

Abstracts

III
International Conference
on
Catalysis in Membrane Reactors

MASTER

September 8-10, 1998
Copenhagen, Denmark

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III International Conference on Catalysis in Membrane Reactors

The III International Conference on Catalysis in Membrane Reactors, Copenhagen, Denmark, is a continuation of the previous conferences held in Villeurbanne 1994 and Moscow 1996 and will deal with the rapid developments taking place within membranes with emphasis on membrane catalysis.

The conference is organised by the Danish Catalytic Society under the Danish Society for Chemical Engineering.

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SCIENTIFIC PROGRAMME - ICCMR '98

Oral Presentations

Tuesday, 8 September 1998

8.00: *Registration*

9.00: *Welcome: P.E. Højlund Nielsen (Denmark)*

9.05: *Plenary*

Membrane Reactor Application to Hydrogen Production
Professor E. Kikuchi, Waseda University, Tokyo (Japan)

PL1

SESSION 1 :

Hydrogen and Synthesis Gas Production

Chairmen: E. Kikuchi and R. Bredesen

10.00: Membrane Performance: The Key Issue for Dehydrogenation
Reactions in a Catalytic Membrane Reactor
H. Weyten, J. Luyten, K. Keizer, L. Willems, R. Leysen (Belgium)

O1

10.30: *Coffee Break*

10.45: The effect of Hydrocarbon Removal on the Performance of
a Membrane Reactor for Methane Steam Reforming
K. Hou, R. Hughes (U.K.)

O2

11.15: Catalytic Dehydrogenation of Hydrocarbons in Palladium
Composite Membrane Reactors
R. Quicker, R. Dittmeyer (Germany)

O3

11.45: Methane Partial Oxidation in a Fast Flow Non-Selective
Membrane Reactor
J. Yun, H. Hahm, M. Alibrando, E.E. Wolf (U.S.A.)

O4

12.15: *Lunch*

13.15: *Plenary*

Biocatalysis in Membrane Reactors
Professor, Dr. C. Wandrey (Germany)

PL2

14.15: Theoretical and Experimental Analysis of Methane Steam
Reforming in a Membrane Reactor
G.S. Madia, G. Barbieri, E. Drioli

O5

14.45: Oxidation of Iso-butane over Supported Noble Metal Catalysts in a Palladium Membrane Reactor **06**
T.M. Raybold, M.C. Huff (U.S.A.)

15.15: *Coffee Break*

15.30: Ultra Pure Hydrogen Production by Catalyst-Membrane Systems **O7**
V.M. Gryaznov (Russia)

16.00: Prospects and Problems of Dense Oxygen Permeable Ceramic Membranes **O8**
P.V. Hendriksen, P.H. Larsen, M. Mogensen, F.W. Poulsen (Denmark)

SESSION 2:

Fine Chemicals, Biological Membranes. Low Temperature Reactions

Chairmen: E. Drioli and G. Jonsson

10.00: Zeolite Containing Catalytic Membranes as Interphase Contractors **O9**
S. Wu, C. Bouchard, S. Kaliaguine

10.30: *Coffee Break*

10.45: Selective Hydrocarbon Oxidation using Liquids Phase Catalytic Membrane Reactors **O10**
G. Langhendries, G.V. Baron, I.F.J. Vankelecom, R.F. Parton, P.A. Jacobs (Belgium)

11.15: Macroporous Catalytic Membranes for Three-Phase Processes: Principles and Applications **O11**
O.M. Ilinitch, F.P. Cuperus, L.V. Nosova, E.N. Gribov (Russia, The Netherlands)

11.45: Dense Catalytic Membranes for Fine Chemical Synthesis **O12**
I.F.J. Vankelecom, K. Vercruysse, P. Neys, D. Tas, K.B.M. Janssen, P-P. Knops-Gerrits, R.F. Parton, P.A. Jacobs (Belgium)

12.15: *Lunch*

13.15: *Plenary* **PL2**
Biocatalysis in Membrane Reactors
Professor, Dr. C. Wandrey (Germany)

14.15: Photocatalytic Membrane Reactor for Removal of Chemicals and Bioaerosols from Indoor Air **O13**
W.A. Jacoby, P.C. Maness, D.M. Blake, E.J. Wolfrum (USA)

14.45: Influence of membrane Selectivity and Operation Conditions on the Performance of an Enzyme UF-Membrane Reactor System **O14**
G. Jonsson (Denmark)

15.15: *Coffee Break*

15.30: Development of a Polytrimethylsilylpropyne based Organophilic Membranes for Membrane Bioreactor Application **O15**
V.V. Volkov, A.G. Fadeev, Ya.A. Selinskaya, J. McMillan, S.S. Kelley (Russia, U.S.A.)

16.00: Molecular Size Recognition with Zeolite Membranes **O16**
M. Matsuka, A. Takahashi, T. Takahashi, K. Ueyama, N. Nishiyama (Japan)

17.00: *Poster Session - parallel with a light buffet meal*

Wednesday, 9 September 1998

SESSION 3:

EU-Sponsored Projects

Chairmen: J.A. Dalmon and J. Ross (France, Ireland)

- 9.00:** Introduction
J.-C. Toussaint (EU Commission)
- 9.20:** An Attractive Option for CO₂ Control in IGCC Systems:
Water Gas Shift with integrated H₂O/CO₂ Separation
(WHIHYS) Process. Phase 1: Proof of Principle **EU1**
Paul P.A.C. Pex (The Netherlands)
- 9.50:** Catalytic Membrane Reactors: Application to Fine
Chemicals Synthesis **EU2**
J.A. Dalmon (France).
- 10.20:** Membrane Reactor for cost Effective Environmental-Friendly
Hydrogen Production **EU3**
R. Bredeesen (Norway)
- 10.50:** *Coffee Break*
- 11.05:** Development of Inorganic Membrane Reactors for Oxidative De-
hydrogenation of Propane and Selective Oxidation of Propane **EU4**
J.C. Volta, C. Mirodatos (France)
- 11.25:** Development of Inorganic Membrane Reactors for Selective
Oxidation of Hydrocarbons to Oxygenates, in particular
n-Butane to Maleic Anhydride **EU5**
Jens Perregaard, P.E. Højlund Nielsen (Denmark)
- 11.45:** European Catalytic Membrane Network **EU6**
E. Drioli (Italy)
- 12.05:** *Lunch*
- 13.00:** *Plenary*
Membrane Catalysis for Liquid Applications **PL3**
J.-A. Dalmon (France)

SESSION 4 :

Selective Oxidation/Dehydrogenation

Chairmen: R. Hughes and J. Santamaria

- 13.45:** The Selective Oxidation of Iso-butene in a Membrane
Reactor with Separate Feed of Reactants **O17**
H. Neomagus, W. van Swaaij, G. Versteeg (The Netherlands)

- 14.15:** Use of Membrane Reactors for the Oxidation of Butane to Maleic Anhydride under high Butane Concentrations
R. Mallada, M. Menéndez, J. Santamaria (Spain) **O18**
- 14.45:** *Coffee Break*
- 15.00:** n-Butane Oxidation to Maleic Anhydride using Membrane Reactors
E. Xue, J. Ross (Ireland) **O19**
- 15.30:** Characteristics and Performance in the Oxidative Dehydrogenation of Propane of a Catalytically Active V-MFI Zeolite Membrane
A. Julbe, D. Farrusseng, C. Guizard, J.C. Jalibert, C. Mirodatos (France). **O20**
- 16.00:** Catalytic Membranes for Oxidation under Mild Conditions
V.M. Linkov, L.A. Belyakova, V. N. Belyakova (South Africa, Ukraine) **O21**
- 16.30:** Effects of Membrane Catalysts on the Activity and Selectivity of Hydrogenation Reactions
W.F. Maier, C. Lange, I. Tilgner, B. Tesche (Germany) **O22**
- 17.30:** *Tour to Louisiana (Museum of Modern Art)*
- 23.00:** *Back in the centre of Copenhagen*

Thursday 10 September 1998

- 8.45:** *Plenary*
Catalytic Membrane Reactors for Spontaneous
Synthesis Gas Production **PL4**
Dr A.F. Sammels (USA)

SESSION 5 :

Perspectives in Membrane Catalysis, incl. Modelling

Chairmen: J. Lercher and J. Rostrup-Nielsen

- 9.30:** Oxidative Coupling of Methane Using an Oxygen-Permeable
Dense Membrane Reactor **O23**
Y. Lu, A.G. Dixon, W.R. Moser, Y.H. Ma,
U. Balachandran. (U.S.A.)
- 10.00:** Electrochemical Coupling of Hydrocarbon Hydrogenation and
Water Electrolysis **O24**
N. Itoh, S. Hara, K. Sakaki, T. Tsuji, M. Hongo. (Japan)
- 10.30:** *Coffee Break*
- 10.45:** Mass Transfer in Gas-filled Porous Support Structures **O25**
J.H. Meldon, H.W. Deckman (USA)
- 11.15:** A Review on Hydrogen-selective Membranes -
Obtained Results and Future Perspectives **O26**
P.E. Hojlund Nielsen, K. Aasberg-Petersen,
S. Laegsgaard Jorgensen (Denmark)
- 11.45:** *Plenary*
Experimental and Theoretical Aspects of Membrane Catalysis **PL5**
Dr. T.T. Tsotsis (USA).

12.30: *Lunch*

SESSION 6 :

Preparation of Membranes and Membrane Reactors

Chairmen: R. Noble and A. Julbe

- 13.15:** Investigation of Sol-gel Methods for the Synthesis of VPO
Membrane Materials Adapted to the Partial Oxidation of n-Butane **O27**
D. Farrusseng, A. Julbe, D. Cot, C. Guizard, S. Mota, J.C. Volta,
J.A. Dalmon (France)
- 13.45:** Preparation and Test of Inorganic Modified Porous Polymer
Membranes in Gas Phase Catalysis **O28**
D. Fritsch, S. Ziegler, J. Theis. (Germany)

- 14.15:** Mordenite-ZSM5-Chabazite Hydrophilic Tubular Membranes
for the Separation of Gas-Phase Mixtures **O29**
E. Piera, M.A. Salomón, J. Coronas, M. Menéndez,
J. Santamaria. (Spain)
- 14.45:** *Coffee Break*
- 15.00:** Fabrication of Dense Pd Composite Membrane for
Hydrogen Separation **O30**
A. Li, W. Liang, R. Hughes (UK)
- 15.30:** Measurements of Surface Exchange Kinetics and Chemical
Diffusion in Dense Oxygen Selective Membranes **O31**
R. Bredesen, T. Norby. (Norway)
- 16.00:** Preparation and Characterisation of Nickel-modified
Porous Ceramic Discs **O32**
H.-B. Zhao, D.J. Draelants, G.V. Baron (Belgium)
- 16.30:** *Refreshments*
- 16.45:** *Round Table Discussion*
T.T. Tsotsis and Lercher
- 18.30:** *Conference Dinner*

POSTER SESSION

- P1:** An analysis of the Performance of Membrane Reactors for the Water Gas Shift Reaction using Gas Feed Mixtures
A. Criscuoli, A. Basile, E. Drioli, S. Tosti, V. Violante (Italy)
- P2:** Hydrogen Permeation Properties through Composite Membranes of Platinum supported on Porous Alumina
M. Kajiwara, N. Hatakeyama, S. Uemiya, T. Kojima, E.Kikuchi (Japan)
- P3:** Steam Reforming of Methane in Membrane Reactors: Comparison of Electroless-Plating and CVD Membranes and catalyst Packing Mode
E.Kikuchi, Y. Nemoto, M. Kajiwara, S. Uemiya, T. Kojima (Japan)
- P4:** Rh- and Ir-Dispersed Porous Alumina Membranes and their Hydrogen Permeation Properties
M. Kajiwara, D. Kurita, S. Uemiya, T. Kojima, E.Kikuchi (Japan)
- P5:** Dehydrogenation of Hydrocarbons by Catalyst Membrane Systems
N.V. Orekhova, M.M. Ermilova, V.M. Gryaznov (Russia)
- P6:** Palladium and Rhenium-Containing Membrane Catalysts of Hydrocarbon Dehydrogenation
M.M. Ermilova, N.V. Orekhova, V.M. Gryaznov, G.P. Karpacheva (Russia)
- P7:** Hydrogenation of Vegetable Oils in a Three-Phase Catalytic Membrane Reactor
J.W. Veldsink (Netherlands), O.M. Ilinitich (Russia), F.P. Cuperus (Netherlands)
- P8:** Ethanol Production in Membrane Distillation Bioreactor
A.W. Morawski, M. Gryta, M. Tomaszewska (Poland)
- P9:** Hydration of Alpha-Pinene over Zeolites and Activated Carbons Dispersed in Polymeric Membranes
J. Vital, A.M. Ramos, I.F. Silva, H. Valente (Portugal)
- P10:** Installation for Production of Ecologically Pure Hard Fats by New Membrane Catalysts
A.P. Mischenko, V.M. Gryaznov, N.R. Roschan, E.M. Chistov (Russia)
- P11:** Oxidative Dehydrogenation of Propane in an Inert Membrane Reactor
R. Ramos, M. Menendez, J. Santamaria (Spain)

- P12:** Vanadium-based Catalytic Membrane Reactors for the Oxidative Dehydrogenation of Propane
M.J. Alfonso, M. Menéndez, J. Santamaría (Spain)
- P13:** Oxygen Transfer and Reactivity of RuO₂-SiO₂ Catalytic Membranes
V. Pârvulescu, V.I. Pârvulesco, C. Niculae, G. Popescu (Romania)
- P14:** Catalyst State in a Fixed-Bed Membrane Reactor for the Selective Oxidation of n-Butane to Maleic Anhydride
S. Mota, M. Abon, J-C. Volta, J.A. Dalmon (France)
- P15:** Performance of a Membrane Reactor for the Coupling of a Dehydrogenation and Hydrogenation Reaction
O. Schramm, A. Tuchlenski, A. Seidel-Morgenstern (Germany)
- P16:** Experimental Study and Numerical Simulation of the H₂/Isobutane Separation in an MFI Zeolite Membrane Reactor
P. Ciavarella, H. Moueddeb, S. Miachon, K. Fiaty, J.A. Dalmon (France)
- P17:** Permeation Characteristics of Butane Isomers through MFI-Type Zeolitic Membranes
T. Matsufuji, N. Nishiyama, K. Ueyama, M. Matsukata (Japan)
- P18:** Simulation and Experimental Study on the Catalytic Polymer Membrane Reactors for the Vapour-Phase MTBE (Methyl Tert-Butyl Ether) Decomposition
J.S. Choi, Y.H. Kim, I.K. Song, W.Y. Lee (Korea)
- P19:** Preparation and Characterization of Palladium-Based Composite Membranes from two Synthesis Methods
H.B. Zhao, G.V. Baron, G.-X. Xiong (Belgium, China)
- P20:** A Membrane Reactor using Carbon Fibers
N. Itoh, K. Haraya (Japan)
- P21:** Mesoporous Alumina Tube with Asymmetric Structure for Membrane Support
N. Itoh, S. Hara, K. Sakaki, T. Asakura, A. Shono, K. Sato (Japan)
- P22:** Preparation of Metallic Double-Layered Membranes for Hydrogen Separation
S. Hara, K. Sakaki, N. Itoh, K. Haraya, T. Kataoka, A. Shono, K. Sato (Japan)
- P23:** Use of Electrocatalytic Membrane Reactor for Synthesis of Sorbitol
Y. Owobi, K. Fiaty, P. Laurent, C. Bardot (France)

- P24:** Ceramic Membrane Reactors for Propane Dehydrogenation: Feasibility Study on the use of High-Selective Membranes
H.M. van Veen, P.T. Alderstein, P.P.A.C. Pex (Netherlands)
- P25:** Study on Oxidation of n-Butane to Maleic Anhydride over Inorganic Membrane Reactor
X. Hongxia, P. Feng, H. Zhouqtao (China)
- P26:** Enzymatic Hydrolysis of a Sunflower Oil in an integrated Ultra-filtration and CSTR Reactor System
O. Gan, H. Rahmat, L.R. Weatherley (UK)
- P27:** Preparing and Characterising Palladium-Silver, Palladium-Nickel and Palladium-Copper Alloy Membranes
J.N. Keuler, L. Lorenzen, R.D. Sanderson
- P28:** Synthesis of Zeolite A Membranes: A New Approach
S.P.J. Smith, R.D. Sanderson, J.C. Jansen (South Africa)
- P29:** Preparation and Characterisation of membranes for Electrochemically Promoted Catalysis and Separations
D.G. Bessarabov, R.D. Sanderson, W. Michaels, J.P. Vermeulen, S. Marais, Y.M. Popkov (South Africa)
- P30:** Solid Polyelectrolyte (SPE)-Supported Membrane Reactor for Anodic Oxidation of Organic Pollutants in Water
R.D. Sanderson, J. Grimm, D.G. Bessarabov (South Africa)
- P31:** Preparation of Beta Zeolite Supported on a Ceramic Membrane for the Isoparaffins/Olefins Alkulation Reaction
M. Torres, J.M. Dominguez, M. Maubert, M. Gutiérrez, A. Mantilla, G. Ferrat, S. Alfaro (Mexico)

Plenary Abstracts

Membrane Reactor Application to Hydrogen Production

Eiichi Kikuchi

Department of Applied Chemistry

Waseda University, Tokyo, Japan.

Hydrogen and syngas are most economically produced nowadays by steam reforming, a reaction between steam and hydrocarbons, using supported nickel catalysts. As methane is a stable hydrocarbon, extremely high reaction temperatures, around 800 °C, are required.

If hydrogen is selectively removed from the reaction system, the thermodynamic position of the reaction system is shifted to the product side, and high conversion of methane to hydrogen and carbon dioxide can be attained even at low temperatures.

We invented a composite membrane consisting of thin palladium layer deposited on the outer surface of porous materials by electroless plating. The palladium layer could completely cover the surface, so that only hydrogen could permeate through the membrane with a 100% selectivity. The membrane has been applied for a polymer electrolyte fuel cell system by Tokyo Gas Co., Ltd. and Mitsubishi Heavy Industries, Ltd., as a membrane reformer.

The limitation of Pd membranes are caused by 1) inherent hydrogen permeance of pure Pd membrane, 2) hydrogen embrittlement, 3) high cost, and 4) poor resistance against sulfur poisoning and carbon deposition. As a possible way to improve them, we propose the application of a CVD technique to deposit precious metals such as Pt and Ru on the surface or inside the

pore of a ceramic alumina tube. The permeability and permeation selectivity of these metal-ceramic composite CVD membranes were investigated in a comparison with electroless-plating palladium membranes, as well as the performance in membrane reactors applied to steam reforming of methane.

The permeation of hydrogen through the CVD membranes is not based on the solution-diffusion transport mechanism but on the surface diffusion mechanism. Although the CVD membranes gave higher conversion of methane than thermodynamic equilibrium, they gave high conversion similar to electroless-plating membranes, only when the membranes showed high H₂/N₂ separation factors.



Biocatalysis in Membrane Reactors

C. Wandrey, J. Beliczey, N. Brinkmann, G. Dudziak, S. Fey, G. Giffels, D. Hahn,
U. Kragl, S. Laue, A. Liese, U. Mackfeld, H. Offermann, S. Rissom
Forschungszentrum Jülich GmbH, Institut für Biotechnologie 2, D-52425 Jülich

A. Advantages and Applications of Membrane-Processes¹

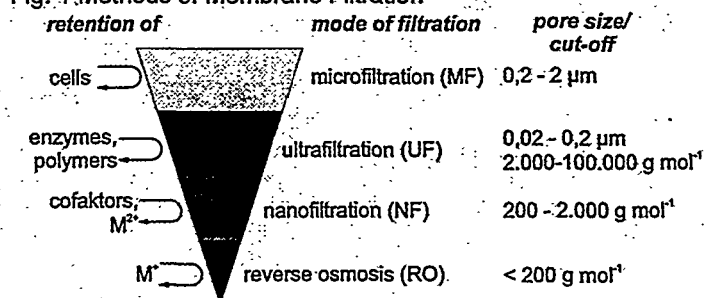
1. Advantages

- Simple and clean removal of reaction products
- Repeated or continuous use of catalysts
- Commercial availability of a multitude of membranes with diverse cut-offs and properties

2. Applications

- Microfiltration: sterilisation, gas-transfer, extraction
- Ultrafiltration: retention of enzymes and macro-molecules
- Nanofiltration: retention of cofactors and homogeneous catalysts
- Reverse osmosis: desalting of reaction mixtures

Fig. 1 Methods of Membrane Filtration

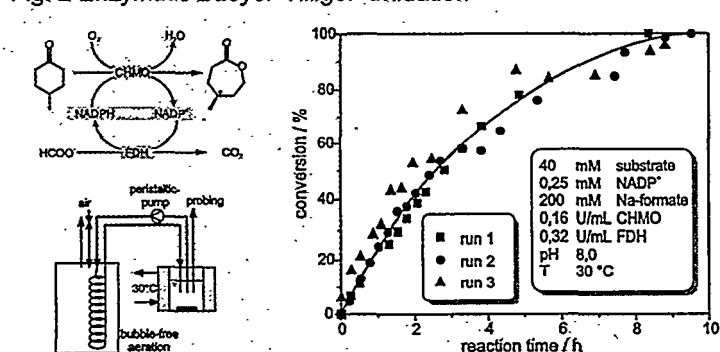


B. Examples of Application

1. Synthesis of Lactones²

- Enzymatic *Baeyer-Villiger*-oxidation of ketones yielding enantiopure lactones using cyclohexanon monooxygenase (CHMO) [EC 1.14.13.22]
- Regeneration of the cofactor NADPH using recombinant formate dehydrogenase (FDH) [EC 1.2.1.2]
- Addition of molecular oxygen by bubble free aeration using a micro-porous silicone tube
- Enzyme stability permits synthesis in triple repetitive Batch without loss of activity
- Total turnover number of the cofactor = 160
- Isolation of 5-methylcaprolactone with >99 % ee

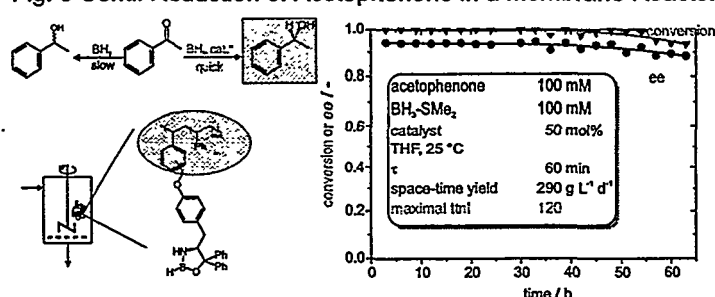
Fig. 2 Enzymatic *Baeyer-Villiger*-Oxidation



2. Reduction of Acetophenone³

- Use of homogeneously soluble polymer-enlarged oxazaborolidin-catalyst
- Increase of the total turnover number by retention of the catalyst using a nanofiltration membrane (Koch MPF 50) up to 520
- Discrimination of the non-catalysed side reaction (blue) by use of a continuous stirred tank reactor (CSTR) operating at low substrate concentrations
- Reaching of high yields (>99%), ee (up to 95%) and space-time yields (up to 1400 $\text{g l}^{-1} \text{d}^{-1}$), simple product isolation

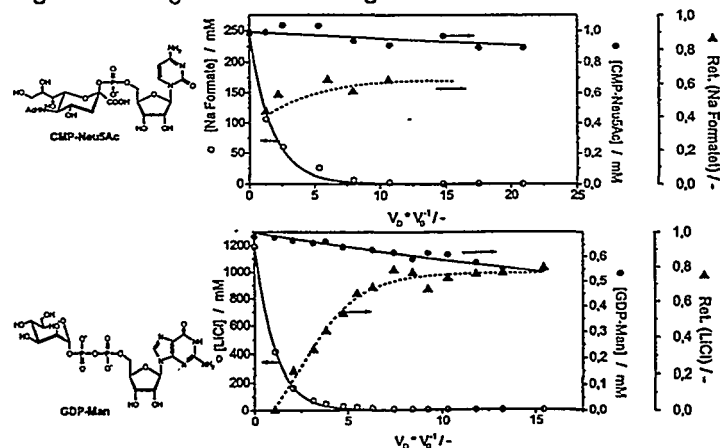
Fig. 3 Conti. Reduction of Acetophenone in a Membrane Reactor



3. Desalting of Nucleotide Sugars⁴

- Nucleotide sugars are important building blocks for the enzymatic oligosaccharide synthesis
- Problem of separation of high salt concentrations in the presence of small amounts of sugar
- Adapted nanofiltration membranes permit the discrimination between salt and sugar
- Purification of GDP-Mannose (GDP-Man) and CMP-Neuraminic acid (CMP-Neu5Ac) up to purities of >95 % in g-scale

Fig. 4 Desalting of Nucleotide sugars



C. Literature

- ¹ M. Mulder: Basic Principles of Membrane Technology, Kluwer, Dordrecht (1996).
- ² S. Rissom, U. Schwarz-Linek, M. Vogel, V.I. Tishkov, U. Kragl: *Tetrahedron: Asymm.* 8 (1997) 2523-6.
- ³ G. Giffels, J. Beliczey, M. Felder, U. Kragl: *Tetrahedron: Asymm.* 9 (1998), 691-6.
- ⁴ G. Dudziak, S. Fey, L. Hasbach, U. Kragl: *J. Carbohydr. Chem.* (1998), in press.

