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Membrane catalysis: where is it now, what needs to be done?

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Abstract

In this overview of the topic, catalysis with metal membrane reactors is reviewed along with an assessment of what still needs to be done. This is still an emerging technology with a need for a lot of fundamental research. Palladium and palladium alloy membrane reactors are compared and discussed with regard to technology limitations and needs. Because of the limitations of palladium metal compositions, there is an emerging effort in less costly but high hydrogen permeable metal membranes such as those composed of tantalum or niobium. Finally an extended discussion is provided with regard to what are the critical issues remaining for the successful commercial application of this technology.

1. Introduction

This overview is an extension of one of the first reviews done in 1988 [1] in the area of permselective inorganic membranes. Since then we have seen hundreds of publications dealing with this topic resulting in a substantial growth of knowledge and additional information that need to be assimilated and assessed. Additional reviews [2–8] have appeared, special issues have been published on this topic, and now we have an entire international workshop focused at this topical area [9].

The driving forces behind the interest in this topic continue to be the use of membranes to catalyze reactions and also to carry out important separations. With regard to catalysis, the opportunity still exists for using a membrane to enhance certain reactions by disturbing the equilibrium product selectivity, thus shifting the steady state concentration of reactants and products away from an otherwise unfavorable equilibrium over the working catalyst. In addition the possibility exists for reacting two incompatible substrates (such as H_2 and O_2) for reactions such as oxydehydrogenation. With a permselective inorganic membrane, one can also generate pure, permeated gas having some potential by-product value. [A permselective membrane is a thin film or layer of material that can selectively pass (or permeate) one component of a mixture.] Major opportunities in membrane catalysis exist if one can use a membrane at temperatures above 200°C where most heterogeneously catalyzed processes occur [1,2].

With regard to the area of separations [3,4,10,11], permselective inorganic membranes allow one to produce ultra pure gases, because of their absolute separation performance. There is a great deal of interest in recovering additional hydrogen value within petrochemical plants while perhaps carrying out some catalysis. Further metal membrane technology has been demonstrated for hydrogen isotope extraction [12]. Membrane sep-

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aration technology is already a key part of many chemical processes, especially using polymer based membranes [4,13,14]; however these membranes are limited in operation to < 200°C.

Currently, there are three popular approaches with regard to the membrane: (1) use inorganic oxide membranes (that are size selective) to contain a catalyst, and (2) deposit a catalytic material on these inorganic oxide membranes in order to provide catalysis at the surface where separation occurs. The third alternative (3) is to use a material that preferentially allows only one gas to permeate through a permselective metal. Here there has been a great deal of pioneering work done by Gryaznov et al. [15–17] using metal membranes of palladium or silver. All these approaches will be discussed below as part of a more detailed overview of how far this field has come and where it appears to be heading. Given the page limitation imposed by the publisher, this overview can only touch upon key points and provide some examples from a large amount of literature on membrane catalysis using inorganic membranes.

2. Types of inorganic membranes

The membrane itself is an important part of any membrane catalysis. To appreciate the opportunities for catalysis, one needs to understand the types of available inorganic membranes. Unfortunately the best commercial membranes have pores of only 40 Å. Until these membranes achieve size selectivity in the sub 10-Å region, they will be of limited value for permselective membrane separations. The work by Burggraaf and co-workers [18,19] as well as that of Xu and Anderson [20] show progress in closing down these pores into the sub 10-Å region. There is a great deal of effort underway to prepare size selective [3], inorganic oxide membranes using sol gel chemistry [11,21,22]. Nonetheless such membranes do not offer absolute selectivity to one particular gas such as that offered by palladium metal. Palladium permeates only hydrogen and silver metal permeates only oxygen [23]. Solid ionic conductors [24–26] are also useful for transporting oxygen but they only perform above 600°C with limited permeability for oxygen. There has been a tidal wave of work on zeolite membranes [27,28] with over 80 publications in the last two years. Currently these materials are still relatively thick (10 microns) and sustained permselectivity has yet to be demonstrated.

