to manufacture methanol fuel. However, it is estimated that this would increase the cost of electricity by a factor of about two for the retrofit of current coal-fired power plants. If in the future major diminution of CO_2 emissions does become required, research on catalytic conversion of CO_2 to fuels offers important opportunities for economic improvements. A primary requirement is that the manufacture of hydrogen for such processes does not generate more CO_2 than is consumed in the overall process.

Gasification of a blend of biomass and coal is proposed to produce CO_2-neutral transportation fuel in an IGCC facility. Biomass is formed by photosynthetic reactions, involving *removal* of CO_2 from the atmosphere. It is possible to produce both atmospherically neutral transportation fuel and electricity without the addition of CO_2 to the atmosphere.

Chapter 8. CATALYSIS FOR CONTROL OF EXHAUST EMISSIONS

Catalysts for pollution abatement represents significant technical challenges for the future. Many aspects where catalysis can positively impact environmental consequences of energy processes are discussed in other chapters of this report. This chapter discusses catalysis for the control of stationary and mobile emission sources associated with combustion processes. Abatement of NO_x emissions is of special concern because of its role in the formation of harmful ozone in the troposphere by secondary photochemical and radical reactions. Countermeasures are 1) catalytic combustion at low temperatures to prevent NO_x formation, 2) catalytic reduction of NO_x in exhaust gases, 3) direct catalytic decomposition of NO_x to harmless N_2 and O_2. Effective catalysts for NO_x abatement remains an important goal for pollution remediation.

Catalytic combustion at low temperature is promising for prevention of NO_x formation when used in conjunction with gas turbine operating.

Automobile pollution control to meet present mandated U.S. standards is provided by control of fuel composition, engine design and operation, and by catalytic converters located in the exhaust system. Research is underway to meet more stringent future standards. Research is recommended to explore the application of catalysis in engines capable of removing NO_x under lean-burn conditions with the objective of both increasing fuel efficiency and environmental protection.

Chapter 9. CATALYSTS FOR LIQUID TRANSPORTATION FUELS FROM PETROLEUM, COAL, RESIDUAL OIL, AND BIOMASS

A cheap and reliable liquid fuel supply has been a fundamental factor in the economy of the U.S., with increasing importance since the close of World War I. However, economic, environmental, and strategic concerns are now combining to drive the liquid fuel supply to more stringent requirements. These include lower aromatics, less sulfur, lower volatility, and more oxygen. Heterogeneous catalysis will be called upon, as it has been in the past, to meet the demands of these more stringent environmental requirements.

This chapter also recognizes the emergence of the trend away from heavy feedstocks, such as coal, tars, and residual oils as a source of liquid fuels. Environmental factors and the flat projections of petroleum pricing threaten to drive this trend into the next century, although projections of this type have been unreliable. Nevertheless, changes in the world order appear to have permanently changed the petroleum supply picture. Moreover, there is a clear trend towards the use of natural gas and methane, either directly or as an alternate source, for liquid transportation fuels. This will require new catalysts and new processes for the cleaning and conversion of CH_4 and natural gases to fuels and chemical fuel additives.

Environmental pressures may eventually lead to the world-wide adoption of a "carbon tax" on CO_2 emitting fuels. Anticipation of this event further drives the trend away from heavy feedstocks to hydrogen-rich feedstocks such as methane and natural gas. Ultimately, CO_2 neutral feedstocks such as biomass or pure hydrogen may become more attractive for the production of transportation fuels. For this scenario, new catalysts and catalytic processes for the production of hydrogen will be required, including better hydrogen utilization and new catalytic routes to hydrogen which do not yield CO_2 as a by-product.

Better understanding of the physical, chemical, and structural causes of catalyst selectivity will be required and new catalyst materials, that are likely to be produced by unconventional methods, will be needed. Among the established materials, zeolites, sulfides, and metal catalysts will continue to play an important role in achieving the above objectives.

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