MEMBRANE REACTORS FOR LIQUID-PHASE CATALYTIC REACTIONS

Jean-Alain Dalmon, Institut de Recherches sur la Catalyse-CNRS

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According to the literature, most of the studies combining membranes and catalysts concern gas-phase catalytic reactions, occurring at relatively high temperatures. This very often leads to limitations due to the membrane thermal stability. In fact, most of the commercial membranes have been designed for liquid phase separations, which are, in principle, low temperature processes. Moreover, in gas-phase reactions, the membrane often also acts as a separator between the different gaseous molecules involved in the reaction. Therefore, the membrane should be not only highly selective, but it should also be permeable enough to give a sufficient separation. The combination of these three requirements: high thermal stability, high separation selectivity and high permeability makes one of the most difficult challenge people have to face in membrane catalysis. Development of new membrane materials with adequate performance seems compulsory and many groups are active in this field.

Liquid-phase catalytic reactions are involved in numerous industrial processes ranging from fine to bulk chemicals syntheses. Environment protection is also concerned, as catalysis is good way of processing liquid effluents. Most of these reactions occur at relatively moderate temperature, typical of those used with state-of-the-art membranes in current applications for liquid separation.

The aim of the present paper is to show the potential of membrane reactors in liquid-phase catalytic applications. Most of the few studies published in this area make use of the unique characteristic of catalytic membranes when compared to conventional catalysts (Fig. 1). Schematically, in a catalytic membrane, the pore containing the active phase presents two mouths, each of them opened on each of the two faces of the membrane (Fig. 1a), when in a conventional catalyst, most of the pores have only one mouth (Fig. 1b). Due to the specific geometry of the membrane (structured as a permeable wall dividing the reactor into two separated chambers), it is therefore possible to use the membrane reactor either as an interfacial reactive contactor [1] or as a flow-through membrane [2].

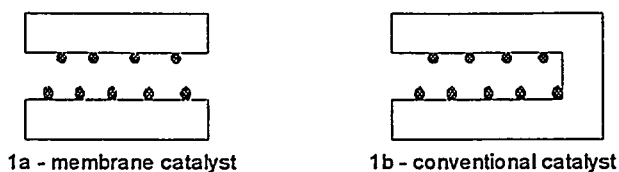


Figure 1 – Schematic of membrane and conventional catalysts

In the interfacial contactor, the two reactants, A and B, are introduced separately from each side of the membrane and the interface A-B is located in the active pore. This is an unique situation when compared to conventional systems (the A-B interface is generally outside the active pore) and may completely change the mass transfers, making easier the transfer of the reactant which limits the reaction in conventional systems.

In the flow-through membrane, the two reactants are both introduced from the same side of the active membrane and the A+B mixture forced to flow through the active pore. The residence time of reactants (and products) in the active pore is therefore controlled by experimental conditions (such as the differential pressure across the membrane). This is also an unique situation when compared to conventional systems, where diffusion processes often control the residence times in the pore and the local concentrations of the reaction partners. In principle, the flow-through membrane seems to be a reactor giving a better control of the catalysis conditions, thus allowing activity and selectivity improvements.

Another advantage of these two types of membrane reactors for liquid phase applications is that, in most cases, they do not need selective separation of the molecules involved in the reaction. This point, combined with the low temperatures often used, generally allows the use of state-of-the art (commercial) membranes as support of the active phase.

To conclude, if few examples have been up till now available, membrane reactors for liquid-phase applications seem to be a very promising area for future investigations.

[1] J. Peureux, M. Torres, H. Mozzanega, A. Giroir-Fendler and J-A. Dalmon. *Cat. Today*, **25**, 409 (1995).

[2] C. Lange, S. Storck, B. Tesche and W.F. Maier *J. Catal.*, **175**, 280 (1998).

Catalytic Membrane Reactors for Spontaneous Synthesis Gas Production

by

Anthony F. Sammells and Michael Schwartz
Eltron Research, Inc.
Boulder, CO 80301 USA

for presentation at

3rd International Conference on Catalysis in Membrane Reactors
in Copenhagen, Denmark - September 9-12, 1998

ABSTRACT

Over the last several years our work has focused upon determining the interrelationship between crystallographic and thermodynamic properties of solid state metal oxides and how they relate to achieving high ionic and electronic conductivity. This work has led to a new class of oxygen anion and electron conducting brownmillerite membrane materials which have demonstrated practical utility for achieving the spontaneous conversion of natural gas (methane) into synthesis gas.

This presentation will describe the solid state chemistry of these membrane materials and their performance in Catalytic Membrane Reactors (CMR's). Reactors have operated continuously at practical rates for one year at 900°C with no evidence of material instability over this time period.

Experimental and Theoretical Aspects of Membrane Catalysis

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Catalytic membrane reactors combine reaction and membrane-based separations in the same process unit. Membrane reactor-based processes belong to the broader class of reactive separation technologies, which also encompass other processes like reactive distillation, sorption and crystallization, etc. Some of these reactive separation processes have already found commercial application (e.g., catalytic reactive distillation), something that has so far, for the most part, eluded catalytic membrane reactors.

This talk will focus on some of the technical challenges that catalytic membrane reactor-based processes still face before they attain broad commercial appeal. The emphasis in this paper will be on reactor design and engineering issues. We will discuss these issues in the context of four general classes of membrane reactors, namely:

- Dehydrogenation Reactors
- Oxidation and Partial Oxidation Reactors
- Liquid Phase Reactors
- Pervaporation Reactors

The driver in optimal reactor design to date has been the enhancement of yield and selectivity. It will be shown in this talk that the separation component is often equally critical or even more important in determining overall process economics.

EU Sponsored Projects

**An Attractive Option for CO₂ Control in IGCC Systems:
Water Gas Shift with Integrated H₂O/CO₂ Separation
(WHIHYS) Process. Phase 1: Proof of Principle**

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In the Joule II programme a novel reactor concept, the water gas shift membrane reactor (WGS-MR) for CO₂ removal in IGCC systems has been investigated. In order to establish full insight in the possibilities of the application of such a reactor, a multidisciplinary technical and economic feasibility study has been carried out comprising system integration studies, catalyst research, membrane research, membrane reactor modelling and bench-scale membrane reactor experiments. The application of the WGS-MR concept in IGCC systems is an attractive future option for CO₂ removal as compared to conventional options. The net efficiency of the IGCC process with integrated WGS-MR is 42.8% (LHV) with CO₂ recovery (80% based on coal input). This figure has to be compared with 46.7% (LHV) of an IGCC without CO₂ recovery and based on the same components, and with 40.5% (LHV) of an IGCC with conventional CO₂ removal. Moreover, an economic analysis indicates favourable investment and operational costs. The development of the process is considered to be technically feasible. However, it became clear that the technology of inorganic high selective gas separation membrane manufacturing and high temperature ceramic materials engineering is not yet mature and that further development in this area remains necessary

Contract N°: BREU-CT91 0406

Project N° 4575

CATALYTIC MEMBRANE REACTORS: APPLICATION TO FINE CHEMICALS SYNTHESIS

Partnership

Institut de Recherches sur la Catalyse, F, (coordinator).
Laboratoire des Matériaux et Procédés Membranaires, F.
Istituto di Chimica Industriale di Genova, I.
Centro di Studio per le Macromolecole Stereordinate ed Otticamente Attive, I.
Laboratoire d'Automatique et de Génie des Procédés, F.
Endorsers:
Société des Céramiques Techniques (SCT-US Filter), F.
Snampromgetti, I.

The catalytic hydrogenation of organic molecules is a key step in the preparation of various fine chemicals. Typical processes generally involve 3 phases: gaseous (H_2), liquid (the organic molecule) and solid (the catalyst). The contact between these three phases, which is obviously necessary to have the reaction, is the major problem of this type of process (especially the transfer of the gaseous reactant). Different reactors are used in the Industry, but all of them present drawbacks due to the difficulties to achieve the contact between the three phases.

There has been consequently considerable interest in the implementation of new types of reactor for gas-liquid-solid applications. It is suggested here that a catalytic membrane reactor, based on a porous membrane separating the two gaseous and liquid reactants and acting as a support for a catalytic phase, can be an efficient alternative to improve the contact between gas, liquid and solid, due to the high gas-liquid interfacial area developed within the catalytic porous membrane. Beside this advantage in mass transfer resulting in a higher efficiency (energy saving), other advantages should be related to the suppression of the catalyst recovery step and also to a decrease in catalyst losses (cost and environment protection).

The progress of the work led to the following results:

- preparation and characterization of defect-free microporous inorganic membrane
- controlled deposition of catalytic platinum within the porous framework of the membrane.
- full design of the catalytic membrane reactor (laboratory and pre industrial scales).
- exploration of the catalytic performance in a model reaction (validation of the concept).
- modelling of the catalytic membrane reactor in 3-phase reactions (for further scaling-up).

During the project it has been shown that the membrane reactor, when correctly used, is a very efficient tool for the transfer of a gaseous reactant to the solid catalyst in presence of a liquid phase. The catalytic membrane acts as an active contactor and surpasses in this respect conventional reactors, in good keeping with the starting hypothesis.

Membrane Reactor for Cost Effective Environmental-Friendly Hydrogen Production

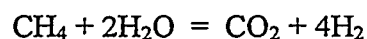
EU-Contract no. BRPR-CT95-0045, Project number: BE95 1930

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Abstract

Inorganic membranes that are stable and have high hydrogen selectivity and flux, can be used in membrane reactors for large-scale production of hydrogen by steam reforming of hydrocarbons. The process is used to produce hydrogen for ammonia (NH₃) production. The reaction may be written



By current technology, this thermodynamically restricted process is carried out in conventional reactors at 850-900°C to a conversion of the methane of 90%. With a membrane reactor where H₂ is taken out of the reaction zone through a hydrogen selective membrane, the same conversion can be obtained at much lower temperature. This process may be significantly cheaper, both with respect to the investment costs for production plants and to the energy consumption of the process, given certain membrane properties and cost limitations.

The objective of this project is to develop a microporous silica membrane with high flux and hydrogen selectivity, and with sufficient chemical and thermal stability, for production of hydrogen by steam reforming at temperatures from 500 - 650°C.

The membranes are prepared using advanced sol-gel technology and deposition techniques on state-of-the art alumina supports. The membrane properties are verified by lab-scale membrane reactor testing in gas mixtures simulating the steam reforming

conditions up to 30 bar pressure and 700°C. Powders of selected and characterised steam reforming catalysts are used in the reactor testing. The membrane stability is followed for several hundred hours, and textural and chemical changes are analysed. A techno-economic evaluation of the membrane reactor concept for production of hydrogen by steam reforming to support ammonia and clean energy production, have been carried out.

Partners are:

SINTEF, Norway, Coordinator

University of Twente, The Netherlands

Vlaamse Instelling voor Technologisch Onderzoek (VITO), Belgium

Institut de Recherche sur la Catalyse (IRC-CNRS), France

Velterop BV, The Netherlands

Norsk Hydro ASA, Norway

KEMA Nederland BV, The Netherlands

Contract JOE3-CT95-0022

DEVELOPMENT OF INORGANIC MEMBRANE REACTORS FOR OXIDATIVE DEHYDROGENATION OF PROPANE AND SELECTIVE OXIDATION OF PROPANE

C. Mirodatos, J.C. Volta

1. Objective and strategy. Any process of direct oxidation of propane into propene and/or acrolein and acrylic acid should overcome the yield limitation in desired products. This programme combines i) fundamental investigation of the reaction mechanism, ii) development of performing catalysts, iii) implementation of membrane reactors aimed at a better control of the selectivity by tuning the partial pressure and contact time within the reacting zone. Beside yield, the potential advantages are safety (low O₂ concentration in the reacting zone) and product recovery (separation effects), and scale up.

2. Mechanistic and kinetic studies. Data concerning the propane-to-propene reaction were obtained with a reference and optimized catalyst V/VMgO. The active phase is essentially formed of isolated tetraedra VO₄²⁻ scattered on the magnesia, mostly free from carbonaceous residues. Basic sites related to bare magnesia may also accumulate part of the formed CO₂ as stabilized carbonates. Other forms of polymeric carbon could also slowly form under oxygen lean conditions. The mechanistic scheme includes all the steps of a redox Mars-van Krevelen process and considers three states of the active sites : reduced, oxidised and superoxidized.

Several sets of kinetic equations (power laws and micro kinetic models) were derived from a large collection of kinetic data, able to predict the effect of oxygen and hydrocarbon concentration on the reaction rate in a membrane reactor.

A similar approach was developed for the reaction propane-to-acrolein, since the reaction propane-to-acrylic acid was found not suitable for reliable kinetics. A batch of standard VPO precursor was prepared and activated under water pressure. Kinetic studies were carried out leading to a simplified power law model for acrolein production. Propene was found to be an intermediate in acrolein formation.

3. Membrane reactor preparation. Two concepts were investigated : i) the inert membrane reactor (IMR) where one of the above described powder catalysts is placed inside a micro or meso porous tube, and ii) the catalytic membrane reactor (CMR) where the active phase is inserted inside the porous zone of the tube. Numerous methods of preparation including use of alkoxides and sol/gel procedures were tested. The optimized procedures lead to stable and crack-free membranes suitable for kinetic and engineering investigations.

4. Membrane reactor testing. IMR performance in ODHP was investigated over a wide range of operating conditions. Improvement in propene selectivity was obtained with the VMgO catalyst. Several CMR reactors were tested both for ODHP and partial oxidation. The nature and morphology of the membranes were found to be determining parameters as well as the operating conditions.

5. Membrane reactor engineering. A computer model was developed to simulate the partial oxidation of propane to propene in an industrial scale membrane reactor. A one-dimensional axial dispersion model was adopted to characterise the hydrodynamics. The performance of an industrial membrane reactor was simulated. Better selectivities are obtained increasing temperature, percentage of oxygen in the shell side and decreasing percentage of propane in the tube side.

Development of Inorganic Membrane Reactors for Selective Oxidation of Hydrocarbons to Oxygenates, in particular n-Butane to Maleic Anhydride

Jens Perregaard (Denmark)

Selective oxidation of methanol to formaldehyde, ethylene to ethylene oxide, propylene to acrylonitril, o-xylene or naphthalene to Phthalic anhydride, and n-butane to maleic anhydride (MA) are important processes that today are carried out by heterogeneous catalysis. Typically the yield is below 80% and for the MA the yield is below 60%.

Membrane reactors offer the potential of controlling the concentration profile of the reactants along the length of the reactor as well as the resident's time.

Thus, the safety issue with respect to an overall feed in the explosion region can be overcome by adding the O₂ along the reaction zone. In addition it will be possible to enhance the performance of the reaction since undesired total oxidation can be limited.

This project is focused on developing a new process for the production of MA based on membrane reactors that are an attractive alternative to existing technology. The main is that an improved yield of MA can be obtained and that it is possible to operate with n-butane concentration far above the normal 1-2%.

As already stated the aim of the project is to develop a membrane-based process for MA production. In order to optimise the process has to be integrated with the membrane and the catalyst has to be able to function under the process conditions in the membrane reactor eq. at higher n-butane concentrations. Thus, the project involves catalyst, membrane, and process development.

EUROPEAN CATALYTIC MEMBRANE NETWORK.

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One of the major activities of the European Science Foundation has been in the past years the creation and sponsoring of Networks on topics of specific and growing importance for the European scientific community.

In 1994 a proposal for an European Network on Catalytic Membrane Reactors, presented by a group of scientists and engineers representing all the research Institute, more involved in the field, was approved and activities started formally on July 1994. To our knowledge at that time this Network was the first example of a multinational coordinated action to promote fundamental research in the area of high temperature inorganic membrane reactors.

During the three years of activity interesting results have been obtained both in membrane preparation and in the application of catalytic membrane reactors to several reactions. Progresses based on studies of new materials and of new technique of preparation have been achieved in designing new membranes, inorganic or polymeric, able to operate at high temperature and/or in non-aqueous media, with interesting selectivities and permeabilities. Studies on transport phenomena which occur in membranes led to a better understanding of the separation mechanism and, then, to a better application in reaction systems.

For several reactions, by modelling the membrane reactors it has been possible to determine the optimal operating and engineering conditions.

Experimental tests carried out on reactions like WGS, partial oxidation of CH_4 , etc. confirmed the advantages of these systems with respect to the traditional ones in terms of conversion, selectivity and overall performance.

Some specific subjects which have been discussed and analyzed in detail during these years are the following:

- Development of membrane reactors for enhanced conversion and selectivity in dehydrogenation and oxidative reactions.
- Zeolite-ceramic composite membranes preparation and characterization.
- Palladium-ceramic composite membranes synthesis and characterization.
- Development of mixed conducting ceramic materials for oxidation processes.
- Studies on the nitrobenzene liquid phase hydrogenation in membrane reactors.
- Studies on the use of three phase catalytic membrane reactors.

The Network on CMR permitted, during the three-year of its duration to increase the role of European research in this important field by encouraging ideas and people to circulate among the different laboratories involved. The cooperation among the different Institutions allowed a continuous exchange of young scientists between groups. The Workshops and seminars organized approximately twice a year and the Newsletters published pointed out the state of the art and the progress made at each stage of the Network actions. All these activities led to an exchange of knowledge in the field and strengthened the contacts among the several participants with an efficient use of the resources.

An evidence of the big interest derived from this coordination can be found in the increasing, during the three years of activity, of the associated members. Academic and industrial groups initially not involved became, in fact, new partners active in the Network; among them GKSS (Germany), University of Liege (Belgium), VITO (Belgium), Royal Institute of Technology (Sweden), University of Torino (Italy), etc.

Oral Presentations

Membrane Performance: The Key Issue for Dehydrogenation Reactions in a Catalytic Membrane Reactor.

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In a high temperature membrane reactor, a conventional catalytic plug-flow reactor is combined with a gas separation membrane. By selectively removing one of the reaction products, the reaction mixture is prevented from reaching equilibrium, and higher conversion can be obtained. Although the principle of the catalytic membrane reactor is easily understood, in practice the concept is much more complex. The three aspects of the membrane reactor and their relationship to each other have to be considered: the membrane performance, the catalyst performance and the process parameters.

In a previous study^[1] a commercial CVI-type silica membrane was used for the direct dehydrogenation of propane in a high temperature catalytic membrane reactor. This H₂ selective membrane had only a moderate permeance ($\sim 140 \cdot 10^{-9} \text{ mol/m}^2\text{Pa.s}$) and a limited H₂/C₃H₈ permselectivity ($\alpha_0 \approx 70\text{-}80$ at 500°C). These experiments proved that (at 500°C) the propane conversion could be improved from the equilibrium value ($\sim 18\%$) to a value that is about twice as high. The increase was however only significant for relatively small values of the weight-hour-space-velocity (WHSV $< 0.25 \text{ h}^{-1}$). The reason for this can be found in the low H₂ permeance of the CVI silica membrane. At high propane feed streams (high WHSV), the H₂ cannot be removed fast enough through the membrane and conversion is limited by the thermodynamic equilibrium. Because of the moderate selectivity of the membrane, some of the propane and propene can diffuse through the membrane into the permeate stream which also limits the performance of the catalytic membrane reactor.

In this study the comparison is made between the performance of the CVI silica membrane and a Pd/Ag membrane when used as the H₂ selective membrane in a catalytic membrane reactor for the dehydrogenation reaction. The membrane performance (H₂ permeation, permselectivity and binary gas separation) of the Pd/Ag membrane is superior to the performance of the CVI silica membrane. H₂ fluxes of more than $0.3 \text{ mol/m}^2\text{s}$ were measured (with a $\Delta p = 0.1 \text{ MPa}$) and the H₂ permselectivity exceeds 3000. Because of the better characteristics of the membrane the performance of the membrane reactor is also much better when it is run under comparable conditions. The increase in propane conversion persists at higher WHSV values ($> 1 \text{ h}^{-1}$). Both reactors (CVI silica and Pd/Ag) were run with the same type (Cr₂O₃/Al₂O₃) and approximately the same amount of catalyst. Because the transport mechanisms through the Pd/Ag and the silica membrane are different it is not easy to make a direct comparison between the performance of both reactors. However it will be shown that the membrane performance is one of the key issues for the performance of a catalytic membrane reactor for the dehydrogenation reaction.

Because the H₂ is selectively removed from the reaction mixture, it is not available for any competitive side reactions. It will also be shown that the production of methane, which limits the propene selectivity in a conventional plug-flow reactor, is much less in a catalytic membrane reactor. This means that the selectivity in the membrane reactor is higher than in the plug-flow reactor when they are run under similar conditions.

[1] H. Weyten, K. Keizer, A. Kinoo, J. Luyten & R. Leysen: "Dehydrogenation of propane using a packed-bed catalytic membrane reactor": AIChE Journal: 43(7), 1819 (1997).

The Effect of Hydrogen Removal on the Performance of a Membrane Reactor for Methane Steam Reforming

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This paper provides the results of a mathematical simulation of methane steam reforming with hydrogen sulphide present in a tubular catalytic reactor with a hydrogen permeable membrane. The emphasis of the simulation is to examine the influence of hydrogen removed on the catalyst deactivation by hydrogen sulphide poisoning and carbon formation. The main variables affecting H_2S tolerance and the tendency of carbon formation, including H_2S level, the proportion of hydrogen removal, temperature and pressure have been investigated. The simulation demonstrates that the hydrogen removed by the membrane may cause the more extensive catalyst deactivation from both H_2S poisoning and carbon formation. In addition the H_2S tolerance drops and the tendency to carbon formation increases as the proportion of hydrogen removed increased. The benefit of using a membrane reactor may be not achieved for feedstream with a high H_2S content and in which a high proportion of hydrogen produced is removed. To compensate for the influence of hydrogen removal on performance of a membrane for methane steam reforming, a higher applied pressure would be a better choice in order to control carbon formation, and it is suggested that a more efficient desulphurisation technique has to be employed to curb the H_2S content in feed to avoid the catalyst poisoning in the membrane reactor for operation at low temperature and with significant hydrogen removal.

Keywords: methane steam reforming, hydrogen removal, mathematical simulation, catalyst deactivation, hydrogen sulphide tolerance and carbon formation

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Catalytic dehydrogenation of hydrocarbons in palladium composite membrane reactors

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Introduction

Palladium membranes have been proposed by many authors to improve the product yield in various equilibrium restricted dehydrogenation reactions [1,2]. Removing hydrogen from the reaction mixture by using permselective membranes allows to drive the reaction closer to equilibrium and hence increases the yield of the desired products. In addition, membranes can help to reduce the demand for high reaction temperatures and low reaction pressures, leading to a cost reduction (less expensive materials, reduced reaction volume). This work describes recent progress made at our laboratory in the preparation of palladium composite membranes (ceramic and stainless steel based), the testing of these membranes in laboratory reactor experiments and in process simulation calculations for two industrially relevant reactions, i.e. the dehydrogenation of ethylbenzene to styrene and the dehydrogenation of propane to propylene.

Results and Discussion

Membrane preparation: Using tubular ceramic substrates (alumina) with different pore size obtained from Inocermic GmbH, Hermsdorf (Germany), palladium composite membranes have been prepared by electroless plating according to Collins and Way [3], although their plating conditions have been modified in order to improve the quality of the membrane layers (adhesion, durability). Before and after use in a laboratory membrane reactor, the membranes were characterized by permeation measurements and SEM, showing that the palladium layer is uniformly deposited with a thickness of typically 3 - 5 μm . The H_2/N_2 -permselectivity of a membrane of 100 mm tube length (diameter: 10/7 mm) typically is in the range of 200 - 300. In addition to ceramic membranes, stainless steel based palladium composite membranes have been prepared using tubular asymmetric porous substrates. Electroless plating and electroplating have been applied to date, but the results indicate that the preparation must be improved before these membranes reach equal selectivity and permeability as the alumina-based membranes.