In addition to the work on precipitation of fine particles of alumina or titania on mesopores supports and with zeolite membranes, there has also been some work with carbon membranes. Commercial carbon materials are mesoporous, and a great deal of fabrication capability is already available. None of these carbon membranes are truly size selective, but they are available in some continuous form suitable for use in a process. In addition, they obviously suffer from limitations with regard to O_2 exposure at high temperatures [2,29,30].

Table 1 describes some limitations of inorganic membranes which have yet to be resolved. For materials that demonstrate size selectivity at the sub 10-Å range, almost all of the research has been focused on thin disks. At some stage, one will have to worry about how to seal these membranes to a device that will feed the gases in and collect the products. Since most of the pore formation is controlled by the precipitation of inorganic oxides, these oxides themselves are chemically reactive. Many of the oxide systems suffer from instability because they are formed from metastable phases that undergo further pore development with higher temperatures. These membranes also undergo a change in porosity upon heating in steam at high temperatures [26,31].

Table 1
Status of inorganic membranes

- Available in only small sizes; scale-up to tubes an issue?
- Few definitive examples with pores < 5 Å; uniformity?
- Need method to measure such small pore sizes
- How will seal to devices be made?
- Surface reactivity with increasing temperature
- Must perform at > 200°C without changing pore size

The focus of our work has been on materials that are truly permselective to only one gas. Such a membrane provides enhanced value by generating a pure byproduct of some value (in this case hydrogen). We began much of our work by focusing on the initial advances by Gryaznov and these efforts are summarized below.

3. Catalysis with palladium membranes

Gryaznov and co-workers demonstrated [23,15–17] a number of examples for membrane catalysis using palladium metal in the form of spirals that offered high surface area. These narrow spiral tubes were not readily available to us in the United States, and in our early efforts some difficulty was encountered with regard to the durability of the spirals that were loaned to us by Professor Gryaznov. Thus, in collaboration with Professor Hank Foley (University of Delaware), a membrane reactor was developed that was composed of a palladium disk [32,33] which was held in place by knife-edge flange fittings. These allowed us to use palladium and palladium alloys foils that were much easier to obtain without having to fabricate a device with an unusual geometry. The seal to the membrane was relatively straightforward and a flow distributor was devised in order to enhance the transport of hydrogen to and through the membrane.

Early work with pure palladium membranes suffered by the different degree of expansion of the alpha and beta forms of palladium metal containing hydrogen. H_2 absorption causes the Pd lattice to expand with micro cracks developing throughout the bulk of the metal. Repeated cycling between these phases leads to embrittlement and membrane failure. Unfortunately this phase transition occurs near room temperature and is a function of the hydrogen partial pressure. To avoid this one has to operate above 300°C where the beta phase is absent. As Gryaznov discovered, one could also avoid the problems of mechanical stability by using palladium alloys. Palladium alloyed with 1–30% Ag, Rh, Ru, or rare earths shift the beta phase so that it is absent above 77°C. These alloy compositions reduce cracking and distortion due to the alpha/beta phase transition. In many cases the hydrogen permeability is reduced, but in some cases it is enhanced. Interestingly, it was demonstrated [34] that the hydrogen which permeates through the membrane is a much more surface active species (prior to re-combination of the atoms to form H_2) than hydrogen that is adsorbed on a palladium supported catalyst. We also reported a similar observation [33] by following ethylene hydrogenation over a Pd/Ru membrane at 150°C. Ethylene conversion is greater by allowing the hydrogen to permeate through the membrane rather than blending both hydrogen and ethylene together on the same side of the membrane or in a non-membrane configuration. We also observed that the permeability of hydrogen varies dramatically with the alloy composition: Pd/Ag/Ru > Pd > Pd/Ru.

Previously, we also reported that hydrogenation of some alkenes in the liquid phase is not very effective over spirals of palladium alloy [35]. Apparently the choice of the substrate is crucial. Using cyclohexene, cyclo-octadiene and cyclo-octadecene, conversions of only 2% were common and never exceeded 5% with a single spiral membrane. In contrast, facile liquid phase hydrogenations with palladium membranes are known for the conversion of acetylenic alcohols [15]. The choice of acetylenics versus selected alkenes, temperature, pressure of hydrogen, the surface area of the membrane, the sorption of the reactants/products, and/or sufficient level of active metal on the surface of the activated membrane are all factors that influence the performance of the membrane for hydrogenation. Studies in the vapor phase with the palladium alloy foil reactors indicated that butadiene was hydrogenated unselectively to give butane and butenes; interestingly toluene is not hydrogenated at all over these palladium membranes at 300°C [33].

Clearly, there are several limitations exhibited by Pd and Pd alloy membranes as catalysts. They do not provide a universal means to hydrogenate olefinic substrates. Instead one must balance reac-

Table 2
Disadvantages of Pd alloys

- Cost
- Limited availability
- Sometimes permeability is reduced
- With multiple temperature cycles, metals (such as Ru) migrate; leading to non-uniformity
- Reduce level of active Pd sites on surface of membrane
- Still require activation
- Impurities, such as CO or H_2S, still poison surface

tor conditions with alloy composition, reactor configuration and the catalysis at hand. There are a number of disadvantages associated with palladium alloys which are summarized in Table 2. Besides their cost and limited availability, the alloying element can migrate yielding non-uniform membranes. At the same time the alloying element leaves fewer active sites of palladium on the membrane surface.

Some of the disadvantages described in Table 2 for palladium alloys can be solved with additional research. However there are some inherent problems with palladium membranes that are summarized in Table 3. Hydrogen permeability is clearly a factor for low temperature reactions (less than 400°C). The alpha/beta phase transition still requires a careful purge procedure before one can lower the temperature of the membrane. Finally there may be a limitation on hydrogen transport through these membranes for kinetic reasons.

In the classic approach used by Itoh [36], he described the use of a palladium membrane containing a 0.5% Pt/alumina catalyst for the dehydrogenation of cyclohexane to benzene at 200°C and 1 atm pressure. Essentially complete conversion of cyclohexane was achieved (versus the equilibrium value of 18.7% without the membrane reactor). What is often forgotten is that a circa 15 minute residence time was required in order to obtain these conversions. Matsuda et al. [37] studied the dehydrogenation of isobutene with chromia/alumina catalyst within a palladium coated alumina tube. At 350–450°C and 1 atm total pressure with 16.7% isobutene in a tubular reactor a steady state conversion of 28.5% was achieved at 400°C. While this was measurably better than the calculated equilibrium conversion of 10.5%, or the conversion of 6% achieved experimentally with the same amount of catalyst in a conventional reactor, the results do not approach those seen with cyclohexane. It does appear that the efficiency of hydrogen transport was high in these cases. Instead the activity of the catalyst simply may not have been sufficient to sustain higher conversions. Raich and Foley suggest [38] that greater efforts need to be spent on the development of new dehydrogenation catalysts that offer higher activity per unit volume and an enhanced resistance to deactivation. Thus with more active dehydrogenation catalysts one can eliminate the activity of the catalyst as a process controlling step. Nevertheless with a membrane reactor comprising a granular catalyst within a palladium coated membrane, one has to consider all the steps that must occur to achieve both catalysis and hydrogen transport. With Pd membranes, Itoh [39] has shown that the H_2 permeation obeyed Siebert's law and the amount of dehydrogenation at the surface of the membrane was small. With a second catalyst phase over which dehydrogenation occurs, some of the hydrogen

Table 3
Inherent problems of Pd membranes

- H_2 permeability is too low at < 100°C
- Require careful purge procedure before lowering temperature
- Useful for only certain substrates
    - acetylenics instead of alkenes
    - hydrogenation of ethylene but not toluene
- Liquid phase reactions are too slow
- Competitive adsorption issues
- Low surface area for catalysis
- Sufficient transport rates for H_2?

will be swept away with the retentate stream. While the presence of a granular co-catalyst within the membrane reactor enhances the catalysis that palladium alone cannot provide, one still has to worry about sufficient transport of the hydrogen to, through and out the permeate side. Thus membranes need to be designed to transport hydrogen very efficiently, to sorb and activate the hydrogen, and to sufficiently catalyze the reaction of choice. A great deal of work has been done with palladium and its alloys, but, as with many of the systems described in this review, they are only permselective to hydrogen. Very little work has been done with oxygen permselective membranes or with membranes that might be permselective to other gases.