Kinetics, simulation and membrane reactor experiments: For both reaction systems kinetic studies were performed with typical industrial catalysts in order to set the

basis for a more detailed simulation of the potential benefits of a membrane reactor in an integrated process. In addition, lab-scale membrane reactor runs were carried out for different process options (nitrogen sweep gas, permeate evacuation, permeate oxidation). The experimental results confirm that in both systems it is possible to increase the yield of the desired products (styrene and propylene, respectively) by removal of hydrogen, but they also demonstrate the dependence on the reaction kinetics, i.e. the sensitivity of the kinetics on the partial pressure of the various products. For example, adsorption of the hydrocarbon products at the catalyst surface can cause a kinetic inhibition, so that under certain circumstances the removal of hydrogen through the membrane does not necessarily speed up the reaction. For the ethylbenzene system, the increase of styrene yield with increasing pressure [4], which was predicted by a simplified pseudo-homogeneous model taken from literature [5], could not be confirmed by experiment. This was explained by a strong adsorption of styrene observed during the kinetic experiments, as reported also by Lebedev for a similar catalyst system [6].

Conclusions

It could be demonstrated, both by experiment and by simulation, that palladium composite membranes offer interesting advantages for hydrocarbon dehydrogenation in terms of an enhanced product yield or less demanding operating conditions when used along with a highly active catalyst. However, additional (long-term) experiments have to be performed to demonstrate the successful operation of the membrane reactor. Moreover, for a reliable prediction of the behavior of an industrial scale membrane reactor sufficiently detailed models have to be used which include all important heat and mass transport processes occurring inside the membrane and within the catalyst bed.

References

- [1] V.M. Gryaznov and N.V. Orekhova, "Reactors with metal and metal containing membranes", in: A. Cybulski and J. A. Moulijn (Eds.) "Structured Catalysts and Reactors", Marcel Dekker, New York, 1998
- [2] H.P. Hsieh, "Inorganic membranes for separation and reaction", Elsevier Membrane Science and Technology Series, Vol. 3, Amsterdam, 1996
- [3] J.P. Collins and J.D. Way, "Preparation and characterization of a composite palladium ceramic membrane", *Ind. Eng. Chem. Res.*, **32**(1993) 3006 - 3013
- [4] Ch. Hermann, P. Quicker, and R. Dittmeyer, "Mathematical simulation of catalytic dehydrogenation of ethylbenzene to styrene in a composite palladium membrane reactor", accepted for publication in *J. Membr. Sci.* (1997)
- [5] B. K. Abdalla und S. S. E. H. Elnashaie, "Catalytic dehydrogenation of ethylbenzene to styrene in membrane reactors", *AIChE J.* **40** (1994) Nr. 12, 2055 - 2059
- [6] N.N. Lebedev, G.V. Odabashyan, V.V. Lebedev, M.G. Makarov, "Mechanism and kinetics of dehydrogenation and by-product formation", *Kinet. Katal.*, **18**(1976), 1441 - 1447

Methane Partial Oxidation in a Fast Flow Non-Selective Membrane Reactor

By J. Yun, H. Hahm, M. Alibrando and E.E. Wolf, Chemical Engineering Department, University of Notre Dame, Notre Dame , IN 46556, USA

The partial oxidation of methane yields high conversions and selectivities to synthesis gas in fast flow reactors operating at millisecond residence times (1). The high gas throughput combined with the reaction exothermicity can sustain autothermal operation. The main drawback of these reactors is the potential for reaching the flammability limit when a low oxygen to methane ratio is used. Under such conditions flame formation can lead to an explosion. To eliminate the safety hazard and operate with the same advantages of premixed reactors, we designed a new reactor configuration that separates the oxidant and reducing feeds prior to contact with the catalyst bed. The reactor consists of a porous membrane tube with one end sealed, which is concentric with a quartz tube. The upper part of the membrane tube is impermeable whereas the lower part near the sealed end is highly porous. The catalyst is placed in the annular section between the porous section of the membrane tube and the external quartz tube. Oxygen is fed into the inner membrane tube and permeates through the porous section of the tube flowing in a cross flow configuration (axial and radial) through the catalyst bed. Methane is fed at the top of the annular section containing the catalyst. Contact between the two reactants occurs only in the region in which the catalyst is located, eliminating the possibility of flame formation that occurs in premix fixed bed reactors. The distribution of oxygen along the porous membrane wall eliminates the formation of hot spots and alters both the temperature and concentration profiles in the catalysts bed.

The catalyst used is in a powder form and contains Rh or Ni supported on TiO₂. The catalyst is ignited by using a temperature programmed method in excess methane. After ignition, the oxygen flow is adjusted to reach the desired methane to oxygen ratio. Results were obtained in a fixed bed and membrane reactors using Rh/TiO₂ catalysts(2). We found that in both reactors, conversion and selectivity are not sensitive to the effect of

catalyst loading, residence time and methane to oxygen ratio. Oxygen conversion was 100% in all cases, whereas methane conversion, and CO and H₂ selectivities vary from 70-90% depending on operating conditions. New results on Ni/TiO₂ have recently been obtained with special consideration to the issue of catalyst deactivation. Catalyst characterization by XRD and XPS and H₂ chemisorption were conducted to ascertain the state of the surface before and after reaction.

An elementary step model similar to the one proposed by Hickman and Schmidt (1) fit the experimental results well when a slightly lower activation energy for CO desorption is used. The model predicts that most of the reaction takes places in a narrow region where the reactants are contacted, which explains the lack of sensitivity of the conversion and selectivity to operating variables (3).

- 1) D. A. Hickman and L.D. Schmidt, *AICHE J.*, 39,(1993) 1164.
- 2) M. Alibrando and E.E. Wolf, "3rd World Congress on Oxidation Catalysis"
R.K. Graselli, S.T. Oyama, A.M.Gaffney and J.E. Lyons Edits., 693-700,
Elsevier 1997.
- 3) M. Alibrando, H.Hahm and E.E. Wolf, *Catal. Lett.* In press.

Theoretical and experimental analysis of Methane Steam Reforming in a membrane reactor

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ABSTRACT

Methane steam reforming is an important process in Chemical Industry. Its products are hydrogen and a mixture of hydrogen and carbon monoxide, named syngas. Methane conversion in traditional reactors is limited by the thermodynamic equilibrium. Moreover, the temperature operative conditions are severe (850-900°C). Membrane reactors incorporate reaction and permeation in a single unit; this configuration can shift the thermodynamic equilibrium (Barbieri and Di Maio, 1997; Barbieri et al., 1997). In this work, experiments were carried out to analyse the thermal effects of membrane reactors in a MSR process. The membrane used is a Pd-Ag (Ag 23%_w) alloy and its infinite selectivity for hydrogen permeation has been verified. Hydrogen permeability follows the Richardson's law. The methane conversion has been analysed in function of various parameters: temperature, reactant feed molar ratio, sweep gas flow rate, reactant feed flow rate. The overall heat transfer coefficient of a traditional reactor has been, also, determined experimentally (190 kcal/m² h °C). The predictions of non-isothermal model are in a good agreement with the experimental results obtained in the lab and the ones present in the literature (Shu et al. 1994). Whereas, the isothermal model predictions are higher than experimental data. Being the MSR a very endothermic reaction and fast on Ni catalyst, the limiting step, on the reaction conversion, is the heat transfer rate.

Shu, J.; Grandjean, B. P. A.; Kaliaguine, S. Methane steam reforming in asymmetric Pd- and Pd-Ag/porous SS membrane reactor. *Appl. Catal. A*, 1994, 119, 305-325

G. Barbieri, and F.P. Di Maio, "Simulation of methane steam reforming process in a catalytic Pd-membrane reactor", *Industrial & Engineering Chemistry Research*, 1997, 36(6), 2121-2127

G. Barbieri, V. Violante, F.P. Di Maio, A. Criscuoli, and E. Drioli, "Methane Steam Reforming Analysis in a Palladium-based Catalytic Membrane Reactor" *Industrial & Engineering Chemistry Research*, 1997, 36(8), 3369-3374

Oxidation of Isobutane over Supported Noble Metal Catalysts in a Palladium Membrane Reactor

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The U.S. government passed several amendments to the Clean Air Act in November 1990 in an effort to curb automotive air pollution. In response to the new requirements, methyl *tert*-butyl ether (MTBE) has emerged as a promising, high octane, oxygen-rich gasoline additive [1]. Since isobutylene is a precursor of MTBE, demand for isobutylene has increased beyond its traditional supply, and the development of additional, efficient methods of producing isobutylene has become advantageous. The typical method of producing isobutylene industrially is by dehydrogenation over a $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst at approximately 650°C [2]. Without catalyst regeneration, isobutylene yields are approximately 20%. A large heat input is required to drive this endothermic reaction and maintain the reaction temperature. In addition, carbon deposition can quickly deactivate the catalyst [3]. The attainable yield of isobutylene is also limited by thermodynamic equilibrium.

Therefore, researchers have proposed conducting dehydrogenation in H_2 selective membrane reactors to remove this thermodynamic limitation by removing the co-produced H_2 and consequently increasing product yield. In such processes, H_2 is selectively removed through a membrane (often Pd), resulting in an equilibrium shift of the dehydrogenation reaction towards products. Improvements of 50% to 400% in isobutylene yield have been achieved by using a membrane reactor [2, 4]. However, many of these membrane reactors operate under kinetic limitation since the dehydrogenation is inherently slow [5].

A route to isobutylene which may alleviate this kinetic limitation is the oxidative dehydrogenation of isobutane. In contrast to the previous reaction system, oxidative dehydrogenation is an exothermic reaction with very fast kinetics. Higher yields of isobutylene can be obtained over a $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst with much less heat input and at shorter catalyst contact times [6]. In these experiments, O_2 is the limiting reactant and is usually consumed very quickly after initial contact with the catalyst. Therefore, while oxidative reactions dominate initially, non-oxidative reactions become increasingly important as O_2 is consumed. The thermodynamic limitation is affected by the co-production of isobutylene and H_2 via oxidative routes. In the absence of this limitation, the overall isobutylene yield will increase.

Our goal is to combine the advantages of oxidative dehydrogenation (fast kinetics) and non-oxidative dehydrogenation in a membrane reactor (relief of thermodynamic limitation) by using a Pd membrane reactor in an oxidative dehydrogenation reaction system. We show that isobutylene yield is indeed improved by the removal of H_2 through a Pd membrane [7]. The extent of isobutylene yield improvement depends primarily on the balance between catalyst contact time and the characteristic time for H_2 diffusion across the membrane. However, the relative importance of the non-oxidative dehydrogenation route in the overall reaction scheme is also an important issue.

REFERENCES:

1. R. Clark, R. Morris, D. Spence, E. Tucci, *Energy Progress* **7**, 164-169 (1987).
2. T. Matsuda, I. Koike, N. Kubo, E. Kikuchi, *Applied Catalysis A: General* **96**, 3-13 (1993).
3. S. Udomask, R. Anthony, *Industrial and Engineering Chemistry Research* **35**, 47-53 (1996).
4. T. Ioannides, G. Gavalas, *Journal of Membrane Science* **77**, 207 (1993).
5. B. Raich, H. Foley, *Applied Catalysis A: General* **129**, 167-188 (1995).
6. M. Huff, L. Schmidt, *Journal of Catalysis* **155**, 82-94 (1995).
7. T.M. Raybold, M.C. Huff, *Industrial and Engineering Chemistry Research* submitted (1998).

Ultra pure hydrogen production by catalyst-membrane systems

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Systems of grained industrial catalysts with hydrogen permeable membranes have been used for ultra pure hydrogen production. The hydrogen porous membranes were palladium alloy foils and thin walled tubes as well as composites prepared by metal or alloy coverage of heat resistant porous supports.

Hydrogen was obtained by dehydrogenation of hydrocarbons over commercially available Pt-Re/Al₂O₃ and alumina-chromia catalysts and steam reforming of methane over nickel industrial catalyst. It was prepared a new catalyst for dry reforming of methane - ultradispersed particles of iron group metals fixed in thermostable oxides. This catalyst converts an equimolar mixture of CH₄ and CO₂ completely into hydrogen and carbon monoxide.

High temperature reactors with system of grained catalyst and membrane permeable for hydrogen only were constructed in co-operation with A.A.Baikov Institute of Metallurgy (Moscow, Russia), Institute of Technical Chemistry (Perm, Russia), Institute of Physical and Inorganic Chemistry (Minsk, Belarus). The reactor shells were made of stainless steel and ceramics. The methods of membranes tightening with reactor shell were elaborated.

Prospects and Problems of Dense Oxygen Permeable Ceramic Membranes

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The prospects of using mixed oxide ionic and electronic conductors in membrane reactors for generation of synthesis gas ($H_2 + CO$) from methane at temperatures in the range of 600 to 800°C have been pointed out in many papers during recent years. The main advantage is that only oxygen can permeate through the compact membranes (in the form of oxide ions with electrons moving in the opposite direction). Focus has been on metal oxides such as $Sr(Fe,Co)_{1.5}O_y$ and $La_{1-x}Sr_xCoO_{3-\delta}$. Good oxide ion conductivity has been documented but problems of mechanical and chemical stability of these compounds have been realized.

The aim of this presentation is to list a number of possible material types and to give a more general analysis of both the prospects and the problems. Both homogeneous and heterogeneous membranes (e.g. mixtures of metals and pure oxide ion conductors) will be discussed.

The prospects will be analyzed in terms of permeation rate as a function of membrane thickness, surface exchange kinetics (exchange current densities), ionic conductivity and electronic conductivity. The significant influence on the three latter properties of gas composition and temperature will be described.

Some problems are common to oxide membrane reactors while others of quite different nature dependent on the type of membrane in question. One common problem is that of thermal expansion coefficient (TEC) mismatch between the thin membrane and the necessary membrane support structure which often will be a porous tube. Another is that of chemical stability in both of the very different atmospheres of methane and oxygen at elevated temperatures.

In case of mixed conducting oxides, problems may arise from changes in defect chemistry with the gradual changes in oxygen partial pressure over the membrane. Thus, in a tubular reactor for syngas production with methane inside and air outside, the molar volume of the ceramic membrane material will change gradually through the membrane. This will result in internal mechanical stresses which may in worst case destroy the membrane.

..In case of a heterogeneous mixture of a pure oxide ionic conductor and a metal the main problem may be cracks and porosities causing gas leakage. The reasons for such cracks and porosities are the differences in TECs and in sintering properties of the two different materials. The problems will be illustrated by concrete examples.

Zeolite Containing Catalytic Membranes as Interphase Contactors

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Zeolitic titanium silicalite (TS-1) was previously found to be a very efficient catalyst for the oxygenation of various organic compounds with aqueous hydrogen peroxide. Nevertheless, in a conventional reactor, where the catalyst particles are suspended, the reaction rates are quite low because of the immiscibility between the organic and aqueous phases. In such a reactor, the use of a co-solvent is required to increase the reaction rate. In this study, a membrane reactor was tested. In this reactor, a zeolite containing catalytic membrane was placed at the interface between the two immiscible phases which allowed adequate transport of reactants on the catalyst surface without using a co-solvent. This concept of zeolite containing catalytic membrane as interface contactor, which may be applicable to numerous multiphase reactions, has been tested for the oxyfunctionalization of n-hexane to a mixture of hexanols and hexanones. Membrane preparation consisted in embedding catalyst (TS-1) particles in a polymeric matrix made of pure or polar functional groups containing modified polydimethylsiloxane (PDMS). The experimental results demonstrate the feasibility of such a catalytic membrane reactor since no loss of catalytic activity was observed when compared to a conventional reactor. Permeation and separation tests were performed which bring some insights into the membrane transport mechanisms. The permeation experiments and the reaction tests show how the different modifications of the polymeric matrix significantly affect the chemical and physical properties of these composite catalytic membranes. Moreover, a kinetic diffusion- reaction model was established in this study. The simulated average reaction rates fit well with the results obtained from the experiments.

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Selective Hydrocarbon Oxidation using Liquid Phase Catalytic Membrane Reactors

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Catalytic oxidation is a major route towards functionalised hydrocarbon chemicals. In recent years, several novel catalysts and reactors were developed for the liquid phase hydrocarbon oxidation. Zeolite-encapsulated iron-phthalocyanine was shown to be a promising selective catalyst for the liquid phase cyclohexane oxidation into cyclohexanol and cyclohexanone. This reaction is carried out at room temperature using acetone as a solvent and a t-butylhydroperoxide (t-BOOH) oxidant. However, effects of polarity were shown to be crucial in alkane oxidation. As a result of the competitive adsorption of the polar components in the reaction mixture (acetone, t-BOOH, oxidation products ...), the cyclohexane substrate is almost completely excluded from the active sites of the catalyst, resulting in rapid decomposition of the organic peroxide and low reaction rates. In an attempt to create a more hydrophobic environment, the zeolite was embedded into a dense hydrophobic poly-(dimethylsiloxane) polymer, substantially improving the catalyst performance [1]. The hydrophobic polymer membrane is then used as a catalytic barrier between the aqueous t-butylhydroperoxide on one side and organic cyclohexane phase on the other side of the membrane, thus avoiding the use of a solvent.

In this presentation, the influence of the polymer membrane thickness and the volume fraction of zeolite-encaged iron phthalocyanine on the catalytic membrane activity and selectivity will be discussed. The oxidation of cyclohexane, cyclododecane and n-dodecane using t-butylhydroperoxide as an oxidant was studied in a catalytic membrane reactor. Cyclohexane products (cyclohexanol and cyclohexanone) were recovered into both aqueous oxidant and organic substrate phases. On the other hand, dodecane oxidation products desorbed preferentially into the organic substrate phase. Hence, using this catalytic membrane reactor configuration, the combination of reaction and separation can be achieved in one single process unit.

REFERENCES

- [1] R. F. Parton, I. F. J. Vankelecom, M. J. A. Casselman, C. P. Bezoukhanova, J. B. Uytterhoeven and P. A. Jacobs, An efficient mimic of cytochrome P-450 from a zeolite-encapsulated iron complex in a polymer membrane, *Nature*, 370 (1994), 541

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MACROPOROUS CATALYTIC MEMBRANES FOR THREE-PHASE PROCESSES: PRINCIPLES AND APPLICATIONS

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In three-phase processes, diffusion of reactants in the pores of solid catalysts often plays an important role, negatively affecting both activity and selectivity. To minimise the internal diffusion limitations, three-phase processes are typically performed in slurry reactors with powdered catalysts. Fixed bed reactors with their relatively large catalyst particles are more attractive from the technical point of view, but have received only limited use in these processes.

We are investigating the membrane reactors to find new ways to improve the reaction performance in three-phase processes. The approach explored in this study presumes the use of *macroporous membranes* as the catalyst support of a specific type. Operated in the regime of *forced flow through the pores*, the catalytic membranes assure more intensive mass transfer compared to the diffusion-driven flow that exists inside pores of conventional catalysts; this results in the *improvements of activity and selectivity*.

With the membranes of the described type, *large working catalytic surface* can be developed in a reactor - orders of magnitude higher than that typical for classic membrane reactors where only external surface of a membrane participates in a reaction. This novel approach has been applied for hydrogenation of vegetable oils [1] and purification of water from soluble inorganic pollutants - sulfides and nitrates.

Oxidative detoxication of sulfides $S^{2-} + O_2 \rightarrow S, SO_3^{2-}, S_2O_3^{2-}, SO_4^{2-}$ is catalyzed by the sodium salt of tetra(sulfophthalocyanine)cobalt(II), briefly Co-TSPC. Although Co-TSPC is very active as homogeneous catalyst, it cannot be heterogenized over conventional porous supports in view of dramatic decrease in the activity resulting from the intraporous diffusion limitations. In our study, the macroporous catalytic membrane containing Co-TSPC has been prepared and successfully tested in the reaction, revealing high activity of the membrane-supported catalyst.

In reduction of nitrates $NO_3^- + H_2 \rightarrow NO_2^- \rightarrow N_2 \rightarrow NH_4$, nearly 100% selectivity towards the target product nitrogen is to be guaranteed to yield the standard quality drinking water. In conventional catalysis, the reaction is affected by intraporous diffusion of the reactants that negatively influences both activity and selectivity. The desired performance can be achieved by tuning the composition of palladium-based catalysts as well as their pore structure and particle size. The use of powdered catalysts in the industrial process of drinking water purification is not desirable, since the catalyst filtration becomes necessary. The catalytic membrane reactors based of the above specified type offer an attractive techno-economic alternative to the solution of the problem.

Reference:

[1] O.M.Ilinitch and F.P.Cuperus, 2nd Int. Conf. Catal. Membrane React., Moscow, 1996, p.34.

Dense catalytic membranes for fine chemical synthesis

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A survey will be given of the potentials of a recently developed type of catalytic membrane consisting of a catalyst immobilised in a dense polymer matrix. In most cases, PDMS (polydimethylsiloxane) is the polymer material of choice, because it combines mechanical, chemical and reasonable thermal stability with high permeability and affinity for the reagents. Two different kinds of catalysts can be incorporated. When homogeneous, catalytically active transition metal complexes are occluded, these membranes constitute a new way of heterogenation for such catalysts.¹ In the case of solid state catalysts, these composite membranes can improve the activity of the catalyst by improving the sorption of the reagents, excluding other compounds from interfering or allowing experimental set-ups without solvent.² Even though the reactions take place in a counter current reactor, these systems don't seem to comply with the general definition of a catalytic membrane reactor, being a combination of a heterogeneous catalyst and a permselective membrane.³ Indeed, in the first system, a homogeneous catalyst instead of a heterogeneous one is built in the membrane and more than one component has to permeate through the PDMS-membrane to make both systems work. If desired, additives can be co-immobilized in the membrane polymer and the catalyst can be regenerated easily.

The concept of this new type of catalytic membrane reactors will be highlighted and its scope and limitations will be discussed by means of selected examples. Focus will be given on how the composite membranes are synthesised and on the interactions existing between the catalysts and the membrane polymer. Reagent sorption and retention of the catalyst in the membrane will be discussed as important factors to make the catalytic performance of these membrane systems superior to their non-membrane resident counterparts. Both catalytic systems - the occluded heterogeneous catalysts and the complexes - will be discussed separately as they possess very specific requirements for synthesis, have their own difficulties under reaction conditions and possess completely different catalyst-polymer interactions.

Examples will be given in the field of oxidation reactions, epoxidations, hydroformylations and hydrogenations. The solid catalysts will be mainly zeolitic materials (TS-1, Ti-MCM-41, zeolite Y). A number of transition metal complexes will illustrate the application of the membranes in chiral synthesis.

Acknowledgments

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¹ I.F.J. Vankelecom, D. Tas, R.F. Parton, V. Van De Vyver and P.A. Jacobs, *Angew. Chem. Int. Ed. Engl.* 35 No 12 (1996) 1346.

² R.F. Parton, I.F.J. Vankelecom, M.J.A. Casselman, C.P. Bezoukhanova, J.B. Uyterhoeven and P.A. Jacobs, *Nature* 370 (1994) 541.

³ J.L. Falconer, R.D. Noble and D.P. Sperry, in: *Membrane Separations Technology Principles and Applications*, Vol. 2, eds. R.D. Noble and S.A. Stern (Elsevier, Amsterdam) ch. 14.

Photocatalytic Membrane Reactor for Removal of Chemicals and Bioaerosols from Indoor Air

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Session 2: Fine Chemicals, Biological Membranes, Low Temperature Reactions.

The most significant contaminants of indoor air are chemicals in solution in air and particulate matter in suspension in air. An effective means of removing both solvated and suspended impurities from air streams would have broad applications. A photocatalytic membrane reactor is developed to meet this challenge. The asymmetric photocatalytic membrane reactor features a thin microporous film of TiO_2 cast on a macroporous support. As the air stream flows through the membrane, the TiO_2 film functions as both a size exclusion filter and a photocatalytic layer. Results pertaining to removal of both solvated and suspended pollutants are presented.

Carbonyl compounds. Photocatalytic oxidation of ppb-levels of the common indoor air pollutants formaldehyde, acetaldehyde and acetone is reported. This is the relevant concentration range in an indoor air quality context. Operation of the photocatalytic reactor at extremely low light intensities ($\sim 0.1 \text{ mW/cm}^2$) is also explored.