4. Alternative approaches

Since my earlier reviews on the topic it is clear that the field is migrating to alternative approaches beyond the earlier ones of Gryaznov et al. One can hope to reduce the cost of a membrane by depositing very thin layers of palladium onto mesoporous supports. The difficulty is that such layers must be thin, flawless, and adhere to the surface upon repeated process and temperature cycles. Kikuchi's group [40,41] has been somewhat successful in coating both palladium and palladium/silver onto mesoporous alumina supports. Kaliaguine and co-workers [42], Collins and Way [43], and Arai and co-workers [44] have also made progress in coating palladium onto a variety of supports. One still has to establish whether these approaches will have sufficient space time yields to be appropriate for commercial operation and whether they are sufficiently durable for the necessary years of operation. Other efforts include the deposition of catalyst particles onto size selective inorganic oxide membranes or to the use of non-palladium, hydrogen permselective metal membranes. Buxbaum and Marker [45] and Bend Research, Inc. [46] have pursued dense, composite membranes and these will be described in the next section.

5. Non-Pd metal membranes

There are several refractory metal membranes which offer good hydrogen permeability. These include niobium, tantalum, zirconium, or vanadium. The hydrogen permeability of these metals along with others are shown in Fig. 1. As shown in Fig. 1 several common refractory metals have much greater hydrogen permeability than palladium but have greater surface resistance to H_2 transport. Metals such as, niobium, tantalum and vanadium are stronger than palladium and are

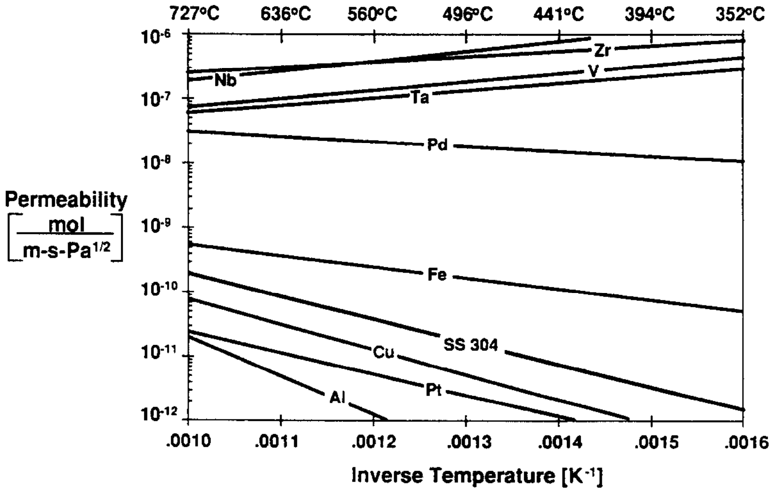

Fig. 1. Hydrogen permeability over a variety of metals as a function of temperature [45].

readily available commercially and can easily be fabricated into tubes and other shapes [45]. Makrides et al. [47] patented the use of precious metal coated refractory metal membrane for reducing surface resistance. Buxbaum has successfully used electroless palladium deposition techniques on refractory metal surfaces to enhance their hydrogen permeability. Tantalum, niobium and vanadium metal disks and tubes have been prepared with a two micron palladium coating. The coated niobium membranes did swell and embrittle at 350°C. Tantalum or vanadium metal membranes were less susceptible to embrittlement. The relative permeability was $Nb > Ta \gg V$ [45]. The hydrogen permeability factor for a palladium coated tantalum membrane was 1.0×10^{-7} mol/m·s $Pa^{1/2}$. Interestingly they report that the permeability of these membranes, like that for palladium, actually increases with temperature, which offers a distinct advantage for higher temperature chemical processes. Presently the long-term performance of these membranes is yet to be established, as well as their space time yields for various chemical reactions.