Bioaerosols. The function of a photocatalytic membrane reactor as a self-sterilizing, self-cleaning filter for bioaerosols is discussed. To achieve this, three sequential steps must occur:

- 1) Separation and immobilization of bioaerosols from an air stream. Results are presented showing that aerosolized bacteria and other particulates are efficiently separated from an air stream and immobilized on a film of titanium dioxide in the photocatalytic membrane reactor via size exclusion or intercalation.
- 2) Killing of bioaerosols on the catalyst surface. The bactericidal nature of the near UV-irradiated titanium dioxide surface is explored. Enhanced killing relative to light only is documented. Microbiological assays are reported that implicate photocatalytically generated hydroxyl radicals in compromising cell membrane integrity, leading to cell death.
- 3) Oxidative decomposition of bioaerosols. Three separate experiments document the oxidative destruction of bacterial cell mass on the surface of illuminated titanium dioxide. Scanning electron microscopy experiments provide a view of the photocatalytic surface and show the disappearance of cells, batch reactor experiments demonstrate evolution of carbon dioxide during the photocatalytic oxidation of bacteria, and ^{14}C radioisotope labeling experiments demonstrate the bacteria to be the source of the carbon dioxide. The photocatalytic membrane reactor is a self-sterilizing and self-cleaning filter for removing solvated organic chemicals and suspended bioaerosols from indoor air. Removal of inorganic chemicals and particulates and deployment strategies are also discussed.

INFLUENCE OF MEMBRANE SELECTIVITY AND OPERATING CONDITIONS ON THE PERFORMANCE OF AN ENZYME UF-MEMBRANE REACTOR SYSTEM

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Ultrafiltration is one possible method when there is a need for a separation between macromolecules of different sizes. This is seen in enzyme membrane reactors, where the enzyme is used to hydrolyse proteins or to depolymerize macromolecules like heparin. In both cases the membrane is retaining the enzyme, while allowing the macromolecule to pass the membrane when its size has been reduced to that which is wanted. In this case the membrane selectivity is crucial for giving the right product. In this presentation two cases will be given:

Standard heparin which has a molecular weight of about 15.000 dalton can be improved in the antithrombotic effect by decreasing the molecular weight to about 5.000 dalton. This can be done by fractionation of the original heparin sample; however, using the enzyme heparinase to depolymerize the heparin molecules in combination with an ultrafiltration process to separate the heparin molecules from the enzyme, when the right molecular weight has been obtained seems to be a much better way. One problem however, is to find a suitable membrane which can retain the enzyme and let the heparin molecules pass through the membrane, when the molecular weight has decreased to about 5.000 dalton. From primary investigations it was found that the best membrane seemed to be a cellulose acetate membrane with a nominal cut-off value of 20.000 dalton. This membrane was used in a closed loop system, where the solution in the thermostated reactor (heparin and heparinase) was recirculated through the UF module. The total volume in the system was kept constant by adding substrate (standard heparin) at the same rate as the product (low molecular weight heparin) was permeating the membrane. In a long-term run (26 hours) steady-state was obtained after a few hours. However, due to a gradual deactivation of the enzyme it was necessary to add more enzyme at certain intervals, to keep the steady-state for the system. HPLC measurements on the total product showed that the obtained molecular weight was very close to 5.000 dalton and that the product had a very narrow molecular weight distribution ($M_w/M_n = 1.41$).

In another study an enzyme membrane reactor was characterized and optimized regarding production of a low molecular weight protein with reduced anti-allergenic properties. Sodium caseinate was hydrolysed under various operating conditions like pH, enzyme type and concentration, caseinate concentration and operating pressure. The influence of these parameters on the molecular weight distribution were measured on HPLC and quantified by measuring flux and protein concentration. Using this enzyme membrane reactor it was possible to produce a product with improved properties compared to conventional batch methods. The product had an average molecular weight of 3500 dalton with a maximum of 5000 dalton.

ABSTRACT

DEVELOPMENT OF POLYTRIMETHYLSILYLPROPYLENE BASED ORGANOPHILIC MEMBRANES FOR MEMBRANE BIOREACTOR APPLICATION.

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This paper presents the results obtained in a joint research and development project, funded by the US Departments of Energy and State through the NIS-Industrial Partnering Program, aiming at the use of pervaporation in order to reduce the cost of industrial biofuel production. The use of ethanol from biomass as a fuel is a very attractive since it can substantially reduce the threat of global warming, decrease sulphur dioxide emission, provide a number of economical advantages in a future. The National Renewable Energy Laboratory is working to make ethanol from lignocellulosic biomass, the most abundant renewable resource on earth. The use of membrane separation unit coupled to a fermenter not only acts as a means of separation, but also as a production enhancer by reducing product inhibition.

In the course of this research, the poly(trimethylsilyl-1-propyne) (PTMSP) samples having different molecular mass were synthesized by polymerization of TMSP using the catalytic systems $\text{TaCl}_5/\text{n-BuLi}$, $\text{TaCl}_5/\text{AlR}_3$ (triisobutylaluminum), and NbCl_5 . Pervaporation characteristics of PTMSP samples were examined using 6 wt% aqueous solution of ethanol, synthetic mixture, and fermentation broth. *Saccharomyces cerevisiae* D5A was used in the yeast fermentations and *Zymomonas mobilis* 39676 (NREL's proprietary strain) was used for the bacterial fermentation. Membrane cell was Minitan-S Millipore system stacked with 10 Minitan plates. The actual membrane area was about 600 cm².

A real fermentation broth contains many organic compounds. In addition to ethanol, glycerol and acetic acid are both presented at low concentrations, e.g., about 2-5 g/l. The behavior of the PTMSP membranes was studied using an ethanol/glycerol/water (6%/0.5%/93.5%) mixture, cell-free fermentation broth which contains additional organic compounds, and fermentation broth. The effect of continuous ethanol removal on the performance of the fermentation reactor has been studied in more detail. The overall fermentation reactor performance is improved by the use of pervaporation for the continuous removal of ethanol. As a result a higher level of total sugar consumption is reached.

Molecular Size Recognition with Zeolitic Membranes

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Introduction

Zeolites have been attracted much attention as a candidate for a component of inorganic membrane reactors mostly because of their unique, uniform micropore systems and catalytic properties. We have been developed a new synthetic method call "Vapor-phase Transport (VPT) method", to crystallize dry amorphous aluminosilicate gels to zeolites in gas phase[1]. Since crystallization after an amorphous thin gel layer is applied on a porous support, we anticipate that the VPT method will be applicable to synthesize a membrane on honeycombs, monoliths and so on. In this study, an MFI-type zeolitic membrane was prepared by the VPT method. Permeation behavior of various hydrocarbons through the zeolitic membrane were evaluated in the wide temperature range from 298 to 773 K.

Experimental

An MFI-type zeolitic membrane was prepared in the following procedure. A parent aluminosilicate gel suspension was prepared by mixing colloidal silica (Nissan Chemical Co., Ltd.), aluminum sulfate anhydride (Wako Pure Chem. Ind. Co., Ltd.), and a NaOH aqueous solution. The composition was 25.0 SiO₂: 1.0 Al₂O₃: 12.2 Na₂O: 600 H₂O in molar ratio. A porous, plate-like α -alumina substrate (NGK Insulators, Ltd.) was dipped in the gel suspension at 303 K for 1 day, and dried to obtain the substrate coated with the gel. The substrate had an asymmetric porous structure, and the mean pore size of the top layer was 0.1 μ m. The coated substrate was treated in vapor of triethylamine, ethylenediamine, and water at autogeneous pressure and 455 K for 4 days to crystallize zeolite at the surface of the substrate. The treated membrane was calcined in air at 773 K for 4 h.

Permeation behavior of hydrocarbon vapors such as methane, propane, toluene, m-xylene and p-xylene was investigated at 298 - 773 K. Hydrocarbons was carried with nitrogen and supplied to the feed side of the membrane. Nitrogen containing 10 ppm of oxygen was supplied to the permeation side. At the outlet of the permeation side, the oxygen concentration was measured with a zirconia oxygen meter. When a flammable component hydrocarbon, permeates through the membrane, the oxygen concentration measured should decrease with the consumption of oxygen on the surface of the zirconia sensing element.

Results and Discussion

The XRD measurement of the product showed that randomly-oriented MFI polycrystalline layer was formed as a top layer on the porous α -alumina support. However, based on the SEM observations, this top layer seemed not to be compact but to be accumulation of MFI particles. The XRD pattern measured after the removal of this top layer by mechanical polishing suggested that a composite of porous alumina and zeolite was formed. The FE-SEM views of the cross section strongly supported that this composite layer might be compact.

Table 1 summarized the permeation results at different temperatures. Permeation was performed both in the presence and absence of 7% steam. As shown in Table 1, smaller molecules like methane and propane permeates in the whole temperature range, irrespective of steam addition into the feed. On the other hand, m-xylene which has a molecular dimension slightly larger than the pore dimension of MFI zeolite was not detected in the permeate side at any temperatures tested. At room temperature, we have tested permeation of p-/m-xylene equimolar mixtures (257 and 243 ppm) and confirmed that p-xylene selectively permeated through the membrane.

Accordingly, we conclude that the MFI-type zeolitic membrane prepared in this study was pinhole-free. Separation of hydrocarbons would be possible with this zeolitic membrane in the very wide temperature range on the basis of a size exclusion mechanism. In addition, it is noteworthy that while toluene is permeable through the membrane up to 423 K, its permeation was hard to detect at 773 K. The effect of temperature on the molecular size recognition should be studied further.

Table 1 Permeation results through an MFI-type zeolitic membrane

Temperature/K		298	423	423	773	773
Water/vol%		0	0	7	0	7
		Permeation				
Gas	Oxygen (20%)	yes	yes	yes	yes	yes
	Methane(1000 ppm)	yes	yes	yes	yes	yes
	Propane (1000 ppm)	yes	yes	yes	yes	yes
	Propene (1000 ppm)	yes	yes	yes	yes	yes
	Toluene (1000 ppm)	yes	yes	yes	no	no
	p-xylene (500 ppm)	yes	-	-	-	-
	m-xylene (500 ppm)	no	no	no	no	no

References

- [1] Matsukata et al., Microporous Materials, 7(6), 299-308(1996), Stud. Surf. Sci. Catal., 105, 2195-2202 (1996), Bull. Chem. Soc. Jpn., 70(10), 2341-2356 (1997), Microporous Mater., 11, 107-116 (1997), AIChE J., 43(11A), 2724-2730 (1997)

The selective oxidation of isobutene in a membrane reactor with separate feed of reactants

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In the past years, a new type of membrane reactor has been developed. This reactor consists basically of two compartments, separated by a (catalytic active) membrane. The reactants are introduced into the reactor on opposite sides of the membrane, and will be transported into the membrane and at the position where they are contacted a reaction occurs. This concept of separate feed of reactants has some distinct advantageous above other types of gas-solid reactors for e.g. reactions that require a strict stoichiometric feed of reactants (Sloot et al. 1990) or kinetically fast, strongly exothermic heterogeneous reactions (Veldsink et al. 1992).

A new application of this type of reactor is the partial oxidation of hydrocarbons in which usually one of the intermediate products is the desired product. It may be possible to improve the selectivity towards this intermediate product, by applying a pressure difference over the two compartments. If the higher pressure is on the 'oxidation-side' of the membrane, the primary formed (and desired) product will be transported opposing to the oxidation zone and therefore it is protected against further oxidation into undesired consecutive products. This concept is tested, theoretically and experimentally for the partial oxidation of isobutene to methacrolein.

The theoretical work concerns modelling of mass-transfer accompanied with chemical reaction, where the mass-transfer in the membrane is described by the Dusty-Gas-Model. The three important structure parameters of the membrane (ε/τ , B_0 and K_0) are each determined experimentally while the physical properties of the gas mixtures are calculated from different well known semi-empirical relations. The kinetic rate expressions of the different reactions are determined from a kinetic study in a fixed bed reactor.

The partial oxidation of isobutene with separate feed of reactants was experimentally studied in two membrane reactors. In one of the reactors the separating device was an alumina membrane impregnated with the catalyst, while in the other reactor an ordinary packed bed of small active particles was placed as physical barrier for the two reactants. Isobutene/nitrogen- and air/nitrogen mixtures could be fed to both sides of the membrane respectively, and a pressure difference could be induced to shift the reaction zone and product distribution in the membrane. The principle of the reactors is illustrated in Figure 1.

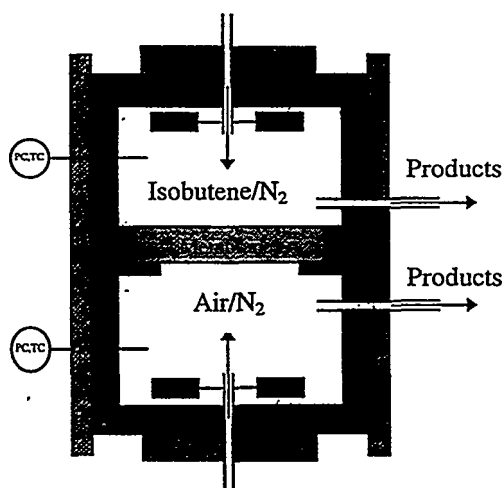


Figure 1: Schematic presentation of the membrane reactor with separate feed of

Use of Membrane Reactors for the Oxidation of Butane to Maleic Anhydride under High Butane Concentrations

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An inert membrane reactor (IMR) has been used for the oxidation of butane to maleic anhydride, under butane concentrations higher than those that can be obtained in a conventional fixed bed reactor. The typical experimental set up consisted of a IMR unit (ceramic membrane tube surrounding a bed of VPO catalyst, contained within an outer stainless steel shell), heated by a 3-zone electrical furnace. The ceramic membranes were prepared by deposition of silica or alumina onto commercial microfiltration membranes using sol-gel techniques. The catalyst bed had an annular cross section (to allow the passage of a thermocouple well), and typically contained between 2.5 and 3.5 g of catalyst. Butane was always fed to the tube side while He and O₂ could be fed to either side or to both simultaneously. All the reactant streams were mass flow controlled. The reaction products were analysed by on-line mass chromatography, with carbon and oxygen mass balances always better than 10%, and usually better than 5%.

Preliminary experiments confirmed the inertness of the membrane reactor under reaction conditions. After these experiments, the membrane reactor has been used under a wide range of operating conditions that included:

i) Different feed configurations (inert gas and oxygen), to optimize the inert gas and oxygen feed configuration by shifting He and/or O₂ from shell to tube side, ii) variable C₄/O₂ ratio, iii) variable GHSV, iv) variable temperature, in the range 375-450 °C, and v) different inert membranes (silica vs alumina-loaded membranes).

The results showed that with the IMR it was possible to operate safely under conditions that would have been within the explosion range in fixed or fluidized bed reactors. Further, the membrane was stable, as shown by prolonged (ca. 1000 h) stability tests at the reaction temperature under a steam-loaded air stream. The maximum maleic anhydride yield corresponded to operating conditions under which part of the oxygen and inert feeds shifted to the tube side, i.e., the optimum feed arrangement involves a split of the oxygen and inert feeds between shell and tube side.

During IMR operation, it was found that due to the gas pressure drop along the bed, preferential permeation of oxygen was taking place near the exit region of the reactor. This is undesirable, as it reduces the conversion and selectivity reached in the reactor. A more even permeation can be achieved by preparing membranes with a non-uniform permeability, via differential deposition of silica or alumina, and some results are also presented in this respect. It must also be taken into account that the use of high butane concentrations in the feed (so far we have used concentrations about 7 times higher than the customary 1.5% butane employed commercially), makes it possible to recycle the unconverted butane, and therefore considerably higher overall (i.e., including recycle) yields can be economically achieved.

n-Butane Oxidation to Maleic Anhydride Using Membrane Reactors

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Abstract

Conversion of n-butane (nB) to maleic anhydride (MA) by means of V-P-O catalysts is an unique catalytic reaction in terms of conversion of an alkane directly to an oxygenate. The current industrial processes for nB oxidation to MA are however carried out mostly in a relatively uneconomic way due to the low nB concentration in feed (about 1~2% of butane in air). Much effort has been made to find better processes and also to improve the performance of the catalyst over a wide range of the reaction conditions, for instance, by operating the reaction in a fuel-rich environment and/or by using a novel reactor configurations such as that of a membrane reactor. This leads to the following questions: what is the maximum MA yield obtainable and which are the important factors determining the process efficiency in terms of MA yield? In this paper, these questions are discussed in the light of theoretical calculations and experimental results.

Based on a simplified reactor model, we have evaluated the performance of an inert microporous membrane reactor in combination with the kinetic study of a commercial VPO catalyst for the catalytic oxidation of nB to MA. Parameters such as the membrane permeability, the feed compositions, the operating pressure and the dimensions of the reactor were examined. It was found that when trans-membrane flow is high, such as in the case of using a membrane with high permeability ($>10^{-5}$ mol/(m²sPa) or one with a moderate permeability but operated at high trans-membrane pressure, the reactor will behave like a plug flow reactor (PFR). The feed compositions and the ratio of nB to oxygen fed to both sides of membrane also critically affect the overall performance of the reactor. A membrane reactor only out-performs to a PFR in terms of MA yield under certain limited conditions. Experimental results obtained for the same system showed generally good agreement with those of the model calculations. The experimental studies also revealed the presence of a significant non-uniform temperature distributions within the reactor when high conversions of the oxygen were achieved. Further studies are being carried out to define the optimum reactor system and operation conditions for catalytic oxidation of nB to MA.

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Characteristics and performance in the oxidative dehydrogenation of propane of a catalytically active V-MFI zeolite membrane

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Zeolite membranes offers the exciting perspective of coupling the separation properties of a microporous material with the specific catalytic properties of zeolites. The insertion of catalytically active elements, such as transition metal ions, into the zeolite during its synthesis is an example of the potentialities of such membranes for applications in catalytic membrane reactors.

In this work, we have investigated the synthesis and characterization of V-MFI membranes supported on α Al_2O_3 tubular supports and tested their catalytic properties for the oxidative dehydrogenation of propane. This reaction is known to proceed on elemental units of V supported on oxides and the consecutive oxidation of propene as a primary product could be limited within the zeolite framework due to a minimized oxygen concentration.

The morphological, textural and single gas transport properties of the V-MFI membrane were found very similar to those of V-free MFI membranes. The vanadium species have been characterized by elemental analysis, XRD, FTIR and ESR. The single gas permeance studies demonstrated a specific ability of the V-MFI membrane to decompose alkanes between 400 and 500°C. The catalytic properties of the V-MFI membrane reactor have been studied for the oxidative dehydrogenation of propane between 400 and 650°C and compared to the performance obtained with unsupported V-based active phases and inert membrane reactor configurations. Preliminary results showed that the V-MFI membrane behaves as an efficient contactor between the reactant and the catalytic sites. Possible side effects due to zeolite acidity were also detected.

CATALYTIC MEMBRANES FOR OXIDATION UNDER MILD CONDITIONS

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Abstract

Preparation of catalytic membranes active in oxidation under mild conditions has been achieved. The ceramic material which consists of 70% Al_2O_3 , 29% ZrO_2 and 1% Y_2O_3 was used as a carrier of catalytic active compounds. The samples have the tubular form and their dimensions are the following: length 50 mm, outer diameter 11 mm, internal diameter 9 mm.

It was shown that the structure of the ceramic tubular membranes and their mechanical durability allow for their use as carriers for the immobilization of catalytically active compounds. The mechanical and chemical durability of prepared ceramic membranes increased by the incorporation of disperse silica in their structure. It was experimentally proved that the effectiveness of the modification of ceramic tubular membranes was significantly increased when dispersed silica was applied.

The selection of homogeneous catalysts for heterogenization on the surface of oxide carriers was based on published data. These catalysts were the d-metal complexes of imidazole and hemin. Investigations into the surface modification processes for aluminium and zirconium oxides by γ -aminopropyltriethoxysilane, cyanuric chloride, dihalogenalkanes, imidazole, hemin and d-metal chlorides were carried out. Several methods of application of metal complex compounds, which have to be catalytically active in the oxidation of organic compounds under mild conditions, on the surface of ceramic membranes, were developed. These methods include the following:

- adsorption grafting of active metal complexes
- chemical assembly of metal complexes on the surface
- coordinate metal complex immobilization
- encapsulation of active compounds
- chemical immobilization of metal complexes.

A variety of modified ceramic membranes were made. They differed in their surface modifications by metal complex compounds. The ranges of their thermal, chemical and hydrolytic stabilities were established.

The modified ceramic membranes obtained were tested in the reactions of cumene and methane oxidation, by molecular oxygen, in the range 25-100 °C and at atmospheric pressure. The course of the oxidation process in the presence of ceramic tubular membranes was established. The method of ceramic material surface modification significantly influences the activity of the oxidation reaction under mild conditions.

Effects of Membrane Catalysts on the Activity and Selectivity of Hydrogenation Reactions

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A significant improvement of the activity and selectivity of heterogeneously catalyzed reactions is one of the advantages expected from membrane reactors. Despite intensive efforts over the past few years, convincing demonstrations of such effects have been rare. We have prepared hydrophobic Pt-containing microporous model membranes to study their effects on reaction kinetics and selectivities of hydrogenation reactions in comparison with conventional batch reactor technology. We have found significant effects of such membranes on selected hydrogenation reaction. The TiO₂-based membranes show the same hydrogenation rate when hydrogen is fed through the alken containing liquid as conventional batch hydrogenations, while a drastic increase in hydrogenation rate occurs, when hydrogen is fed through the catalytically active membrane. In such experiments no effect of membrane catalyst on hydrogenation selectivity was noticeable. However, it was found that the micropores of the membrane could be used to effectively prevent the backmixing of initial products with the starting materials, when both, hydrogen and alkene were forced to pass through the membrane. Here, secondary reactions could be suppressed completely and surprising hydrogenation selectivities, unknown for Pt-catalysts in conventional hydrogenation reactions, were observed. Membrane preparation, characterization and hydrogenation reactions together with appropriate control experiments are here presented.

Literature:

- I.-C. Tilgner, C. Lange, H.-W. Schmidt, W. F. Maier, *CIT*, 69 (1997) 1776.
C. Lange, B. Tesche, S. Stork, W.F. Maier, *J. Catal.* 175 (1998) 280-293.

OXIDATIVE COUPLING OF METHANE USING AN OXYGEN-PERMEABLE DENSE MEMBRANE REACTOR

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Direct conversion of methane to C_{2+} hydrocarbons has been one of the most active research subjects in the catalysis field in the past 15 years. Compared to a conventional co-feed reactor, reactors with distributed feed of oxygen through a membrane or multiple injection feed points could reduce the oxygen partial pressure and thus result in higher C_2 selectivity. Ceramic materials of the Sr-Fe-Co-O system exhibit both electronic and ionic conductivities. The dense membrane reactors made of these materials allow selective passage of oxygen gas to the reaction zone, thus a cheaper oxygen source such as air, rather than pure oxygen, can be used without contaminating the product by nitrogen and nitrogen oxides.

Oxidative coupling of methane was studied with an oxygen-permeable dense membrane reactor. The dense membrane was a non-perovskite ceramic material with both oxygen ion and electron conductivities. A ceramic powder was prepared by solid state reaction of the constituent cation salts and the dense membrane tube used was made by extrusion, with a geometry of i.d. = 4.5 mm, o.d. = 6.5 mm, and length = 12-18 cm. The flux of oxygen through the dense membrane tube was measured with air fed in the shell side of the reactor module and helium in the membrane tube. The oxygen flux was about 0.04 cc(STP)/min cm^2 at 950°C under non-reaction conditions. The oxygen flux increased with an increase in either helium sweep flow rate, the air flowrate, or temperature. When methane was fed into the tube side and air into the shell side, only CO_2 with no detectable C_2 hydrocarbons was observed in these experiments at temperatures of 770 to 910°C, which suggested that the dense membrane material is a total oxidation catalyst. When reactions take place in the membrane tube, the oxygen flux was found to be about four times higher than that observed under non-reaction conditions.

La/MgO catalyst was prepared by a precipitation method as the coupling catalyst. A shell-and-tube reactor was used to study the oxidative coupling of methane. The membrane tube served as the "tube", and a quartz tube served as the shell side of the shell-and-tube reactor. Catalyst was packed inside of the dense membrane tube. Methane mixed with helium

flowed in the tube side, while air was fed to the shell side. A perovskite oxide material ($\text{BaCe}_{0.6}\text{Sm}_{0.4}\text{O}_3$) was coated on the inner wall of the dense membrane tube to reduce the total oxidation of hydrocarbons catalyzed by the dense membrane material. The oxygen flux values under non-reaction condition were only about 30% of those obtained with an un-coated dense membrane tube. Compared with the co-feed reactor configuration at the same methane conversion level, the membrane reactor gives higher C_2 selectivity in the low methane conversion region. However, the C_2 yield was still lower than that of the conventional co-feed quartz tube reactor. Although the reactor performance was improved by coating $\text{BaCe}_{0.6}\text{Sm}_{0.4}\text{O}_3$, the C_2 yield obtained was still less than that obtained by the conventional packed-bed reactor due to the fact that the surface was not completely covered by the coating material.

ELECTROCHEMICAL COUPLING OF HYDROCARBON HYDROGENATION AND WATER ELECTROLYSIS

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Abstract

In the "World Energy Network (WE-NET)" project started in Japan since 1993 as a part of the New Sunshine program led by the Ministry of International Trade and Industry (MITI), the goal is to find out the most efficient (economical) way of producing, transporting and utilizing a large amount of hydrogen. In this project, hydrogen is planned to be produced mainly by means of electrolysis in areas blessed with hydropower, solar, geothermal and wind power. Hydrogen is recently revived as clean and renewable energy source (fuel) since generating thermal power without discharging carbon dioxide, which is closely related to the global warming.

In the WE-NET project, liquid hydrocarbons such as methanol, cyclohexane and ammonia, which can be dehydrogenated and then reversibly hydrogenated, are selected as the candidates of hydrogen carriers in terms of their long-distance transportability and long-term storability. Common problem among those reaction systems is that the hydrogen evolution (dehydrogenation) reaction is limited thermodynamically. To solve such inevitable problems, we have already proposed a palladium membrane reactor which considerably improve the dehydrogenation conversion and lower the reaction temperature by selective separation of hydrogen produced during the reaction through Pd membrane.

Next target is the hydrogenation process, in which hydrogen will be supplied from water electrolysis using polymer electrolyte. Our idea is to combine the water electrolysis and hydrogenation in a polymer electrolyte cell. Such a direct hydrogenation process is expected to be more efficient because hydrogen generated on cathode during water electrolysis is in-situ utilized. On both sides of Nafion 117 membrane used for polymer electrolyte, Rh and Pt electrocatalysts were respectively deposited by means of chemical reduction and subsequent electroplating. So far, it is found that benzene could be hydrogenated to cyclohexane on the Rh electrode in a water electrolytic cell.

Mass Transfer in Gas-Filled Porous Support Structures

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- Support structures for catalytic membrane reactors (CMRs) and other inorganic membranes are generally selected to have large pores (i.e., diameters of order 0.1-1 micron) to minimize mass transfer resistance.

Nonetheless, performance of composite structures is often noticeably limited by transport through the support - e.g., when a supported CMR is itself highly permeable. To predict and correct for mass transfer through support structures, we have developed a generalized transport analysis, based on the Dusty Gas Model, that allows for surface, Knudsen and molecular diffusion, plus convection and multicomponent interactions. Calculated results have been used to identify operating regimes in which mass transfer in the support occurs primarily via individual transport mechanisms, and when such mass transfer can be expected to limit overall separation and/or reaction performance.

A Review on Hydrogen Selective Membranes - Obtained Results and Future Perspectives.

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The principle of combining a hydrogen selective membrane with a catalytic reaction such as dehydrogenation or steam reforming of hydrocarbons is attractive, because the combination of separation and catalytic reaction makes it possible to increase the conversion of equilibrium limited reactions, to influence the product-selectivity, to lower the reaction temperature and/or to reduce the required investment of downstream gas separation. However, no large scale industrial membrane reactors have emerged yet. One of the reasons being the lack of low cost membranes with sufficient mechanical strength, high stable permeabilities and selectivities towards hydrogen. Moreover, the presence of a membrane induces several process-related problems, such as the need for transport of heat to the catalytic reaction zone, and in some cases the need for regeneration of the membrane.

At Haldor Topsøe A/S we have studied the possibility of applying hydrogen selective membranes in combination with catalytic reactions. Bench scale experiments in the field of dehydrogenation and steam reforming have been carried out. In this paper we will review the results and underline the advantages and perspectives of applying a catalytic membrane reactor. A review of several process studies, where catalytic membrane processes have been compared to conventional technology, indicate however, that the membrane technology will not be feasible from an economic point of view, unless the applied membranes are optimised with respect to cost and also have very high perm selectivities.

As a result, the application of membranes mainly seems to be attractive in small scale applications. Such applications could typically be reforming of methanol or hydrocarbons for generation of pure hydrogen for fuel cells. In all cases however, the ability to manufacture membranes with high specific permeance to hydrogen is an obstacle that has to be overcome. Our experiments indicate that 1-5 micron thin supported palladium membranes have the intrinsic property of being highly permeable to hydrogen, as permeabilities in the order of $2\text{-}300 \text{ Nm}^3/\text{hr}/\text{m}^2/\text{bar}^{0.5}$ have been measured on membranes prepared in the laboratory. The selectivity of these membranes needs further improvement. At present values around 100 or more for separating nitrogen from hydrogen, are typical.

We expect that values between 1000 and 10000 should be achievable. We will then reach a situation where the cost of palladium becomes insignificant compared to the cost of other components/materials for a hydrogen generator, based upon e.g. catalytic methanol decomposition or steam reforming of LPG. The eventual application of such units is on the other hand, strongly coupled with the advances in fuel cell technology, notably with respect to the Polymer fuel cell.

Concerning larger units for the production of hydrogen or for dehydrogenation of lower alkanes, the advantages of a low cost hydrogen separation technology may not be so pronounced. Problems with supplying the heat for these endothermic processes may be overwhelming. The main challenge in membrane technology is that the ability to push beyond the "equilibrium" value is tied up with the need to supply heat for the process.

Investigation of sol-gel methods for the synthesis of VPO membrane materials adapted to the partial oxidation of n-butane

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The catalytic membrane reactor concept is of typical interest for partial oxidation reaction either by acting as a distributor (control of oxygen feeding) and/or as an active contactor (reactant/catalytic membrane). In both cases, the kinetic of the reaction may be controlled and allow a potential increase in the reaction selectivity and yield. The objective of this work is the development of a catalytically active membrane able to be used in the partial oxidation reaction of n-butane to maleic anhydride.

The largely studied vanadium phosphate (VPO) catalysts, and in particular the $(VO)_2P_2O_7$ phase, are efficient catalysts for selective oxidation of n-butane to maleic anhydride. The oxygen atoms from the VPO lattice are the main oxygen source for the reaction and are restored by the gas phase. A large number of methods have been used to prepare vanadium phosphates. It appears that both the nature of the vanadium precursor (V_2O_5 , V_4O_9 , V_2O_4 , VCl_3 ,...) and of the synthesis media (aqueous or organic) influence the structure (crystallinity rate, crystalline phases, V^{5+}/V^{4+} ratio), texture (grain sizes and morphology) and consequently the catalytic performance of the VPO catalyst. All the classical VPO synthesis methods which are based on the precipitation of VPO powders are not adapted to membrane synthesis.

In this work, we have investigated the sol-gel methods in order to prepare supported vanadium phosphate films. Two methods have been studied : the colloidal route starting either from NH_4VO_3 or $VO(OR)_3$ in aqueous media and the polymeric route starting from $VO(OR)_3$ in organic media. In both methods, homogeneous sols were obtained and deposited on/in porous tubular supports. The structure and texture of the membrane materials have been characterized by TGA, TDA, FTIR, LRS, ESR, ^{31}P NMR MAS & Spin Echo Mapping, SEM and N_2 adsorption-desorption. The main characteristics and catalytic performance of the membrane materials will be discussed and compared to those of the VPO catalysts reported in the literature.

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Preparation and Test of Inorganic Modified Porous Polymer Membranes in Gas Phase Catalysis

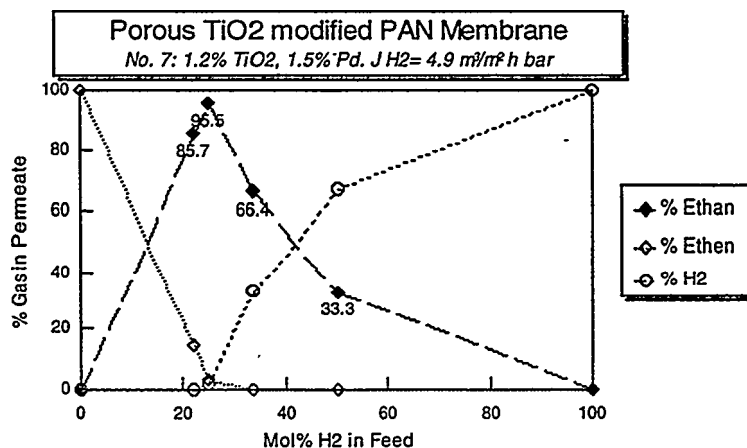
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Polymer membranes are seldom used as active membranes in catalytic membrane reactors. This may suffer from low thermal or oxidative stability during reactions, however, by selecting the appropriate polymer and reaction stability will be sufficient and the advantage of low price compared to similar inorganic membranes will favour polymer type membranes.

To start with inexpensive materials already optimised polymer membranes available at GKSS were chosen. The variety includes polyvinylidene fluoride (PVDF), polyetherimide (PEI) and polyacrylonitrile (PAN) with gas fluxes from 150 to 300 m³/m² h bar. As inorganic modifier Ti(OEt)₄ was taken. The inorganic component has a twofold meaning: (i) to narrow the pore, reduce therefore the flux and increase the selectivity (ii) to incorporate the catalyst and decouple it from the polymer environment for expected better stability to oxidation reactions. The Ti(OEt)₄ was incorporated into the pores, subsequently hydrolysed and dehydrated to TiO₂. The dry membranes were treated with Pd-salt solution and reduced with NaBH₄/MeOH solution, washed and dried. A variety of TiO₂- and Pd-concentrations are possible (PVDF: 0.5-1.8 % TiO₂; 0.2-3 % Pd; J_{N₂} ca. 200 m³/m² h bar. PEI: 0.6-3 % TiO₂; 1-2.5 % Pd; J_{N₂} = 5-90 m³/m² h bar. PAN: 0.75-1.5 % TiO₂; 0.25-3 % Pd; J_{N₂} = 0.1-30 m³/m² h bar). The fluxes of the PVDF membranes were considered to be too high even for fast reactions. Therefore, PEI and PAN membranes with the lowest fluxes were selected and used in the test reaction.

As test reaction was employed the hydrogenation of ethene to ethane. This reaction is not of industrial interest but ideal as test because it is fast, easy to perform and highly exothermic. It matches therefore the needs of examining the quality of the membranes in respect to reactivity and thermal stability. In the Figure below are summarised some results. By increasing the H₂ amount in the feed the maximum in conversion (% ethane) is detected at about 35 mol% H₂. This correlates well with the Knudsen selectivity. In other words the stoichiometric amounts (1/1) needed for complete reaction are provided by the membrane by enrichment of H₂ from 35% to 50% at the membrane interface. At higher H₂ levels in the feed the excess of H₂ permeates to the permeate side (e.g. feed 50 mol% H₂ (1/1) the permeate contains 33 mol% non-reacted H₂).



Mordenite-ZSM5-chabazite hydrophilic tubular membranes for the separation of gas-phase mixtures

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Separation of the different species contained in the exit stream from a chemical reactor constitutes one of the issues that often determine the commercial viability of new processes. A renewed interest is being focussed onto the use of microporous membranes, and among these, of zeolitic membranes for separation purposes. In general, zeolite membranes have been used for the separation of organic/organic [e.g., 1], permanent gas/vapor [e.g., 2] and water/organic (or polar/non-polar) [e.g., 3] mixtures, and separations are explained in terms of differences in kinetic diameters, adsorption strengths and relationship between the organophilic or hydrophilic character of the zeolite and the polarity of the permeating compounds.

In this work, mordenite-ZSM5-chabazite membranes were prepared by liquid phase hydrothermal synthesis onto α -alumina tubular support with 200-nm diameter pores. The hydrophilic character of the membranes prepared will be considered as their most important property. Details concerning the preparation and characterization of these membranes have been given elsewhere [4]. Gas phase separation experiments were carried out using ternary water/alcohol/O₂ mixtures, with methanol, ethanol and propanol as the alcohols. Water was the fastest permeating molecule because the hydrophilic character of the composite mordenite-ZSM5-chabazite membrane. In addition, the performance of this membrane was compared with that of a less hydrophilic, pure-ZSM5 membrane. Also, the effect of the mixture composition, temperature and total pressure on permeances and selectivities has been studied. Table 1 shows that the composite membrane was even able to separate water from methanol, the alcohol with the highest polarity. Finally, good water/propanol separation was found at temperatures up to 473 K, which can be useful for some catalytic processes.

Table 1. Water permeance and water/methanol selectivity

Membrane	H ₂ O Permeance	Water/Methanol
	[mol/(s·m ² ·Pa)]	Selectivity
ZSM-5	3.4·10 ⁻⁷	2.3
Mordenite	2.8·10 ⁻⁷	4.4

(*) Temperature= 298 K, partial pressure [kPa]: water= 2.4; propanol= 0.36

1. J. Coronas, J.L. Falconer and R.D. Noble, *AIChE J.*, **43**(7) (1997) 1797.
2. M.D. Jia, B. Chen, R.D. Noble and J.L. Falconer, *J. Membrane Sci.*, **90** (1994).
3. H. Kita, K. Horii, Y. Ohtoshi and K. Okamoto, *J. Mater. Sci. Lett.*, **14** (1995) 206.
4. M.A. Salomón, J. Coronas, M. Menéndez and J. Santamaría, *Chem. Commun.*, in press.

Fabrication of dense Pd composite membrane for hydrogen separation

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Abstract

Pd-based membranes are expected to possess high thermal and mechanical stability due to the metallic identity of palladium. Also, Pd-based membranes are expected to have appropriate hydrogen permeability and 100% hydrogen selectivity due to the unique hydrogen solubility of palladium and the solution-diffusion mechanism for hydrogen permeation through Pd films. Therefore, Pd-based membranes have the potential to separate hydrogen at high temperatures and pressures or act as a catalytic membrane reactor for the selective removal and separation of hydrogen. In order to improve hydrogen permeability of the palladium membranes, thin Pd films are required since the hydrogen flux through the membranes is expected to increase with decreasing thickness. Generally, Pd composite membranes are synthesised by coating a thin layer of palladium on a porous thermally and mechanically stable support by several methods, such as CVD, magnetron sputtering and electroless plating technique. The usual preparation method for Pd composite membranes is the electroless plating technique, which provides strong advantage such as uniformity of deposits on complex support shapes, hardness, low cost as well as very simple equipment.

However, defects in the Pd film, deposited by electroless plating technique, usually occur when the support's surface is not uniformly activated prior to electroless plating or when impurities are present in plating solution. Defects such as single pores or pinholes in the Pd layer can substantially decrease hydrogen selectivity and the efficiency of the membrane. In this work, a technique, combining electroless plating with osmosis technique, was employed to repair the defects formed during the electroless plating process or formed during the application of the composite membrane at high temperature. A significant improvement in the denseness of the Pd layer was achieved by this repair technique. For example, a Pd/ α -Al₂O₃ composite membrane was originally prepared by electroless plating technique. The permeation results with hydrogen and nitrogen showed that the hydrogen/nitrogen permeation flux ratio of the originally prepared composite membrane at 450 °C was only about 10, which implies that the composite membrane was far from dense or defect-free. However, after the composite membrane was repaired, the hydrogen/nitrogen permeation flux ratio of the repaired composite membrane was drastically increased to over 1000 without leading to obvious decrease in hydrogen permeation of the composite membrane. These facts indicate that repairing can improve the denseness of the composite membrane without causing increases in palladium film thickness. This also was confirmed by SEM characterisation before and after repairing.

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Measurements of surface exchange kinetics and chemical diffusion in dense oxygen selective membranes

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During recent years mixed oxygen ion and electron conducting materials for dense oxygen selective membranes have received increasing interest in industry. These membranes can be used for production of pure oxygen, and may be integrated directly into high temperature reactors. Particular interest has so far been on production of oxygen for synthesis gas production, however, numerous other applications are also relevant for these membranes.

In synthesis gas production the membrane will be exposed to very different chemical conditions, i.e. air on one side, and CH₄, H₂O, H₂, CO and CO₂ on the other. The large chemical gradient across the membrane, as well as thermal gradients across and along the membrane, combined with a mechanical pressure difference on the two sides, add on to the very demanding operating conditions of the membrane.

Membranes of SrFe_{1.5-x}Co_xO_y have shown promising results in terms of oxygen permeability. Very high values, in the order of 1-10 cm³/cm² min, for the oxygen flux have been reported [1] in methane conversion experiments of 1000 hours duration. So far not very much has been reported about the composition dependence of the oxygen flux.

In this work the overall oxygen transport has been studied by so-called transient thermogravimetric measurements carried out on thin membranes of SrFe_{1.5-x}Co_xO_y, x<0.5. The measured weight changes as a function of time have been fitted to a model [2] involving both bulk diffusion and surface exchange kinetics. The surface exchange reaction rate constants on the air side and on the reduced side (fuel side) have been determined, as well as the chemical diffusion in the membrane materials in the temperature range of 850-1050°C. The results will be presented and discussed in light of the membrane composition and operating conditions.

1. U. Balachandran, P. S. Maiya, B. Ma, J. T. Dusek, R. L. Mieville and J. J. Picciolo. *Development of mixed-conducting ceramic membranes for converting methane syngas*. Proc. 4th Workshop on Catalytic Membrane Reactors, Ed. R. Bredesen, May 30-31, 1997, Oslo Norway, p. 15-26.
2. J. Crank. *The mathematics of diffusion*. Oxford Science Publications, 1975 p. 61-62.

Preparation and Characterization of Nickel-modified Porous Ceramic Discs

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The Integrated Gasification Combined Cycle (IGCC) is one of the most attractive options for electricity generation from biomass or coal. Thorough gas cleaning (particles, tar, ammonia, alkali metals) of the product gas is however essential for reliable and environmentally sound operation. To obtain the highest energy efficiency, the gas cleaning should be carried out at high temperatures. In this paper we discuss the preparation and characterization of nickel-modified ceramic discs which will be used for the development of a novel high temperature biomass gas cleaning step. This could result in a further simplification of the hot gas cleaning process.

Porous α - Al_2O_3 ceramic discs were prepared by a dry-pressing procedure. The morphology, the pore volume and specific surface area of the discs were determined by scanning electron microscopy (SEM), mercury intrusion and gas adsorption, respectively. The preparative variables of the discs (additives, pressing force and calcination temperature) were tested. The pore shape of the discs was shown to be irregular because of the irregularity of the α - Al_2O_3 particles. The resulting disc had a narrow pore size distribution with an average pore size of about 20 μm and a pore volume of 0.11 cm^3/g by close packing of the 100-160 μm α - Al_2O_3 particles. A BET specific surface area of 0.4 m^2/g was available for nickel deposition.

Incorporation of nickel into the porous α - Al_2O_3 ceramic discs was performed by precipitation-deposition. In this procedure, the disc was impregnated with a salt solution containing the nickel precursor and urea as precipitant. By the in situ generation of the hydroxyl ions during the thermal decomposition of urea, the precipitation of the nickel salt can occur almost exclusively inside the pore volume of the disc. It was found that heterogeneous nucleation for the nickel precipitation could take place in the presence of the α - Al_2O_3 particles. The method parameters involving the kinetics of the nickel precipitation and the effect of the urea/nickel ratio were intensively investigated in a system of nickel salt/urea/ α - Al_2O_3 particles. The kinetics of the nickel precipitation showed an exponential curve, and attained chemical equilibrium after 24-hours reaction time. The kinetic curve was correlated by a second-order reaction equation. It was observed that the effect of the urea/nickel ratio on the nickel precipitation was related to the reaction time. The amount of nickel precipitate increased as the molar urea/nickel ratio increased, and attained a constant value when the ratio was larger than 2 with 6 hours reaction time. However with 24 hours reaction time, the amount of nickel precipitate as a function of the urea/nickel ratio displayed a peak at 1.5-1.7 molar urea/nickel ratio. The fixation degree of nickel by precipitation reached 80% at the optimum conditions.

The nickel loading in the disc can be increased by multiple precipitation-deposition cycles. The amount of nickel incorporated was 3.3 wt% in NiO by the one-time process, and increased to 11.2 wt% in NiO by the four-time process. SEM observations on a five-times impregnated sample showed that the NiO was deposited onto the pore walls of the disc. In addition, it was shown that some pore plugging in the disc occurred at those high Ni loadings. This pore obstruction is detrimental to a flow-through catalytic disc because it prevents part of the deposited catalyst from being reached by the permeating gas. For this reason, one should make a balance between a higher nickel loading and a lower pore volume.

Poster Presentations

Hydrogen Permeation Properties through Composite Membranes of Platinum Supported on Porous Alumina

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The authors have so far reported that a CVD composite membrane consisting of platinum dispersed on a porous alumina gave high hydrogen fluxes comparable to palladium-based composite membranes by CVD and electroless plating. Nevertheless, information on hydrogen permeation through platinum membranes is not enough at present and furthermore a hydrogen flux through a commercially available dense platinum membrane with a thickness of 500 μm is too low to measure without error. In this work, the hydrogen permeation mechanism of our CVD platinum membrane is discussed in comparison with a developed composite membrane of a dense thin platinum film supported on a porous alumina by electroless plating.

Using the CVD, platinum particles were dispersed in the pores of the porous alumina tube (average pore size, 200 nm) and platinum grains were coalesced on its outer surface. Considerable numbers of ten nanometers order pores existed between the grain boundaries so that all gases could permeate through via the Knudsen diffusion mechanism. On the other hand, using the electroless plating, the surface of the porous alumina was mostly covered with about 8 μm of a platinum layer, though some pinholes still remained. The ideal separation selectivities of hydrogen to nitrogen were 120 and 4.4 at 673 K for the CVD and electroless plating membranes, respectively. The Knudsen diffusion mechanism as well as solution-diffusion mechanism contributed to hydrogen permeation; therefore, true hydrogen permeation coefficient contributed by the platinum layer can be calculated on the basis that the amount of permeated hydrogen permeated via the Knudsen diffusion mechanism is 3.7 times higher than that of nitrogen. The true hydrogen fluxes were calculated to be 1.81×10^{-1} and 8.72×10^{-4} $\text{mol m}^{-2} \text{s}^{-1}$ at 673 K for the CVD and electroless plating membranes, respectively. The true hydrogen coefficient for the electroless plating membrane is consistent with both a reported value for a dense platinum membrane and experimentally obtained value for the electroless-plating membrane prepared in this work, indicating that hydrogen permeated by the traditional solution-diffusion mechanism. On the other hand, the CVD composite membrane gave 10^3 - 10^4 times higher hydrogen permeation coefficient than the electroless plating membrane. This large difference of hydrogen permeation coefficient will be resulted from difference in hydrogen transport phenomena, namely solution-diffusion and surface diffusion mechanisms. The hydrogen transport phenomena on platinum surface and the relationship between platinum structure and hydrogen permeation behavior are now being investigated.

Steam Reforming of Methane in Membrane Reactors: Comparison of Electroless-Plating and CVD Membranes and Catalyst Packing Mode

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Hydrogen and syngas are most economically produced nowadays by steam reforming, a reaction between steam and hydrocarbons, using supported nickel catalyst. As methane is a stable hydrocarbon, extremely high reaction temperatures, around 1073 K, are required for endothermic reaction ($\text{CH}_4 + \text{H}_2\text{O} = \text{CO} + 3\text{H}_2$). Carbon monoxide is further reformed with steam to carbon dioxide and hydrogen by exothermic reaction ($\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$).

If hydrogen is selectively removed from the reaction system, thermodynamic positions of these reactions are shifted to the product side, and high conversion of methane to hydrogen and carbon dioxide can be attained even at low temperatures. The produced hydrogen is free of carbon monoxide, so that it can be applied to the fuel cell with polymer electrolytes.

We have proposed a composite membrane consisting of thin palladium layer deposited on the outer surface of porous materials by electroless-plating. The palladium layer could completely cover the surface, so that only hydrogen could permeate with a 100 % selectivity. Although the electroless plating gives membranes with excellent permeability of hydrogen to enable an efficient performance of membrane reactor, some drawbacks have been pointed out: one is the embrittlement of palladium due to the formation of hydrogen-rich β -PdH phase during heating and cooling cycles, the other is high cost of palladium metal.

Firstly, a CVD technique was applied to deposit precious metals such as Pt and Ru on the surface or inside the pore (average size, 200nm) of a alumina tube at atmospheric pressure. The permeability and permeation selectivity of these CVD membranes were investigated in a comparison with electroless-plating palladium membranes, as well as the performance in membrane reactors applied to steam reforming of methane. The CVD membranes gave higher conversion of methane than thermodynamic equilibrium. The permeation of hydrogen through the CVD membranes, however, is not based on the solution-diffusion transport mechanism but on the surface diffusion mechanism. Therefore, they gave high conversion similar to electroless-plating membranes, only when the membranes showed high hydrogen selectivity.