Although Pd reduces the surface resistance to H_2 dissociation, H_2 transport is slower through Pd than these refractory metals; this contributes to some loss in permeability (30–50% drop vs. pure metal). Factors which might influence the magnitude of the loss include the thickness of the Pd layer and oxide contaminants at the Pd–refractory metal interface.

Publications from Bend Research, Inc. [46] describe a composite-metal membrane that seems to offer promise for easy scale-up as well as lower cost. As shown in Fig. 2, a base metal layer is coated with thin, intermetallic diffusion barrier (such a SiO_2 applied via plasma or sol gel deposition) and hot-pressed with a thin H_2 permeable metal. These composites are claimed to offer stable flux at elevated operating temperatures, chemical compatibility with various process streams, and lower cost. Other issues remain such as the ability to fabricate a coated membrane into the appropriate shape for commercial operation, the cost of such a membrane, the seals necessary to attach these membranes to a device, the resistance of the refractory metal to embrittlement, and the durability of the palladium coating on the membrane.

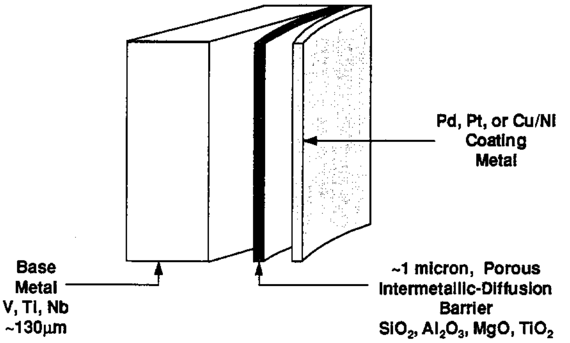

Fig. 2. Intermetallic-diffusion barrier composite membrane [46].

6. Types of catalysis

Palladium and palladium alloy membranes have been used for a variety of reactions. These include hydrogenation of alkenes and aromatics, dehydrogenation of alkanes to alkenes, the dehydrogenation of alcohols, dehydrocyclodimerization, and the hydrogenation of acetylenic alcohols [3,5,11]. One intriguing opportunity that emerges with hydrogen permselective membranes is to carry out coupled reactions. Basov and Gryaznov first demonstrated [48] this for the simultaneous endothermic dehydrogenation of cyclohexanol to cyclohexanone over one side of the membrane and the exothermic hydrogenation of phenol to the same product over the other side of the membrane. Using a Pd/Ru membrane at 137°C, he reported 39% conversion of phenol with 95% selectivity to the ketone. In this case one never has to handle the hydrogen since it is consumed by the dehydrogenation reaction as soon as the H_2 permeates the membrane. There ought to be more opportunities like this available to demonstrate the potential utility of this concept; however it is specific to a certain pair of reactions which limits its utility. In a related experiment Ito et al. showed [49] that one could enhance the dehydrogenation reaction of cyclohexane fed over a 0.5% Pt/Al_2O_3 catalyst contained within a tubular palladium membrane

Table 4
Types of materials for membrane reactors

Type	Permselective?	Limits?	Status [a]
● Polymer	Yes	Temperature	Com
● Zeolite in polymer	No	Temperature	Dev
● Permselective metal	Yes	Brittle; cost, etc.	Com
● Solid inorganic oxide	Yes	Need lower temp.	Dev
● Porous oxide	No	Thermal stability	Com
● Thin coating on any above	Yes/no	Thickness; durability	Fund

[a] For membrane availability: Com = commercial; Dev = development; Fund = fundamental research.

by replacing the argon sweep on the permeate side with 10% O_2/argon. Compared to the equilibrium value of 19% for this reaction at 200°C, the conversion now jumps from 50% with the argon sweep to >99% with the O_2/argon sweep. They suggest that the exothermic generation of water serves to enhance the conversion of the reaction. This is an approach which can be used in a number of examples to enhance dehydrogenation reactions, and in this regard it is similar to oxydehydrogenation reactions.