Secondly, the effect of catalyst packing mode was investigated to save the sectional-area of membrane or to reduce the cost of membrane. The catalyst bed in a reactor was split into a hydrogen-permeation part and a non-permeation part (in front). This configuration gave higher conversion of methane with the same amount of catalyst and the same membrane area than the normal way of catalyst packing. Promotion of membrane reactor efficiency with the variation in catalyst packing is discussed in terms of computer simulations.

Rh- and Ir-Dispersed Porous Alumina Membranes and Their Hydrogen Permeation Properties

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It is well-known that palladium-based membranes are permeable solely to hydrogen. Composite membranes consisting of a thin pure palladium film supported on a porous glass or ceramics have so far been developed by the authors. Their hydrogen permeability and applicability to membrane reactor system have been also investigated. The composite membranes showed enough hydrogen permeability to be incorporated into membrane reactors; however, some drawbacks such as hydrogen embrittlement due to α - β phase transformation, rapid deactivation by impurities, e.g. sulfur compounds, and economically high cost still exist.

In the present work, rhodium and iridium were used as novel membrane materials for hydrogen separation. The composite membranes consisting of these metals dispersed in the pores of a porous alumina tube (o.d., 10 mm; i.d., 7 mm; length, 250 mm; average pore size, 200 nm) were prepared by CVD technique. $\text{Rh}(\text{acac})_3$ and $\text{Ir}(\text{acac})_3$ complexes were selected as CVD sources. Preparation conditions, especially sublimation and decomposition temperatures of the CVD sources, strongly affected membrane structure and consequently membrane performance for hydrogen separation. Under the conditions where metal particle nucleation in gas phase hardly occurs, microporous structure with pore sizes of ten nanometers order still remained for the CVD composite membranes prepared.

The hydrogen and nitrogen permeation fluxes were measured at the temperatures of 573-773 K and the pressure difference of 49-196 kPa between the feed and permeate sides. Here, the permeation side was kept at the atmospheric pressure. The hydrogen fluxes of rhodium and iridium membranes were 0.155 and 0.178 mol m⁻² s⁻¹ at 773 K at pressure difference of 98 kPa, respectively, which were comparable to those of palladium composite membranes prepared by electroless plating and CVD. At that time, ideal selectivities of hydrogen to nitrogen (SH_2/N_2) were 83 and 26 for rhodium and iridium, respectively. The hydrogen fluxes of both the composite membranes showed square-root pressure dependency. This reveals that hydrogen molecules adsorbed on metals dissociate into the atomic form and successively the hydrogen atoms diffuse through the metal layer. Higher hydrogen selectivity than the Knudsen value of 3.7 for H_2/N_2 will be resulted from contribution of selective adsorption and diffusion of hydrogen on the metallic surface.

Dehydrogenation of hydrocarbons by catalyst-membrane systems

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The system combined a catalyst and membrane selectively permeable to only one of the reagents proposed in 1964 and the advantages of that are well known now. Some later this conception was extended to the systems combining the catalytic membrane and conventional grained catalyst. It was shown in particular the sufficient intensification of some dehydrogenation reactions over grained catalysts by hydrogen selective removal through membrane. The most effective proved to be the coupling of dehydrogenation reaction ($C=D+H_2$) on grained catalyst and hydrogenation ($A+H_2=B$) on membrane catalyst surface.

The aim of the present work was to show some additional peculiarities of hydrocarbons dehydrogenation by the systems of grained and membrane catalysts.

The experiments were carried out in a plug flow-type membrane reactor with the 100 micron foil membrane of palladium alloy. The grained dehydrogenation catalyst (Cr_2O_3/Al_2O_3 or $Pt-Re/Al_2O_3$) was placed in one of the chambers where the substance C to be dehydrogenated (butane or cyclohexane, respectively) was supplied in argon flow with the rate U_C . A pure argon or its mixture with an accepting hydrogen substance A (air or pentadiene-1,3, respectively) was supplied to the other chamber with the rate V_A .

The varying of V_A value shows that hydrogen removal increases the dehydrogenation efficiency as higher as more the degree of hydrogen removal (d). Thus for butane dehydrogenation the C_4H_6/C_4H_8 ratio in dehydrogenation products increases with V_A value.

At the d value more than 0.5 the benzene yield from cyclohexane surpass the equilibrium one and at higher degrees of hydrogen removal it is possible to transform cyclohexane into benzene almost quantitatively. The maximal possible hydrogen removal degree is much higher by coupling of cyclohexane dehydrogenation with pentadiene hydrogenation.

Palladium and rhenium-containing membrane catalysts of hydrocarbon dehydrogenation

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Activated carbon is usually used as a support of many industrial catalysts. This material is very fragile and a formed carbon dust depresses the quality of the products of catalytic reaction. The aim of this work is creation of a membrane catalyst on a strong carbonaceous support with high surface area.

Palladium and rhenium containing catalysts were first prepared by infra-red irradiation of a mixture of the mentioned metals compounds and polynitriles solution. The properties of an obtained film on a membrane strongly depend on molecular mass of polymer, the film thickness and temperatures of its annealing and quenching.

The transformations of polymer with polyconjugated system production take place simultaneously with ultradispersed metal powder production. One may cover any porous thermostable membrane by thin carbonaceous layer with Pd or Re particles catalysts.

Hydrogen permeability and catalytic activity of such systems for cyclohexane dehydrogenation have been studied.

HYDROGENATION OF VEGETABLE OILS IN A THREE-PHASE CATALYTIC MEMBRANE REACTOR

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Presently, heterogeneous hydrogenation of vegetable oils, to structure the fat and to obtain a better oxidative stability, is gradually replaced by other processes such as fractionation, blending and interesterification. The reason for the replacement of the classical fat hardening process is undesired formation of trans isomers. However, hydrogenation of fats and oils is still the most versatile method to change the oil's melting behaviour and, hence, new catalysts and processes should be developed which strongly reduce the amount of trans fatty acids.

The reaction scheme for the hydrogenation of linoleic acid - the constituent of many oils - comprises a set of consecutive and parallel reactions. Besides hydrogenation of double bonds, also isomerisation reactions occur, such as cis-trans isomerisation. Therefore, several selectivities can be defined, for instance the preferred hydrogenation of linoleic acid over monoenoic fatty acids (oleic and elaidic acid) (S_I) or the tendency of a catalyst to form trans isomers rather than cis. Limited interfacial hydrogen transfer and intraparticle diffusion limitation of oil molecules have been recognized to strongly influence both S_I and the formation of trans fatty acids (TFA) [1]. Interfacial mass transfer limitation of hydrogen promotes the formation of trans fatty acids, whereas intraparticle diffusion limitation of triacylglycerols reduces S_I . New hydrogenation catalysts should guarantee high S_I and minimize formation of TFA; hence, any mass transport limitations should be avoided.

In a three-phase catalytic membrane reactor (3-CMR) explored in this study the catalyst was positioned in a very thin, $<0.1 \mu\text{m}$, layer, so that interfacial mass transfer of hydrogen was enhanced due to the presence of the catalyst in the boundary layer, and intraparticle diffusion limitation of triacylglycerols was also minimized. Additional advantages of the membrane reactor are: i) operational flexibility, for instance multipass operation with different P_{H_2} /pass, dynamic operation with periodically oscillating P_{H_2} , ii) continuous vs. batch operation, iii) operation with either premixed or separated reactants. Hence, the three-phase catalytic membrane reactor might be advantageous to use in the hydrogenation of vegetable oils.

We performed hydrogenation of sunflower oil in the 3-CMR using an inorganic membrane, which consisted of a metal support and an alumina top-layer. The membrane was a disk of 30mm diameter. The metal was coated with a top-layer of Pd on $\gamma\text{-Al}_2\text{O}_3$ as the active catalyst. In a first series of hydrogenation experiments, the CMR was operated in the packed bed mode, to test the activity and performance of the small particles of the catalyst. Hydrogenation experiments were carried out at different hydrogen pressures. At 0.3 MPa, $S_I = 4$ and TFA = 16% at iodine value IV=75. The obtained S_I corresponds well with industrial selectivities at lower temperatures ($S_I=5$), but the TFA is reduced by a factor of 2-3. The observed strong reduction of TFA in the 3-CMR looks promising. Currently, experiments are being carried out with a tubular 3-CMR that comprises Pd-loaded commercial tubular Al_2O_3 membranes with a mesoporous top-layer ($d_p=5 \text{ nm}$) and operates with hydrogen and oil separated by the membrane.

Reference:

- [1] Veldsink et al., *Catal Rev.- Sci Eng* **39**(3) 258-319 (1997).

Ethanol production in membrane distillation bioreactor

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Introduction

Many fermentations are inhibited by high product concentration that is commonly known as "end product inhibition". For ethanol fermentation the major limitation of the conventional process arises from ethanol inhibition. When the ethanol concentration of the fermentation broth reaches ca. 12 % (vol.), both specific growth and specific production rates fall down, the cell density in the fermentation remains low and concentrated sugar solution cannot be completely fermented. Therefore conventional processes of ethanol production are limited by above phenomena.

This problem may be resolved by integration of fermentator with a separator for both selective and continuous removal of the fermentation products (ethanol). The purpose of this work is to study of effect of direct-contact membrane distillation (MD) application on ethanol productivity in fermentation membrane bioreactor.

Experimental

A microporous capillary hydrophobic polypropylene (PP) membranes were used for MD. The diameters of membranes, nominal pore diameter and porosity were as follows:
 $d_{out}/d_{in} = 2.6/1.8$ mm, 0.2 micrometer and 73 %, respectively.

Two types of periodic fermentation experiments were carried out: the conventional free-cell fermentation, as the standard process and the fermentation in that produced ethanol was extracted continuously by membrane distillation from the membrane bioreactor. A commercially available dry distillery yeast (*Saccharomyces cerevisiae* - BC16a) manufactured in Poland was used as the microorganism, without earlier pre-cultivation.

Results

In the course of fermentation experiment cells deposition on the membrane surface was not observed.

The ethanol permeate flux across the PP membrane changes with ratio 1-4 kg/m²d and it was dependent on the ethanol concentration in the broth and its temperature. Two fermentation temperatures were studied - 303 and 309 K. The ethanol yield expressed by alpha coefficient (delta weight of ethanol to delta weight of sugar) in the membrane bioreactor was higher (alpha = 0.46) than using conventional fermentation (alpha = 0.35). Also in MD fermentator system the lower final sugar concentration (C_{end}) in the post-fermentation solution was obtained. For initial sugar concentration 150 g/dm³ we find C_{end} = 41 mg/dm³ without MD supporting and C_{end} = 20 mg/dm³ in MD bioreactor after 48 hrs of fermentation period.

The detailed results will be presented.

HYDRATION OF α -PINENE OVER ZEOLITES AND ACTIVATED CARBONS DISPERSED IN POLYMERIC MEMBRANES

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The acid catalysed hydration of α -pinene yields a complex mixture of monoterpenes, alcohols and hydrocarbons. By controlling the reaction variables is possible to make it selective to the terpenic alcohols, namely α -terpineol.

In previous works, the effects of extra-framework aluminium species generated in USY zeolites by hydrothermal treatments, on the isomerization and hydration of α -pinene were studied. The hydration of α -pinene over zeolite beta and modified activated carbons was also studied.

Although zeolite HY is not active for the hydration of α -pinene, zeolite beta and USY show a reasonable activity and selectivity to α -terpineol.

On the other hand, the composition of the solvent has a pronounced effect on the activity and selectivity of the catalysts. For acetone-water, when the amount of water increases selectivity to α -terpineol passes through a maximum while selectivity to the bicyclic alcohol borneol increases.

In this work, we report the performance of catalytic membranes obtained by dispersing the zeolite or activated carbon in a polymeric matrix, regarding the hydration of α -pinene.

Essentially, two types of matrixes are used: polydimethylsiloxane and polyamide. In the last case, the particles of carbon are grafted with hexamethylenediamine and incorporated in the polymer network.

Effects of solvent, membrane thickness and catalyst loading on the activity and selectivity, are studied.

Installation for production of ecologically pure hard fats by new membrane catalysts.

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It is constructed assembled and proved a block type pilot plant installation with new palladium - indium - ruthenium membrane catalyst with a porous superficial layer.

A reactor has a system of liquid reagent spiral circulation above the membrane catalyst and hydrogen introduction from outer side to central part.

The installation is tested for sunflower oil Hydrogenation eatable and perfumery into hard fats at much lower temperature than by the known catalysts. That is why the obtained hard fats are free from cancerogenic products of sunflower oil destruction. Because of mechanical strength of new catalysts the produced hard are not polluted with heavy metals.

The installation is designed for work at pressure up to 10 atm. Its productivity is 10 tons of hard fat per year and may be increased by more blocks addition.

Oxidative Dehydrogenation of Propane in an Inert Membrane Reactor

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Oxidative dehydrogenation of propane yields propene as the selective reaction product, although CO and CO₂ can also be obtained through non-selective oxidations of both propane and propene. This is a typical example of a series-parallel oxidation network with an intermediate valuable product. In such systems it is often found that the use of a low partial pressure of oxygen often favours the selective versus the nonselective reactions. An Inert Membrane Reactor (IMR), in which an inert ceramic membrane acts as an oxygen distributor to a fixed bed of catalyst can be used for this purpose.

The experimental set up consisted of a IMR unit (ceramic membrane tube surrounding a bed of V/MgO catalyst, contained within an outer stainless steel shell), heated by an electrical furnace. The catalyst bed had an annular cross section (to allow the passage of a thermocouple well), and typically contained 2.2 and 2.5 g of catalyst. The membranes used were commercial alumina microfiltration membranes (SCT) loaded with either γ -Al₂O₃ or SiO₂ by impregnation with the appropriate boehmite or silica sols. Further, the chemical inertia of the membranes at the reaction temperature was improved by the use of dopants, generally Li or Na salts (the role of the membrane is limited to oxygen distribution, without direct participation in the reaction). The membranes were characterized by mercury intrusion porosimetry, BET measurements, SEM, and permeation measurements.

The reaction experiments have included the study of the optimum reactor feed configuration (what percentage of oxygen and inert diluent should be fed to tube and shell sides), the effect of feed composition (propane to oxygen ratio, overall dilution), space time and temperature (between 450 and 550°C). The results obtained so far are promising (propene yields in excess of 15%), and they can be further improved by optimization of the membrane performance. In addition, when membranes of a suitable permeability were used (see below), the selectivities obtained at a given conversion were considerably better than those in a fixed bed reactor using the same catalyst, temperature and overall feed composition.

The best results obtained with membranes of uniform permeability correspond to membranes presenting a high pressure drop of the permeating gas, i.e., mainly silica-impregnated membranes, or alternatively inert membranes with high alumina loadings. This is due to the fact that a sufficiently high pressure drop across the membrane reduces the permeation flux maldistribution (the permeation flux increases towards the exit region of the reactor) that is caused by the pressure drop of the gas stream flowing on the tube side. Alternatively, the deviation of the permeation flux can be corrected by using a membrane with a non-uniform permeability, i.e., a membrane in which the permeance decreases along its length. Results with non-uniform membranes will also be presented at the meeting.

Vanadium-based Catalytic Membrane Reactors for the Oxidative Dehydrogenation of Propane

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Catalytic Membranes with catalytic material supported on a porous membrane tube have been described in several experimental works dealing with selective oxidations (e.g., 1-3). Theoretical works (4) have also shown that it is possible to find improvements in selectivity if the catalyst is located near one of the surfaces of the membrane. The aim of this work is to prepare a catalytic membranes for the oxidative dehydrogenation of propane and to study their performance under reaction conditions.

Several membranes have been studied, varying the amount and the radial distribution of catalyst. Two kinds of membrane have been prepared: a) V/MgO membranes, where the alumina support pores are filled with MgO by several cycles of impregnation-calcination and later impregnated with V, and b) V/Al₂O₃, where the alumina supports are impregnated with a boehmite sol before the V impregnation. In both cases the impregnation with V is carried only from the internal side of the porous tube, and for a short time, in order to achieve a radial distribution of the active material.

The effect of the operating variables on the performance under reaction conditions for the prepared membranes has been tested, varying the reaction temperature, the feed flowrate and composition and the reactor feed arrangement (i.e. the distribution of gases fed at either side of the membrane). Regarding the type of membrane, it has been found that the best V/MgO membranes are more selective but less active than the best V/Al₂O₃ membranes among those prepared to date in our laboratory.

Yields to propene up to 15% have been obtained, which can be considered as an encouraging result. Previously reported yields using catalytic membrane reactors were lower than 6%. Otherwise, it is clearly possible and necessary to optimise the method of preparation in order to obtain a better control of the of the Vanadium distribution across the membrane. There is also scope for optimization of the operating conditions, and results concerning this point will be presented at the meeting.

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1. Pantazidis, A. , Dalmon, J.A., Mirodatos, C. Catal. Today 25 (1995) 403.
 2. Herguido, J.; Lafarga, D.; Menéndez, M.; Santamaría, J.; Guimon, C., Catal. Today 25 (1995), 263.
 3. Capanelli, G., Carosini, F., Cavan, F., Monticelli, O, Trifiro, F., Chem. Eng. Sci. 51 (1996) 1817
 4. Harold, M.P., Zaspalis, V.T. Keizer, K and Burggraaf, A.T. Chem. Eng. Sci. 48 (1993) 2705

Oxygen Transfer and Reactivity of RuO₂ - SiO₂ Catalytic Membranes

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Ruthenium-based catalysts are well known as being very active in many catalytic reactions and most of the research has been done in hydrogenation ones. Many of these studies report about the influence of the metal dispersion and of the interaction of Ru with support in such processes [1]. Ru-based catalysts are also active in reactions involving active oxygen but in these cases the stability of these catalysts is very low because of its high volatility.

One of the possibilities to improve the stability of these catalysts is to incorporate Ru in very stable frame which should reduce its volatility. A solution in this sense could be the use of the sol-gel technique, in which the incorporation of the active metal could be carried out during the gelation. Previous studies concerning the preparation of the catalytic membranes containing ruthenium have already shown the advantages of this technique. Following this routine we have already reported about the preparation of thin Ru layers permeable for oxygen [2,3]. Catalytic tests carried out in the presence of isopropyl alcohol showed an increase of the stability compared with catalysts prepared by impregnation technique but also, which is very interesting, of the selectivity versus acetone.

In this paper we report on the permeability of oxygen and catalytic performances of RuO₂ - SiO₂ membranes supported on alumina. The later ones were appreciated in the oxidation of the low isoalcohols (C₃ - C₅) using air as oxidant agent. We also report the effects of the textural characteristics and reaction conditions upon the activity and selectivity of these membranes.

The catalytic membranes were prepared using sol-gel technique. SiO₂ sol was prepared by hydrolysis of tetraethoxyortosilicate (TEOS). Introduction of ruthenium was carried out by adding solutions of RuCl₃.H₂O, in ethyleneglycohol or ethyl alcohol, to the TEOS derived sol. Various ruthenium dispersions in the sol or gel oxidic phase were obtained by adding surfactants (as tetrabutylammonium bromide-TBAB) in the sol step. The content of

ruthenium in these catalysts varied in the range (1-10%). The sols, with adapted binder/plasticizer, were deposited, on microporous support using spin coating technique. After drying the membranes were calcined at 873K.

$\text{RuO}_2/\text{SiO}_2$ and Ru/SiO_2 sol-gel prepared membranes were characterised by IR and UV-Vis diffuse reflectance spectroscopy, X-ray diffraction and nitrogen adsorption-desorption isotherms. Measurements of the effective diffusion coefficients and oxygen permeability through the catalytic membranes were determined by the stationary method in a Wicke-Kallenbach cell. The oxidation of the alcohols was carried out in the gas phase using a reactor with plane membrane. The reactions were conducted under a difference of pressure between the two sides of the membrane ranging within 0-1 atm (air was introduced on the side with higher pressure) and in the temperature range 40-150 °C.

Mass transfer process through the membranes (diffusion and permeability) were found to be influenced by the pore diameters and the pressure gradient between the two sides of the reactor. The values of the effective diffusion coefficients are low compared to the permeability coefficients. Variation of the permeability with the preparation variables was significant in the case of the membranes prepared with surfactants.

The increase of the oxygen permeability and the length of the hydrocarbon chain exhibited a positive influence upon the catalytic activity. The permeability was tuned by modification of the gradient pressure and of the textural characteristics of the membranes. However, this increase was effective up to a gradient pressure between the two sides of the membrane of 60 mmH₂O and for the pore diameter lower than 2 nm. Over this limit of the gradient pressure it was determined a strong decrease of the selectivity to ketones.

The experimental data showed that the incorporation of Ru in the silica layer by sol-gel led to an activated transfer of the oxygen. One should also note that after long term experiments, the chemical analysis of the investigated membranes indicated no weight loss of ruthenium. Previous studies using impregnated Ru membranes showed that under similar conditions of pressures and temperatures a such loss occurred.

References

1. T.Lopez, P.Bosch, M.Asomoza and R.Gomez, J.Catal., 133 (1992) 247.
2. V.Pârvulescu, V.I.Pârvulescu, G.Popescu, A.Julbe, C.Guizard and L.Cot, Catal.Today, 25 (1995) 384.
3. V.Pârvulescu, V.I.Pârvulescu, Em.Angelescu and G.Popescu, *ICIM₃ '94, Proc.Third International Conference of Inorganic Membranes, Worchester, 1994*, Y.H.Ma et al.(Eds.), p.571.

CATALYST STATE IN A FIXED-BED MEMBRANE REACTOR FOR THE SELECTIVE OXIDATION OF N-BUTANE TO MALEIC ANHYDRIDE

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When combining a fixed-bed catalyst and a membrane, the catalyst may be placed in a reactive atmosphere which differs from that of a conventional reactor, and therefore behave differently [1]. This is for instance the case in dehydrogenation reactions, where the removal of hydrogen through the membrane may affect the stability of the catalyst. In the literature on membrane catalysis, few studies concern this specific behaviour.

In this contribution, a membrane is used to feed in a distributed way a reactant A in the catalyst bed (Fig. 1). Using this principle, it is possible to limit the partial pressure of A and keep a low A/B ratio, which favours the selectivity towards the primary product of addition of A to B.

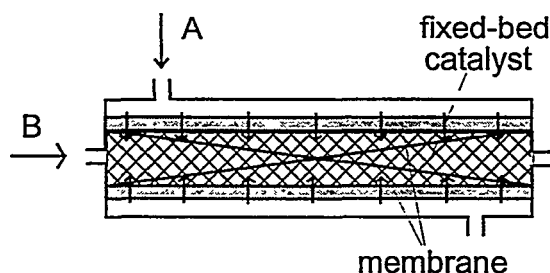


Fig. 1: Schematic of the membrane reactor

The reaction studied here is the selective oxidation of butane to maleic anhydride (MA). Oxygen (A) is distributed through a tubular zeolite membrane prepared by pore-plugging of a macroporous α -alumina commercial support [2]. Butane (B) is introduced in the fixed-bed catalyst made of a VPO mixed oxide [3].

In a first step, the catalyst bed of the membrane reactor has been modelled using the following approach and starting hypotheses:

- i) the total amount of O_2 distributed in the membrane reactor fits the conventional O_2/C_4 ratio of the reaction (i.e. $O_2/C_4 = 12$).
- ii) the catalyst bed is divided in 10 successive layers. The O_2/C_4 ratio is ca. 1 at the inlet of the membrane reactor (1st layer).
- iii) taking into account the permeability of the membrane for oxygen at 400°C (the reaction temperature), which fixes the butane flow rate and assuming for the catalyst a constant activity (as deduced from [3]), an O_2/C_4 near 20 can be calculated at the outlet of the reactor.

A conventional microreactor, fed with O_2/C_4 mixtures corresponding to different layers, has been used to simulate the local conditions of the catalyst bed of the membrane reactor. When using O_2 lean conditions (inlet of the membrane reactor), the catalyst is selective towards butane ODH and mainly consists of V^{4+} species (as shown by SEM-NMR). At the outlet (fuel-rich conditions), MA is the main product and V^{4+} and V^{5+} species are present.

The performance of the membrane reactor will be discussed on the basis of the results obtained in this simulation.

[1] J-A. Dalmon, Handbook of Heterogeneous Catalysis, G.Ertl, H.Knözinger and J.Weitkamp Eds., VCH Publ. (1997), Chapter 9.3, 1387.

[2] A. Giroir-Fendler, J. Peureux, H. Mozzanega and J-A. Dalmon, Studies Surf. Sc. Cat, Elsevier, 1996, 101A, 127.

[3] M. Abon and J-C. Volta, Appl. Cat. A, 1997, 157, 173.

PERFORMANCE OF A MEMBRANE REACTOR FOR THE COUPLING OF A DEHYDROGENATION AND A HYDROGENATION REACTION

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The coupling of the equilibrium limited dehydrogenation of cyclohexanol and the hydrogenation of cyclohexene is studied to assess the performance of a membrane reactor. For this purpose a laboratory reactor was developed consisting of two well mixed compartments separated by a planar membrane. To design and optimize the combination of chemical reaction and separation both processes have been investigated separately.

In the first part of the study the reaction kinetics of the dehydrogenation of cyclohexanol and the hydrogenation of cyclohexene were measured in a temperature range between 150°C and 200°C. $\text{Al}_2\text{O}_3/\text{Pd}$ -Pellets placed in spinning baskets served as catalyst for both reactions. The reaction kinetics of the dehydrogenation reaction could be described by a model of the Langmuir-Hinshelwood type. The hydrogenation reaction was found to be in equilibrium characterized by almost complete conversion.

Further the mass transfer through several porous membranes was investigated experimentally. Transport in the gas phase and on the surface contributes to the total flux through these membranes. To describe the transport of multicomponent gas mixtures the Dusty-Gas-Model (DGM) was applied. The parameters of this model were determined by steady state experiments. To include additional effects of surface diffusion a Generalized Stefan-Maxwell-Model (GSM) was applied. The surface diffusion coefficients of cyclohexanol and cyclohexanone were determined using transient experiments. The required adsorption isotherms of the components were measured independently. It turned out that under certain conditions the contribution of surface transport can be larger than the contribution of gas phase transport.

Considering the process of coupling reaction and transport in the membrane reactor the influence of the ratio of the two volumetric feed flow rates and the type of sweep gas (cyclohexene as reactive sweep gas or nitrogen as inert gas) were studied experimentally. Based on the numerical solution of the mass and energy balance equations formulated for both compartments of the reactor and using the above mentioned reaction and separation parameters a simulation of the process was performed. Comparing experimental conversions and simulations a good agreement was obtained. The results confirmed the fact that using a reactive sweep gas offers the potential for further increase of conversion.

EXPERIMENTAL STUDY AND NUMERICAL SIMULATION OF THE H₂/ISOBUTANE SEPARATION IN A MFI ZEOLITE MEMBRANE REACTOR

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The dehydrogenation of isobutane is an important reaction and a key step for producing isobutene, a starting material for the MTBE octane booster production. This reaction is thermodynamically limited and the use of catalytic membrane reactors can improve the isobutene yield by continuous and selective hydrogen removal through a membrane. For this application, zeolite membranes seem to be an attractive solution [1] and research efforts in order to increase stability and permeability have shown promising results [2]. A modelling of the membrane reactor is necessary in order to determine the operation process parameters for an optimal reactor performance. The complete modelling of the membrane reactor is based on a combination of the kinetics rate and mass transfer equations through the membrane, both being generally obtained in separate studies. This contribution is mainly devoted to the study of mass transport phenomena in a tubular zeolite membrane reactor in the absence of reaction.

In this work, the gas phase mass transport through the zeolite membrane is described by a generalised Maxwell-Stephan approach. The molar flux of the non adsorbable gas is obtained from the mass conservation balance. The molar flux of the adsorbed gas is modelled by using the Langmuir isotherm. The model obtained in steady state with adequate boundary conditions is made of a set of partial differential equations which is transformed into a set of algebraic equations by means of an orthogonal collocation method [3].

Separation experiments of iso-butane/hydrogen mixtures were carried out as a function of temperature. The separation factor strongly depends on temperature. At 25°C, both permeation fluxes are similar. This is a consequence of the isobutane adsorption which blocks the pores of the membrane and decreases the hydrogen transfer through the zeolite. When comparing with a mixture of n-butane/hydrogen under similar experimental conditions [3], the isobutane permeation is 15 times smaller than the n-butane one. This can be explained by the different permeation behaviour between these two isomers which have different adsorption capacities and kinetics diameters. When increasing the temperature, the isobutane occupancy decreases considerably, therefore the hydrogen flux is no longer blocked by the isobutane adsorption and increases rapidly. At 450°C (a typical temperature for isobutane dehydrogenation) high separation factors (>500) were obtained. The MFI zeolite crystal possesses channels of approximately 0.55 nm, which is comparable to the isobutane kinetic diameter (0.5 nm). This leads to the inhibition of the isobutane permeation and to the improvement of the H₂/i-C₄H₁₀ separation factor.

The performance of a fixed bed membrane reactor (zeolite membrane + conventional fixed-bed catalyst) will be discussed and compared to the model.

[1] D. Casanave, A. Giroir-Fendler, J. Sanchez, R. Loutaty and J-A. Dalmon, *Catalysis Today* 25, (1995), 309-314.

[2] A. Giroir-Fendler, J. Peureux, H. Mozzanega and J-A. Dalmon, *Studies Surf. Sc. Cat*, Elsevier, 101A, (1996), 127.

[3] H. Moueddeb, P. Ciavarella, K. Fiaty and J-A. Dalmon., submitted to *J. Memb. Sc.*

Permeation Characteristics of Butane Isomers through MFI-type Zeolitic Membranes

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MFI zeolitic membranes were prepared by a vapor-phase transport method ¹⁾ on porous α -alumina flat disks. For evaluating compactness of MFI membranes, the pervaporation of 1, 3, 5-triisopropylbenzene (TIPB), which has a kinetic diameter of 0.85 nm larger than the pore dimensions of MFI (0.53 x 0.56 nm), was carried out for 10 h at room temperature. No permeation of TIPB through an MFI membrane was detected by a FID gas chromatograph, leading to a conclusion that this membrane was pinhole-free.

The permeation behavior of pure n-butane and i-butane was studied with two types of gas permeation measurements at 300-400 K: Pressure gradient (PG) and concentration gradient (CG) methods.

In the PG method, fluxes were measured at a given pressure gradient. Fig. 1 shows the fluxes of butane isomers as a function of temperature with the PG method. The fluxes of butane isomers greatly increased with increasing pressure of the feed side. The ideal separation factor of n-butane to i-butane was, however, 2.9 at 300K and 2.3 at 400 K, respectively.

The measurements using the CG method were performed at atmospheric pressure. Helium was used as a sweep gas. Fig. 2 shows the effect of feed composition on permeance and separation factor of n/i-butane mixture at 400 K. The ideal separation factor of n-butane to i-butane reached 270, which was much greater than that in the PG method, 2.3. These results indicate that the ideal separation factor depends on the method of gas permeation. The permeation measurements of n/i-butane mixtures show that the MFI membrane prepared in this study can separate a mixture of butane isomers at 400 K. The separation factors of n-butane to i-butane were ca. 20.

1) Nishiyama, N., K. Ueyama, and M. Matsukata, *Microporous Mater.*, 7, 299-308 (1996)

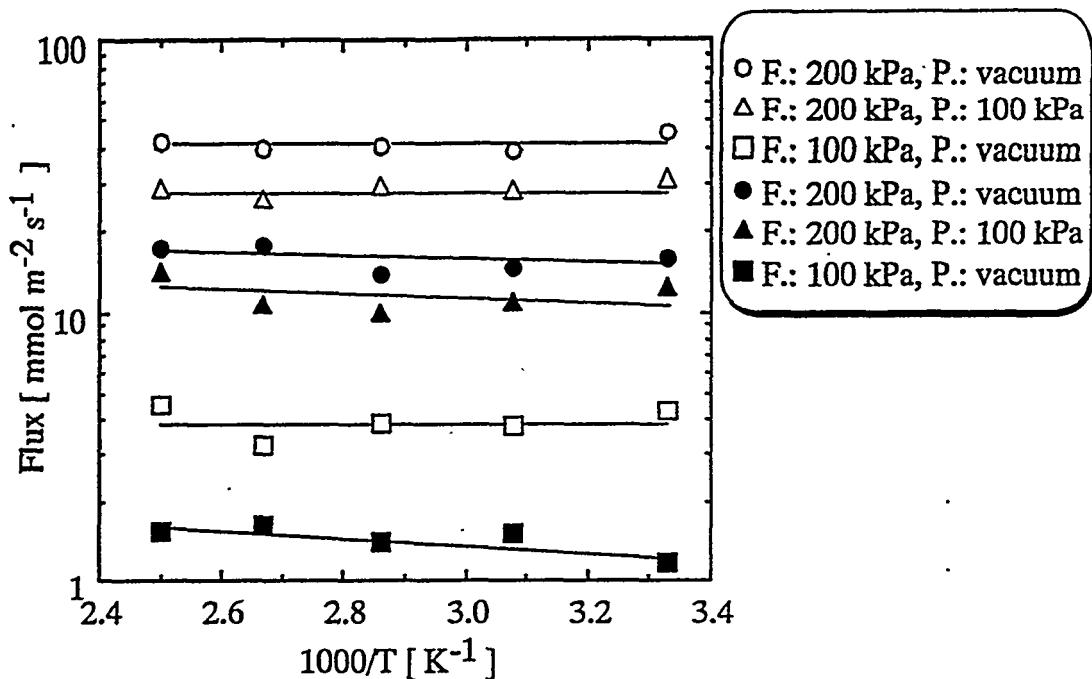


Fig. 1 Single-gas permeances through MFI membrane.
 Open key: n-butane; Solid key: i-butane.
 F.: feed side, P.: permeation side.

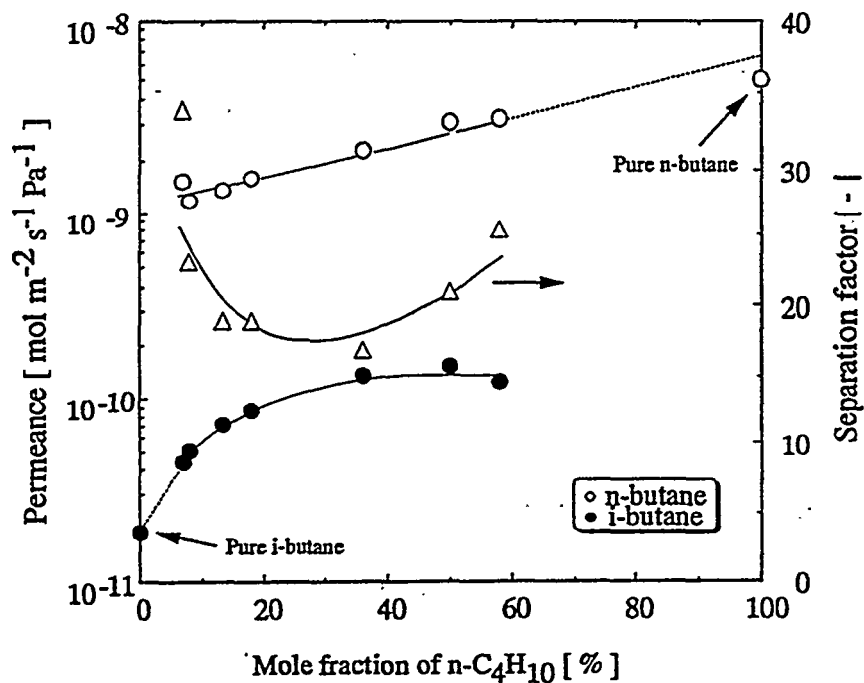


Fig. 2 Permeances and separation factor of n/i-butane mixture through MFI membrane as a function of n-butane mole fraction in the feed.
 Detection limit: Permeance $< 1.0 \times 10^{-12} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$.

Simulation and Experimental Study on the Catalytic Polymer Membrane Reactors for the Vapor-Phase MTBE (methyl tert-butyl ether) Decomposition

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Objective of this research is to develop a simulation program based on solution-diffusion model that depicts real reactions in catalytic polymer membrane reactors. A shell and tube type membrane reactor comprising heteropolyacid catalyst and polymer membrane was examined in this work for its application to the vapor-phase MTBE (methyl tert-butyl ether) decomposition. 12-tungstophosphoric acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) was used as an active catalyst for reaction. PPO (polyphenylene oxide), PSF (polysulfone) and CA (cellulose acetate) were used as membrane materials. Polymer solution was coated on the inner surface of alumina tube to form a corresponding membrane and $\text{H}_3\text{PW}_{12}\text{O}_{40}$ was packed in the tube side. The permeated stream in the shell side was continuously removed by the sweeping gas. Reaction kinetics over $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and permeabilities through each membrane were obtained prior to the simulation. Equilibrium conversions and product selectivities in a membrane reactor were compared with those in a packed bed reactor. Polymer membranes were characterized by thermal analysis and SEM.

It was revealed that all the polymer membrane reactors showed enhanced MTBE conversions compared to equilibrium conversions. PPO membrane reactor showed the best performance among three membrane reactors in terms of MTBE conversion and isobutene selectivity. Perm-selectivities of methanol to isobutene or MTBE through each polymer membrane were in the following order ; $\text{PPO} > \text{PSF} > \text{CA}$. The effects of reaction temperature, pressure and sweeping gas on the reactor performance were also investigated in a systematic way. Conversions and isobutene selectivities in a membrane reactor were increased with the increase of reaction temperature. Isobutene yields in all the membrane reactor showed the maximum points with respect to reaction temperatures. Performance of the membrane reactor was also improved with the introduction of sweeping gas.

Experimental details are now in progress to confirm the simulation results with the variation of temperature, pressure and sweeping gas flow. Taking advantage of a property that heteropolyacid catalyst is highly soluble in some solvents, a composite catalytic polymer membrane coated on the inert membrane of porous alumina tube is being designed as a new research area by using a homogeneous heteropolyacid-blended polymer solution.

Preparation and Characterization of Palladium-Based Composite Membranes From Two Synthesis Methods

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Palladium-based membranes continue to be of great interest for hydrogen recovery from hot hydrogen-containing process streams and catalytic reactions at high temperature. In this work, palladium-based composite membranes were prepared by the electroless plating and the plasma sputtering method, respectively. The membranes were characterized by scanning electron microscopy (SEM) and hydrogen permeation measurements. Furthermore, their performances in hydrogen permeation were compared.

The electroless plating procedure mainly consists of the activation of a substrate and the deposition of palladium on the pre-activated substrate. In this work the activation of porous alumina substrate was made by the sol-gel process of a palladium-modified boehmite sol. Using a plastic filter device, the deposition of palladium on the pre-activated substrate was carried out at the optimum conditions. The as-prepared palladium composite membrane with a thickness of 1 μm was gas-tight for helium at room temperature.

A single-target plasma sputtering system equipped with turbomolecular pump was used to perform the deposition of a Pd-Ag (24 wt%) alloy on the porous alumina substrate. The porous alumina substrate used in this work was commercially available microfiltration membranes with an average pore size of 1.6 μm . The surface roughness of the substrate was improved by depositing $\gamma\text{-Al}_2\text{O}_3$ coating with the sol-gel process of boehmite sol. The optimized condition (a deposition pressure of 20 mtorr and a substrate temperature of 400°C) was obtained for the deposition of the Pd-Ag alloy, resulting in the helium gas-tight Pd-Ag alloy composite membrane with a thickness of 1 μm .

The transport of hydrogen and nitrogen through two types of the palladium-based composite membranes at elevated temperatures was determined. The palladium composite membrane by electroless plating had a hydrogen flux of 1.8-87 $\text{m}^3/\text{m}^2\cdot\text{hr}$, and a hydrogen selectivity of 20-130 for H_2/N_2 at temperature 314-450°C. The palladium-silver alloy composite membrane from plasma sputtering exhibited 1.3-42.8 $\text{m}^3/\text{m}^2\cdot\text{hr}$ hydrogen flux, and 51.5-1000 hydrogen selectivity for H_2/N_2 in a temperature range of 350-450°C. It should be mentioned that the palladium composite membrane produced by the electroless plating remained stable after use in the hydrogen permeation measurements. However, the palladium-silver alloy composite membrane prepared by the plasma sputtering suffered from peeling off after use in the similar condition.

A MEMBRANE REACTOR USING CARBON FIBERS

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Abstract

Carbon fiber membrane could successfully be prepared by carbonizing hollow fibers made of polyimide and the like, and showed a large permselectivity for inorganic gases and light hydrocarbons. Carbonized materials can be stable at high temperatures and resist chemical attack, so that its application is expected to spread over not only separations of hydrocarbon mixtures but also membrane reactors. Membrane reactors, in which a chemical equilibrium shift can be realized via selective product removal, have a possibility of playing an important role in establishing an energy-efficient process in the future petrochemical and chemical industries. Carbon membrane gaining a great interest recently is one of the candidates as membrane materials with high permselectivity for membrane reactors. In this study, an application of carbon membranes to a membrane reactor is experimentally discussed.

Twenty carbonized hollow fibers (0.29 mm in diameter, 140 mm long) were bundled and located at the center of a tubular reactor (30 mm i.d.). Catalyst pellets (0.5wt% Pt/Al₂O₃) were packed in the concentric annular space. Gas permeabilities using pure gases (H₂, Ar) and mixtures (H₂ - Ar, C₆H₆ - H₂) were measured. Dehydrogenation of cyclohexane was carried out at 175 °C. The ideal separation factor measured was 69.5 for H₂/Ar at 175 °C, where hydrogen permeability was 106 cm³(STP)/min/bar. It was found that the conversion of the dehydrogenation in the carbon membrane reactor was enhanced by selective hydrogen separation.

MESOPOROUS ALUMINA TUBE WITH ASYMMETRIC STRUCTURE FOR MEMBRANE SUPPORT

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Abstract

We have already succeeded to prepare an anodic aluminum oxide tube with perforated straight pores by both internal and external anodizing methods. Thus obtained alumina membrane tube leaving metallic aluminum parts is expected to be used as a porous membrane or a support for composite membranes because of easier installation to a membrane container. One of the next interests in development of porous anodic alumina tube is to prepare one with an asymmetric structure, in which a thin layer composed of smaller pores is formed on the large pore layer. This type of structure is common in inorganic porous membranes realizing high permselectivity. In this study, therefore, an attempt to prepare an asymmetric type of porous membrane by a stepwise anodizing method was made, and the relation between the asymmetric structure of porous tube and gas permeability was examined.

An aluminum tube (99.5% purity) used was 45mm long, 0.5mm thick and 6mm in outer diameter. After pretreatment, the inside of the tube was oxidized on anode in an aqueous solution of 4wt% oxalic acid. The anodizing voltage was stepwise changed from 60 volts for first 120 min to 40 volts. The period of 40 V anodizing was changed to see a change in the structure. Next, central 13 mm of the outer aluminum and a thin barrier layer of aluminum oxide were dissolved. The gas permeation mechanism through the two mesoporous layers consisting of 68 nm- and 45 nm-pores was discussed in association to the pore structure observed by SEM.

PREPARATION OF METALLIC DOUBLE-LAYERED MEMBRANES FOR HYDROGEN SEPARATION

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Abstract

It is considered that a composite membrane composed of a thin hydrogen permeable metal layer and a macroporous support is the most promising as a hydrogen permeable membrane. However, fabricating thin metallic layers on inorganic porous supports or polymer films is accompanied by some difficulties, that is, pinholes remaining in the metal layers and cracks due to embrittlement under hydrogen atmosphere. In the present study, metallic double-layers composed of hydrogen permeable Pd alloy toplayers and less permeable Pt underlayers were deposited on nonmetallic supports in order to explore ways of obtaining thin membranes resistible to the hydrogen embrittlement.

Two kinds of supports were used: polyimide film (Kapton, 25 μ m thick, Toray Du Pont Co., Ltd.) for gas permeation experiments, and slide glass for examining the stability against hydrogen embrittlement. Metal layers were deposited at an ambient temperature by an r.f. sputtering apparatus from Pd₈₅Ag₁₅ alloy or pure Pt targets. The r.f. power was 50 W, corresponding to a deposition rate of about 0.1 nm/s. The membrane obtained was mounted in a gas permeation cell, where pure H₂ or He was introduced to the metal-deposited side of the membrane while the gas permeated to the other side was swept away with argon of 15 cm³(STP)/min. The sweep gas containing H₂ or He was analyzed by gas chromatography to determine gas permeation rates.

All the metal films with a Pd alloy thickness more than 75 nm were peeled from glass supports after exposure to hydrogen (1 atm) for an hour regardless of the presence of Pt layers. For thinner metallic membranes, although a lot of cracks were generated in the metal film without Pt underlayers after the hydrogen exposure, no cracks were found in the metallic double-layered membranes with 10-nm Pt underlayers. It is considered that stronger adhesion between Pd alloy and Pt compared with that between Pd alloy and glass results in a resistance to the hydrogen embrittlement, where the Pt layer plays a role of depressing deformation attributed to a stress generated in the Pd alloy layer during repeated absorption and desorption of hydrogen. Moreover, the hydrogen permeabilities of the Pt-inserted membranes were not so small compared with those of the membranes without Pt layers because the intermediate Pt layer was thin enough.

Use of electrocatalytic membrane reactor for synthesis of sorbitol

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During the recent years research in inorganic membrane reactors for a variety of different reactions has been intensive. Even some applications in the fields of biotechnology are described in the literature, the most important works are focussed on catalytic hydrogenation and dehydrogenation reactions. As mentioned by Zaman and Chakma (1994), the potential applications for membrane reactors included steam reforming of methane, water gas-shift and various hydrocarbons dehydrogenation. Most of these applications are studied in gas phase at high temperature.

Electrosynthesis of organic compounds is an interesting route to transform raw materials, typically the components of the biomass such as alcohols, carbohydrates, etc..., in more economically profitable products.

In this work a membrane reactor with electrocatalytic activity has been used for the electrochemical transformation of fructose and /or glucose into sorbitol, mannitol and gluconic acid at ambient temperature and atmospheric pressure with a Pt-based catalyst. The sorbitol has many applications in foodstuff and is formerly carried out on industrial scale as an electro-organic chemical process. But for economic viability this process has been replaced since the war by the catalytic hydrogenation, under pressure (50-60 bars) and at temperature between 130° and 160°C. By this way, the reduction and oxidation products are in the same reaction mixture. The membrane reactor developed in this work offers the possibilities in one hand to operate at ambient temperature and atmospheric pressure, in other hand to separate simultaneously oxidation products from reduction one. The electrochemical membrane reactor developed is constituted of two porous tubular and coaxial electrodes. Each tubes is made up of conducting particles and can be used during experiments as anode or cathode. Internal electrode is made with membrane support or support and membrane in graphite type M5 from TechSep with 6 mm inner diameter, 4 mm of thickness, 0.2 µm of pore average size and a porosity of 0.32. Another membrane support in graphite type M2 (TechSep) with 3µm of pore average diameter and porosity of 0.16 is also used. This electrode is the working electrode. The counter-electrode (external tube) is a graphite support from Union Carbide with 22 mm of inner diameter, 1.2 mm of thickness, porosity of 0.26 and an average pore diameter of 4 µm. The saturated calomel electrode (SCE) is the reference electrode. The electrolyte which is an aqueous solution of fructose or/and glucose, flowed in the annular compartment of the reactor, while anolyte and catholyte (permeate) were collected in a reservoir placed on an electronic balance and interfaced to a computer to collect and record time and mass data. The electrolyte is contained in a tank of 2 liters and its mixing was ensured by magnetic stirring bar. The entire retentate stream is recycled back to the feed reservoir. pH of the electrolyte was controlled. Samples of the catholyte and anolyte were withdrawn at different intervals and were analysed by HPLC to follow and determine the concentration of the products involved in the reaction and evaluate the products selectivity and the reaction conversion. Effect of operating parameters such as pH and temperature of electrolyte, working electrode potential, electrolyte flow rate are studied. The effect of the electrode material and structure (porosity) are also investigated.

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Ceramic Membrane Reactors for Propane Dehydrogenation: Feasibility Study on the Use of High Selective Membranes

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Due to shift of the equilibrium hydrogen selective inorganic membranes can be used to increase to conversion of gas phase dehydrogenation reactions. In several publications the results with respect to the feasibility of low selective, Knudsen diffusion type of membranes, or high selective noble metal type of membranes have been presented . Nearly all of this work predominantly concerned technical lab scale research and some general estimate of the foreseen overall process efficiency. In this study the technical and economic feasibility of inorganic membranes in enhancing the dehydrogenation of propane is being evaluated in detail on the scale of a complete production plant. The focus will be on items which seem to be important when scaling up the membrane process to commercial sizes. The influence of membrane selectivity on the process and especially the capital costs will be discussed. Furthermore coke formation on the membranes and steam stability of the membranes will be dealt with. One of the main items in using inorganic membranes in the process mentioned is the permeate pressure in combination with membrane selectivity and permeability. This pressure mainly determines the membrane area needed, but also the size of the permeate compressor system. Coke formation on the membranes under realistic conditions appears to be very strong, especially for alumina type of membranes. Also start up of the system triggers coke deposition on the membrane. Steam stability of the membrane mainly depends on the membrane material used and can be a problem for microporous membranes which are not hydrothermally stable. A reduction in propylene production costs is possible compared to a conventional dehydrogenation plant.