Table 4 summarizes the current status of a variety of membrane materials potentially useful for membrane catalysis. The relative permselectivity features are shown with some indication of the crucial limitations to the application of these membrane devices. The final column of Table 4 summarizes the commercial availability of the membranes themselves. This last column does not refer to the status of their use as a membrane reactor but simply to the availability of the membrane so that others can evaluate it in membrane reactor configurations. One observes that there is an entire spectrum of research work in this area ranging from very fundamental through commercially developed membrane systems.

7. Critical needs and issues

Since my review articles in 1988 [1] and 1992 [2], progress has been made in the field but many critical issues still remain unresolved and deserving of more attention. In the past I have highlighted the major challenges remaining for membranes to be used in catalytic devices. These include:

- Need for crack-free, uniform, sub 8-Å microporous inorganic membranes which are:
  - stable to extended use from 200–600°C;
  - chemically inert.
- Fabrication of very thin, flaw-free layers over large areas.
- Sealing the membrane into a device operating at >250°C:
  - high temperature seals needed.
- Adherence of membrane layer to support under repetitive temperature cycling.
- Use of large amounts of sweep gas.
- Limited availability of microporous (<10 Å) inorganic membranes.
- Susceptibility to poisoning and fouling.
- As pores get smaller, permeability decreases.
- Pd offers limited activity for a variety of hydrogenations.
- Techniques for measuring pore sizes.
- Limitations of Pd to only H_2 permselectivity.

These issues are elaborated in greater detail in ref. [2]. Given this imposing list of challenges, it is necessary to focus in on the most important issues that really need to be resolved. The following high priority issues are what this author believes are the most important issues that need to be resolved in order for the field to move into commercial practice. *More attention needs to be spent on collecting real performance data with real membrane catalytic systems.* A great deal of effort has been spent accumulating simulation data and trying to estimate performance; now we need to see whether that performance lives up to its expectations. Clearly membrane catalysis as it applies to hydrogenation and dehydrogenation reactions has been shown repeatedly; what remains to be done is *to demonstrate that there are other conceptual applications of this technology that offer real value.* Research in this area should focus on distinctive product opportunities where the unique capabilities of catalytic membrane reactors can be exploited to produce a value added product. Additional research in the field of membrane catalysis really should address the major challenges highlighted above. In particular, inorganic membranes are not going to work in catalytic reactors unless one can *generate inorganic membranes with sub 8-Å pores in a reproducible manner.* Any process for preparing a mesoporous, inorganic oxide or pore size selective membrane *must ultimately be scalable to the sizes anticipated in commercial units with reasonable cost/performance attributes.* Future fundamental work *with dense metal oxides for transporting oxygen should be focused* at the key barrier: the need to come up with membranes *that perform at* $<500°C$ because of issues of materials of construction and the added heat needed to drive the membrane performance. Another key critical issue is how to handle the need (and process issues, as well as cost) *for a sweep gas in a membrane reactor.* One certainly cannot afford to apply a vacuum to the permeate side in order to get the large pressure differences needed to drive membrane separation processes, so instead a sweep gas is used. However the cost of the sweep gas can be a factor and this needs to be considered carefully in any proposed application of a membrane catalytic reactor. Interestingly the field is shifting towards thinner membranes where there is certainly is an obvious need, but *what is the maximum thickness of any membrane coating*? Clearly 50 to 100 micron coatings are much too thick to permit sufficient flux of any permeate stream, but what is the maximum coating needed for a particular system? Is it 1 micron or 100 Ångstroms? Finally one question raised in 1992 still remains largely unanswered. If membranes for size selective separations are going to be used, *better techniques are needed to measure the pore sizes of these membranes.* It is exceedingly difficult to accurately measure porosity below 10 Å even for a powdered material. Some advances [50] are being made in using a variety of models to solve this dilemma, but in their absence the performance of a membrane to pure gases is still the best way of determining its size selectivity. However, this can be deceptive because combinations of certain gases often do not perform like the individual pure gases themselves.

Table 5
High priority challenges which need to be addressed

- Produce flawless, uniform <8 Å pores, reproducibly
- Ability to scale any size selective inorganic oxide membrane
- Produce dense oxides which transport O_2 rapidly $<500°C$
- How to handle need [and process issues, cost] for sweep gas
- Better techniques to measure membrane pore sizes at <10 Å
- What is the maximum thickness of any membrane coating?

8. Conclusion

From this summary and analysis on membrane catalysis given above one can see that there are certainly lots of opportunities and lots of promise, but there are lots of hurdles. Researchers in the field need to drive at what the critical issues are with regard to advancing the technology and others need to be worried about developing any of these fundamental membrane devices into commercial operations. High priority issues are highlighted in Table 5. Nonetheless it is clear from the enormity of the task at hand that it will be many years before any commercial application of a membrane is used within a catalytic reactor.

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References

[1] J.N. Armor, Appl. Catal., 49 (1989) 1–25.

[2] J.N. Armor, CHEMTECH, (1992) 557–563.

[3] I.K. Song and W.Y. Kim, Catal. Lett., 9 (1991) 339.

[4] G. Saracco and V. Specchia, Catal. Rev. Sci. Eng., 36 (1994) 305–384.

[5] J. Shu, B.P.A. Grandjean, A. Van Neste and S. Kaliaguine, Can. J. Chem. Eng., 69 (1991) 1036–1060.

[6] M.P. Harold, C. Lee, A.J. Burggraaf, K. Keizer, V.T. Zaspalis and R. S.A. de Lange, MRS Bulletin, (April 1994) 34–39.

[7] N. Itoh, Sekiyu Gakkaishi, 33 (3) (1990) 136–146.

[8] H.P. Hsieh, Catal. Rev. Sci., Eng., 33 (1991) 170.

[9] Proceedings of the First International Workshop on Catalytic Membranes, Sept. 1994, Lyon, France. Some of the presentations are published in this issue.

[10] B.Z. Egan, S.P.N. Singh, D.E. Fain, G.E. Roettger and D.E. White, Gas Separation Using Inorganic Membranes, Report of Oak Ridge National Labs.: DE 92 014 929 (1992).

[11] R.R. Bhave, Inorganic Membranes Synthesis, Characteristics and Applications, van Nostrand–Reinhold, New York, 1991.

[12] E.F. Hill, Feasibility Study: Removal of Trituim from Sodium during the MDEC Process by Oxidative Diffusion, Argonne West, DOE N707T1830035 (1982).

[13] For example W.J. Koros and G.K. Fleming, J. Membr. Sci., 83 (1993) 1–80.

[14] R.W. Spillman and M.B. Sherwin, CHEMTECH, (1990) 378–384.

[15] V.M. Gryaznov and N.V. Orekhova, Catalysis of Precious Metals, Nauka, Moscow, 1989.

[16] A.N. Karavanov, N.N. Mikhalenko and V.M. Gryaznov, Dokl. Akad. Nauk. SSSR, 286 (1986) 102.

[17] V.M. Gryaznov, M.M. Ermilova, L.S. Morozova et al., J. Less-Common Met., 89 (1983) 529.

[18] Y.S. Lin and A.J. Burggraaf, J. Am. Ceram. Soc., 6 (1991) 219; Y.S. Lin, K.J. deVries and A.J. Burggraaf, J. Mater. Sci., 26 (1991) 715.

[19] K. Keizer, V.T. Zaspalis and T.J. Burggraaf, in P. Vincenzini (Editor), Ceramics Today —Tomorrow's Ceramics, P. Vincenzini (Editor), Elsevier, 1991, p. 2511.

[20] Q. Xu and M.A. Anderson, J. Mater. Res., 6 (1991) 1073.