Study on Oxidation of n-Butane to Maleic Anhydride over Inorganic Membrane Reactor

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Inorganic membrane reactor can combine reaction and separation in single stage at high temperatures to overcome the equilibrium limitations experienced in conventional reactor configurations, they also can offer the possibility to accurately control the reactant supply to the reaction zone and to active reactant molecules. Such attractive features can be advantageously utilized in a number of reactions, such as dehydrogenations, hydrogenations, oxidations and et al. In this paper, the preparation process of stable g-AlOOH sols with ultrafine particle and narrow particle size distribution was described, the influence of preparation conditions on the quality of g-AlOOH sols and mesoporous g-Al₂O₃ membrane was investigated, and the matching relationship between the viscosity of dipping sols and structure parameters of ceramic tubes were preliminary approached. V-P-Co-Ce-O multi-component metal oxide membrane over mesoporous g-Al₂O₃ membrane was prepared by impregnation method, and was applied in a non-fuel cell type catalytic membrane reactor to study the feasibility and the reaction characteristic of n-butane oxidation to maleic anhydride.

I. preparation and characterization of g-AlOOH Sols

g-AlOOH Sols were prepared by destabilization of colloidal solutions method (DCS). First, the ground Al(OC₃H₇)₃ was dripped slowly g-AlOOH precipitate. Second, appropriate amount of HNO₃ was added into the g-AlOOH precipitated to peptize the precipitate. After aging, stable g-AlOOH Sol formed. the results of experiments indicate that the optimal preparation conditions of g-AlOOH Sol are: hydrolytic temperature = 80 °C, using HNO₃ (0.07~0.09 M) as peptizator, [H₂O] / [Al(OC₃H₇)₃] = 90 ~ 110 mol/mol, using HNO₃ as catalyst, aging temperature = 90 °C, aging time = 12 hour.

g-AlOOH Sol formed under the optimal preparation conditions possesses the smallest particles (mean particle size is about 60 nm), the narrowest particle size distribution and shortest gelation time. The colloid is Newton fluid, colloidal particles are spherical, apparent viscosity is constant, not changing with shear rate.

II. Preparation and characterization of g-Al₂O₃ membrane

The scheme of preparation procedure for supported and unsupported g-Al₂O₃ membrane is shown in Figure.1.

The optimal preparation conditions of g-Al₂O₃ membranes are: using PVA-124 as binder and glycerine as plasticizer, the viscosity of dipping sol = 89.26 mPa·s, dipping time = 10s, drying heating rate = 0.8 °C/min, calcination heating rate = 5 °C/min.

The supported g-Al₂O₃ membrane prepared under the optimal conditions is very stable, crack-free, pinhole-free and with concentrated pore size distribution.

III. Preparation and Characterization of V-P-Co-Ce-O multi-component metal oxide membrane

V-P-Co-Ce-O multi-component metal oxide membrane is prepared by impregnation method. The impregnating liquid is aqueous solution containing required catalytically active components. The impregnating liquid is used to dip-coat mesoporous g-Al₂O₃ membrane, after drying and calcination, supported V-P-Co-Ce-O multi-component metal oxide modified g-Al₂O₃ membrane is obtained. EDX results show that there are not catalytically active components in the porous supported layer, catalytically active components are constrained in the top layer. Gas (O₂, N₂ and H₂) permeation through membrane is controlled by Knudsen diffusion, while n-butane permeation through membrane is jointly controlled by Knudsen diffusion and laminar flow. XPS results show that the properties of fresh and used membrane catalyst, such as the crystalline structure, the surface oxidation state and the distribution of active oxygen species, are same as those traditional V-P-Co-Ce-O catalyst.

IV. Application of V-P-Co-Ce-O multi-component metal oxide membrane in n-butane oxidation to maleic anhydride

Enzymatic Hydrolysis of A Sunflower Oil in An Integrated Ultrafiltration and CSTR Reactor System.

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Summary

An experimental study has been carried out on an integrated reaction system consisting of a continuous stirred tank reactor (CSTR), a deemulsifier and an ultrafiltration (UF) unit for simultaneous reaction and product separation in the enzymatic hydrolysis of sun flower oil. The study focuses primarily on how UF performance and enzymatic activity are affected by different constituents in the aqueous oil hydrolysis product and by operating parameters of the integrated system. An evaluation was also conducted of the system productivity and process synergy existing between the kinetics of the hydrolytic reaction, demulsification, and product separation in the heterogeneous two phase liquid system with the free state enzyme functioning at the interface of the oil/water emulsion. In contrast to theoretical expectations, no significant gain in productivity and yield was observed in the operation reaction and separation simultaneously where the glycerol produced was continually removed from the system. This was explained by complex mass transfer processes occurring at the membrane/liquid interface and due to unsuccessful separation of the produced free fatty acids from both the deemulsified aqueous and oil phases. The reactor operating parameters were also recorded including oil/water molar ratio and impeller stirring rate and their effect upon the UF flux performance and the stability of the lipase activity was determined. The work confirmed the process synergy between the reaction and separation processes.

Key words: ultrafiltration, integrated system, simultaneous reaction and separation

Preparing and characterising palladium-silver, palladium-nickel and palladium-copper alloy membranes.

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Abstract

Palladium coated alumina membranes have high hydrogen permeability rates. Conversion in dehydrogenation reactions can be enhanced by shifting the reaction equilibrium towards the product side. Palladium is expensive, but the film cost can be reduced by alloying palladium with other suitable materials, reducing the film thickness and optimising the electroless plating process.

In the electroless plating process, various interactions exist between operating variables such as Pd source, reducing agent concentration, stabiliser concentration, temperature and buffer pH. This requires a proper choice of conditions to ensure bath stability and to maximise conversion. Conversions exceeding 80 % can be obtained after 3 hours of plating. Near optimal values (> 95 %) were also achieved within a three hour reaction period for a very specific choice of variables (optimum conditions). Surface uniformity and purity of the deposited film were excellent.

Multilayer films were prepared by successive plating steps with palladium and either silver, nickel or copper. The metal films were heat treated for 5 hours in a hydrogen atmosphere at 650 °C to promote diffusion across metal layers. A scanning electron microscope (SEM) was used to study the topography of the metal coating and cross section of the film (before and after heating). X-ray diffractometry (XRD) was used for characterising the crystal structure of the alloy coatings. Since both SEM and XRD provide only surface information, PIXE (particle induced X-ray emission) was used to extract depth information of the alloy coating. Concentration profiles across the thickness of the films were constructed. From these profiles, penetration into the support membrane pores and diffusion of the coated layers during the heating step could be determined.

A multitube membrane reactor with water cooled ends has been developed. Gas tight sealing was obtained at temperatures in the reaction zone of up to 700 °C. A maximum of four 10 mm outer diameter membranes (length 300 mm) fit into the reactor with three K-type thermocouples controlling temperature. Mass flow controllers and a syringe pump allow for both gas and liquid reactants to be fed to the reactor. Exit lines from the reactor are heated to keep products in the gas phase. A gas chromatograph (GC) and mass spectrometer (MS) are used for product analysis. The catalytic effect of metal films, without catalyst packing inside the membrane tube, has been studied. It has been found that the contribution of the film towards catalysis is small compared to that of the catalyst packing. The effect of the palladium alloy composition and film thickness on the permeability and selectivity of the film is currently being investigated.

Synthesis of zeolite A membranes: A new approach

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ABSTRACT

A new approach was used to synthesize a zeolite A (NaA) membrane. The main consideration here is to achieve a continuous crystallization front of the zeolite at the interface of the individual nutrient pools. These pools are separated by the porous wall of an alumina tube performing as the interface site and as a support. The parameters studied were, concentration, time and reversal of the source solutions. Mixtures of the nutrients were also used and results compared.

INTRODUCTION

In recent years numerous strategies have been adopted to produce a zeolite membrane, for example precipitation crystallization [1] and impregnation crystallization [2] of synthesis mixtures *on* and *in* a porous support, respectively, as well as sol/gel methods [3]. In most such cases the continuity and a constant thickness of the zeolite phase was difficult to achieve. Closure of pinholes requires additional nucleation and crystallization between existing crystals, which actually consume the nutrient phases rather than reacting inertly with respect to the local crystallization in the pinholes. It also resulted in the undesired thickening of the zeolite layer.

A classic CVD technique is used in this study. Individual nutrient pools are placed at both sides of the porous wall of the tube. When the nutrient pools become separated by the first crystal formation, crystallization stops in the crystallization front in the pores, resulting in a thin crystal layer. The driving force required to close pinholes is the very high concentration available in the separated nutrient pools from both sides of the pinhole. This technique, to our best knowledge, has not been previously used in membrane synthesis.

EXPERIMENTAL

The NaA syntheses were conducted at 80°C on α -alumina tubes (Atech Innovations GmbH), which had a wall thickness of 2 mm and an outer diameter of 10 mm. The inner and outer compartments, with the individual nutrient pools, were separated by the porous wall of the tube, and both had the same volume.

RESULTS AND DISCUSSION

The results were based on the amount of crystals grown in the wall, on the outer surface and on the inner surface of the tube, as observed by SEM. A crystal concentration gradient, probably diffusion controlled, was frequently observed across the wall, with the highest concentration of zeolite A crystals on the side of the Si source. The higher the individual nutrient concentration and/or the synthesis time, the higher was the crystal concentration at the crystallisation front. The mixtures yielded almost no crystal growth on either of the surfaces of the alumina tube.

CONCLUSIONS

The crystallisation front could be shifted by changing the concentrations of the two nutrient pools. With this technique very high nutrient concentrations can be used. It is noted that, in contrast to the mixtures, individual nutrients wet or activate the surface of the tube, thereby mediating crystal growth on the substrate particles. This is further indicated by the fact that the nucleation point of the crystals is located on the surface of the alumina particles. The absence of crystals on the support in the case of the mixtures, indicates that the nucleation in the gel phase is so much preferred that no growth could be achieved from the alumina surface itself.

REFERENCES

1. E.R. Geus, M.J. den Exter and H. van Bekkum, J. Chem. Soc. Faraday Trans. **88**, 3101 (1992).
2. Y. Yan, M.E. Davis and G.R. Cavalas, Ind. Eng. Chem. Res. **34**, 1652 (1995).
3. M. Matsukata, N. Nishiyama and K. Ueyama, Microporous Mater. **1**, 219 (1993).

Preparation and characterisation of membranes for electrochemically promoted catalysis and separations

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Abstract

An objective of this work is the development and characterisation of novel composite solid polyelectrolyte (SPE)-based membranes containing nanoparticles of catalytically-active metals, such as Pt, Ir, Pd or Cu, distributed within the polymeric matrices.

These novel composite membranes are both ionically and electronically conductive due to the presence of the metal nanoparticles. These membranes were used for catalytic processing of petrochemical mixtures, ozone generation and electrochemically promoted gas and vapour separations.

Cation- and anion-exchange flat-sheet and hollow-fibre membranes have been used. Prior to platinum deposition different pre-treatments of the membranes were carried out. These included boiling the membranes in water and mixtures of water and various alcohols. Modification of cation-exchange Nafion-like membrane surfaces by ethylene diamine (EDA) was also studied. It was shown that maximum Pt loading was achieved when membranes had been pre-treated by being boiled in a mixture of alcohols with water.

Transmission-, scanning- and atomic force electron-microscopy as well as Rutherford back-scattering (RBS) and particle-induced X-ray emission (PIXE) techniques were used to characterise the microstructures of the membranes and distribution of the metals within the membranes. Dielectric analysis has been used to examine dielectric properties of the membrane samples.

Fractal dimensions (FD) of the membrane surfaces were obtained to describe the catalytic activity of SPE-based membranes. Power spectral densities (PSD) of the surface roughnesses were also computed.

An idealised theoretical model describing ionic and electronic conductivity due to the presence of nanoparticles of Pt in the membrane is formulated.

References

- Bessarabov, D.G. et al, *Ind.Eng.Chem.Res.*, 1997, 36, 2487-2489
Bessarabov, D.G., *Membr.Techn.*, (Int.Newsletter), 1998, (# 93)
Bessarabov, D.G. et al, *Sep. & Purif. Techn.*, in press, 1998

Solid polyelectrolyte (SPE)-supported membrane reactor for anodic oxidation of organic pollutants in water

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Abstract

An objective of this work is the development and characterisation of novel composite thin-film electrodes and membranes for anodic oxidation of organic pollutants in water in a specially designed membrane reactor. The electrochemical oxidation of phenol in water as a model contaminant has been studied by means of cyclic voltammetry and UV/VIS spectroscopy using different membrane-electrode materials (Ebonex/PbO₂, Ti/SnO₂).

The catalytic films on the porous membranes were prepared by a sol-gel dip-coating technique. Best results have been obtained with doped SnO₂-films. Improvements of the conductivities of the films and higher current densities for the oxidation were obtained by doping the film sol-gel solution with 10% Sb. Cation-exchange perfluorinated membranes were used as an SPE support.

Analysis of the membrane reactor performance with an on-line fibre-optic spectrophotometer proved the electrochemical production of ·OH-radicals by using p-nitrosodimethylaniline (RNO) as a radical scavenger. Those radicals have been reported in the literature as essential for the electrochemical combustion of organics. Kinetic studies were carried out by using state of the art soft-ware.

References

- Grimm, J. et al, *Desalination*, 1998, 115, 295-302
Bessarabov, D.G., *Membr. Techn.*, (Int.Newsletter), 1998, (# 93)

PREPARATION OF BETA ZEOLITE SUPPORTED ON A CERAMIC MEMBRANE FOR THE ISOPARAFFINS/OLEFINS ALKYLATION REACTION

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Abstract

1. Introduction.

Aluminum Chloride, Boron Trifluoride, Sulfuric Acid and Hydrofluoric Acid are widely used as acid catalysts for carrying out Friedel-Crafts reactions such as hydration, hydrolysis, etherification and alkylation (1). However, the use of these acids provokes corrosion, toxicity and troubles in storing and recovering. (2,3). Alternatively, solid acids are more convenient for handling and they are less corrosive and environmentally more friendly. Materials such as mordenite, modified silicates, sulfonated zirconias and zeolites have shown good acidity and selectivity properties. Zeolites are frequently used as catalysts, as well as molecular sieves for gas separation and purification. Because of its composition and three-dimensional channel system, beta zeolite has the acidity and mass transport properties required for most of those applications.

In the last years, several research groups have developed membranes coated with zeolite films, for example ZSM-5 (4,5), MFI (6), Y (7) and silicalite (8), which have shown adequate transport and gas separation properties as well as potential catalytic properties.

On the other hand, the alkylation of isobutane with olefins is an important reaction for the obtention of high-octane compounds for ecological fuels. Among others, Beta zeolite has been employed in this reaction (9,10), which leads to high octane alkylated compounds (RON >92).

2. Experimental.

The zeolitic membranes were synthesized by "in situ" crystallization on a tubular γ -alumina support (S.C.T). The support had pore sizes of 5 and 200 nm, 25-cm length, external diameter of 1 cm and internal diameter of 0.65 cm.

The precursor gel of zeolite beta was prepared as follows: sodium hydroxide (> 99% Mallinckrodt) was dissolved in distilled water, then Aluminum (99.9%, Merck) was added to the solution, followed by stirring with slight heating until complete dissolution. A mixture of TEAOH (35% Aldrich) and potassium hydroxide (Merck) was added to the

solution and, finally, silica (Merck) was included. This preparation was stirred at room temperature until homogeneity and the resulting gel was left aging for 48 h. The hydrothermal synthesis was carried out in a stainless steel autoclave coated with Teflon lining. The γ -alumina membrane was placed inside and the sol-gel precursor was poured on the membrane, covering the whole surface. The autoclave was closed and heated at a rate of 5 °C/min until reaching 165 °C.

The synthesis was carried out in static mode under autogeneous pressure for three days. After this treatment, the autoclave was immersed in cold water and then depressurized. The zeolitic membrane was washed fully with distilled water and brushed in order to remove spare crystals from its surface. Finally it was dried at 80°C for 24 h. The procedure for the membrane preparation is shown in Figure 1

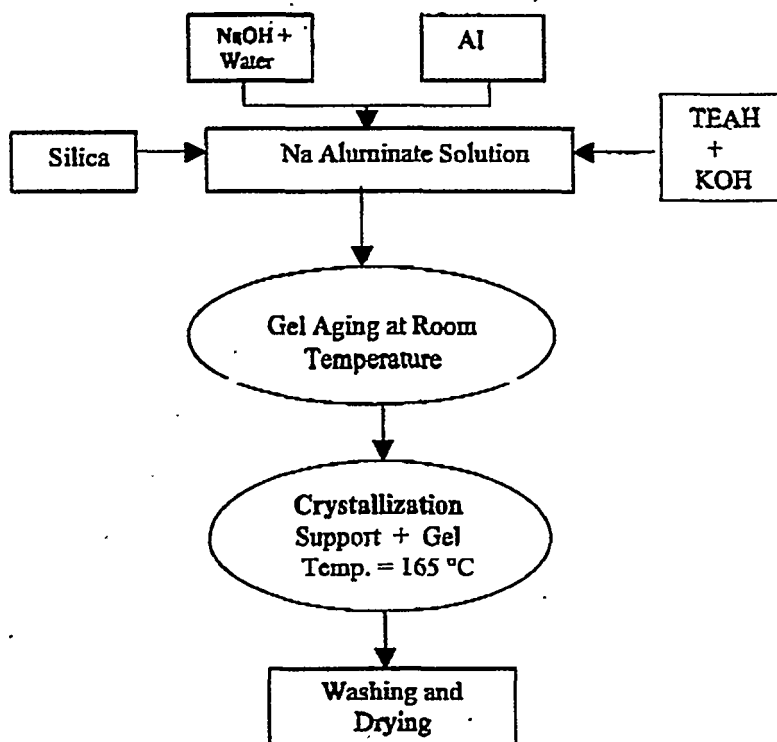


Fig. 1 Schematics for the preparation of Beta zeolite membrane by "in situ" crystallization

3. Results and discussion.

Figure 2 shows two SEM pictures of the cross section (a) and the top view surface (b) of the membrane. The dense membrane film consisted of zeolitic polycrystals which were randomly orientated. The thickness of the membrane was less than 5 μm and the particles of zeolite were 350 nm size. The observation of the material by SEM did not show any particular defect.

Figure 3 shows the X-ray diffractograms of beta zeolite with Si/Al ratios of 60 and 90, respectively.

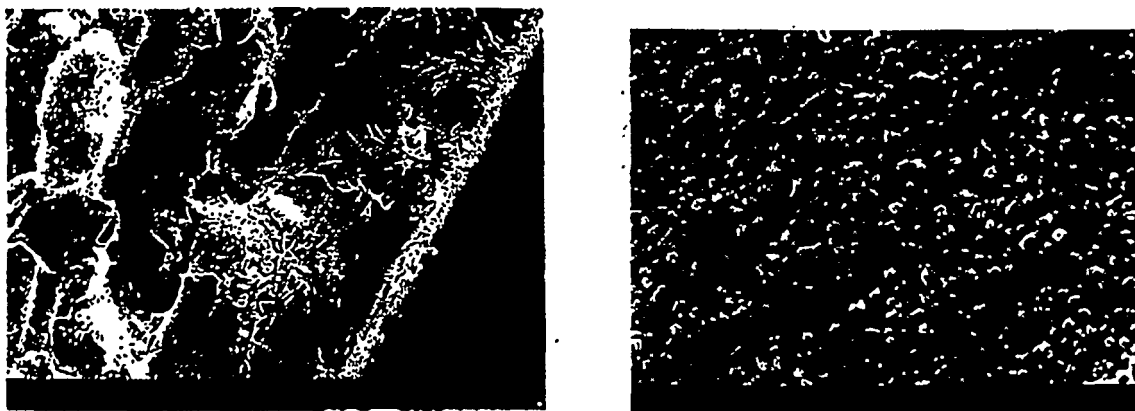


Fig. 2 Scanning Electron Micrographs (a) cross section of the membrane (b) Top view of the zeolite membrane surface.

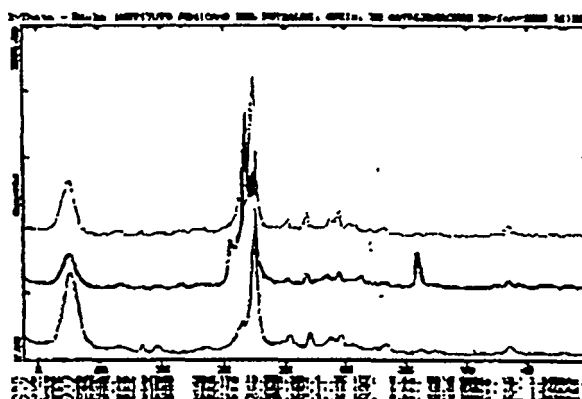


Fig.3 X- Ray diffraction pattern of beta zeolite with 60 and 90 Si/Al ratios.

4. Conclusions.

A defect-free crystalline film of beta zeolite ($< 5 \mu\text{m}$) was prepared employing two different Si/Al ratios (60 and 90). When a Si/Al ratio equal to 30 was employed some defects showed up. A zeolite beta with high Si/Al ratio should exhibit higher thermal and hydrothermal resistances and the three dimensional channel system of the zeolite should allow the diffusion of reactants through the crystal. In future work we will develop a

broaad distribution of acid sites in the zeolite framework by ionic exchanging ammonium solutions. The use of zeolite for the alkylation reaction of olefins with isoparaffins is underway and will be reported soon.

Bibliografia.

1.-George Olah

Friedel Crafts Chemistry

Chap. II., Pags.25-168

Ed. John Wiley & Sons, 1973.

2.- Pradip Rao, and Sorab R. Vatcha

Solid Acid Alkylation: Catalyst and Process Performance Criteria and R&D Guidelines

Symposium on New Chemistry With Solid- Acid Catalysts in the Alkylation of Isobutane Whith Olefins

212 Th National Meeting, American Chemical Society, Orlando, Fl, August 685-691, 25-29, 1996

3.- Avelino Corma and Agustín Martínez

Chemistry, Catalysts, and Processes for Isoparaffin-Olefin Alkylation: Actual Situation and Future trends

Catal, Rev-Sci. Eng. 35(4), 483-570 (1993)

4.- Yushan Yan, Mark E. Davis, and George R Gavalas.

Preparation of zeolite ZSM-5 Membranes by In-Situ Crystallization on Porous α -AL₂O₃.

Ind. Eng. Chem. Res. 1995, 34, 1652-1661.

5.- Joaquín Coronas, Richard D. Noble, and John Falconer

Separation of C4 and C6 Isomers in ZSM-5 Tubular Membranes

Ind. Eng. Chem. Res. 1998, 37, 166-176.

6.- Z.A.E.P. Vroon, K Keizer, M.J. Gilde, H. Verweij, A.J. Burggraaf

Transport properties of alkanes trough ceramic thin zeolite MFI membranes

Journal of Membrane Science 113 (1996) 293-300.

7.- Katsuki Kusakabe, Takahiro Kuroda, Atsushi Murata, and Shigeharu Morooka

Formation of a Y type Zeolite Membrane on a porous α -Alumina tube for Gas Separation

Ind. Eng. Chem. Res. 1997, 36, 649-655.

8.- Richard D Noble, John L. Falconer

Silicalite -1 zeolite composite membrane

Catalysis Today 25 (1995) 209-212.

9.- Hans H. Funke, Michael G. Kovalchick, John L. Falconer, and Richard D. Noble.

Separation of hydrocarbon isomer Vapors with Silicalite Zeolite
Ind. Eng. Chem. Res. 1996, 34, 1575-1582.

10- K.I. Patrylak and O.M. Taranookha

New Developments Concerning the Nature of the Zeolites Catalytic Activity and Isobutane With Butenes Alkylation Mechanism.

Symposium on New Chemistry With Solid- Acid Catalysts in the Alkylation of Isobutane With Olefins

212 Th National Meeting, American Chemical Society, Orlando, FL, August 678-681, 25-29, 1996

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