[21] R.J.R. Uhlhorn, K. Keizer and A.J. Burggraaf, J. Membr. Sci., 66 (1992) 271–287.

[22] B.Z. Egan, Using Inorganic Membranes to Separate Gases, Report of Oak Ridge National Labs, Order No. DE 90 004 386 (1989).

[23] V.M. Gryaznov, V.I. Vedernikov and S.G. Gul'yanova, Kinet. Katal., 27 (1986) 142.

[24] For example, European Patent 405 288A (1991).

[25] D.J. Clark, R.W. Losey and J.W. Suitor, Gas Sep. Purif., 6 (1992) 201–205.

[26] Y.S. Lin and A.J. Burggraaf, J. Membr. Sci., 79 (1993) 65–82; J. Zaman and A. Chakma, J. Membr. Sci., 92 (1994) 1–28.

[27] W.O. Haag and J.G. Tsikoyiannis, US Patent 5 019 263 (1991).

[28] E.R. Geus, H. van Bekkum, W.J.W. Bakker and J.A. Moulijn, Microporous Materials, 1 (1993) 131–147.

[29] H.L. Fleming, Presented at the Sixth Annual Membrane Planning Conf., Cambridge, MA, November (1988).

[30] E. Schindler and F. Maier, US Patent 4 919 860 (1990).

[31] G.R. Gallaher and P.K.T. Liu, J. Membr. Sci., 92 (1994) 29–44.

[32] H.C. Foley, A.W. Wang, B. Johnson and J.N. Armor, Am. Chem. Soc., Symp. Ser., 517 (1993) 168–84.

[33] J.N. Armor and T.S. Farris, in L. Guzzi, F. Solymosi and P. Tetenyi, (Editors), New Frontiers in Catalysis, Proc. of the 10th Int'l. Congress on Catalysis, 19–24 July, 1992, Budapest, Hungary, Elsevier, Amsterdam, 1993, p. 1363.

[34] H. Nagamoto and H. Inoue, Bull. Chem. Soc. Jpn., 59 (1986) 3935.

[35] T.S. Farris and J.N. Armor, Appl. Catal. A: General, 96 (1993) 25–32.

[36] N. Itoh, AIChE J., 33 (1987) 1576.

[37] T. Matsuda, I. Koike, N. Kubo and E. Kikuchi, Appl. Catal. A: General, 96 (1993) 3–13.

[38] B.A. Raich and H.C. Foley, Appl. Catal. A: General, 29 (1995).

[39] N. Itoh, W. Xu and K. Haraya, J. Membr. Sci., 66 (1992) 149.

[40] S. Uemiya, N. Sato, H. Ando, Y. Kude, T. Matsuda and E. Kikuchi, J. Membr. Sci., 56 (1991) 303.

[41] S. Uemiya, T. Matsuda and E. Kikuchi, J. Membr. Sci., 56 (1991) 315.

[42] J. Shu, B.P.A. Grandjean, E. Ghali and S. Kaliaguine, J. Membr. Sci., 77 (1993) 181–195.

[43] J.P. Collins and J.D. Way, Ind. Eng. Chem. Res., 32 (1993) 3006–3013.

[44] M. Chai, M. Machida, K. Eguchi and H. Arai, Appl. Catal. A: General, 110 (1994) 239–250.

[45] R.E. Buxbaum and T.L. Marker, J. Membr. Sci., 85 (1993) 29–38.

[46] D. Edlund, D. Friesen, B. Johnson and W. Pledger, Gas Sep. Purif., 8 (1994) 131–136.

[47] A.C. Makrides, M.A. Wright and D.N. Jewett, US Patent 3 350 846 (1967).

[48] N.L. Basov and V.M. Gryaznov, Membr. Katal., (1985) 117.

[49] K.M. Ito, Y. Shindo, K. Haraya, K. Obata and K. Wakabayashi, Sekiyu Gakkaishi, 32 (1989) 47–50.

[50] C.L. Lin, D.L. Flowers and P.K.T. Liu, J. Membr. Sci., 92 (1994) 45–58.