

# Membranes for High Temperature Hydrogen Separations

Richard J. Higgins (higgins@ceramem.com; 781-899-4495 x.23)  
CeraMem Corporation  
12 Clematis Avenue  
Waltham, MA 02453

## Introduction

High-temperature, highly permselective inorganic membranes are of special interest for many coal-fired power production processes that are currently under development. Such processes require separation and/or purification of hydrogen from mixed gas feeds at elevated temperatures and pressures. Relevant applications include:

- Synthesis gas (H<sub>2</sub>/CO) ratio adjustment
- H<sub>2</sub> removal from gasifier gas for feed to gas turbines or fuel cells, or as feedstock for liquid fuels production
- Upgrading of hydrogen-lean streams, e.g. carbonate fuel cell anode exhaust
- Catalytic dehydrogenation reactors
- H<sub>2</sub> recovery for recycle in petroleum processing

Although a variety of membrane chemistries are being actively developed for these applications, cost-effective modules incorporating such membranes are non-existent. The overall objective of this SBIR Phase II program is development of such modules, which will incorporate membranes with high selectivity and high permeance for hydrogen at elevated temperatures.

## Program Objectives

Specific objectives of this research program include the following:

1. Development and demonstration, through extended simulated process tests, of highly hydrogen-selective membranes based on ultramicroporous silica that are chemically stable under exposure to water and other potential process contaminants to at least 350°C (and preferably 500°C). Such membranes should retain a selectivity of hydrogen compared to nitrogen of greater than 40 and hydrogen permeance of at least  $5 \times 10^{-3} \text{ cm}^3/(\text{cm}^2\text{-s-cm Hg})$  at 350°C after continuous exposure for at least 2,000 hours at 350°C or higher to a simulated hydrogen purge gas stream containing water vapor at 20 cm Hg partial pressure.
2. Development and demonstration, using membranes supported on commercial tubular modules, of the capability of ultramicroporous silica membranes modified with small (i.e., cost-effective) amounts of palladium and/or platinum to perform as catalytic membrane reactors having

commercially viable selectivity and activity properties for selected dehydrogenation reactions and/or direct methane coupling.

3. Development, using low-cost, highly compact, high-membrane-area monolithic ceramic supports with ca. 1200 cm<sup>2</sup> membrane area, of a defect-free asymmetric membrane support structure with top layer characteristic pore size of ca. five to ten nm suitable for application of thin, ultramicroporous silica-based hydrogen-selective membranes.
4. Demonstration of achievement of successful application of ultramicroporous silica-based hydrogen-selective membranes on the low-cost, highly compact monolithic support structures through extended gas permeation tests at 400°C or greater that show high permselectivity for hydrogen with respect to nitrogen.

## Project Description

Paralleling the objectives listed above, the program is comprised of three parallel experimental areas:

1. Fabrication and testing of thermally stable, chemically durable, high permselectivity inorganic membranes, utilizing commercially available tubular ceramic ultrafiltration supports.
2. Fabrication and evaluation of precious metal-doped “catalytic” membranes for facilitated hydrogen membrane transport and in selected catalytic membrane reactor applications.
3. Fabrication and evaluation of low-cost highly compact hydrogen separation membrane modules, using multi-channel honeycomb monolith extrudates as support materials.

## Results and Discussion

### A. Development of Gas Separation Membrane Chemistries

CeraMem has been utilizing microporous silica-based materials as permselective membranes for small gas molecules (hydrogen and helium) at temperatures up to 500°C. These membranes are fabricated via sol-gel processing using straightforward techniques that are amenable to facile membrane manufacturing on large-area supports. Membrane synthesis involves controlled hydrolysis and polymerization of alcoholic solutions containing tetraethoxysilane (TEOS) to produce oligomers with a low degree of branching. These sols, when cast on porous supports having pore sizes less than the size of the oligomers, form very thin (e.g., < 100 nm thickness) membrane layers containing extremely fine micropores after thermal treatment above 350°C. The synthesis, microstructural, and transport properties of such membranes have been widely studied, especially by groups at Sandia National Laboratories/University of New Mexico<sup>1</sup> and Twente University in the Netherlands,<sup>2</sup> and in previous research by this organization.<sup>3</sup> Attributes of these inorganic gas separation membranes

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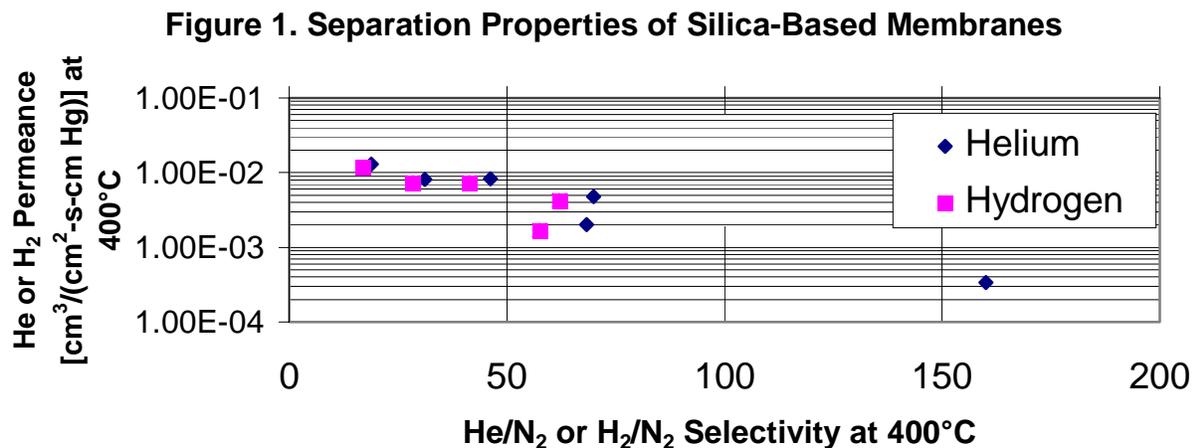
<sup>1</sup> For example, C.J. Brinker et al., “Sol-gel Processing of Amorphous Nanoporous Silicas: Thin Film and Bulk,” in Access in Nanoporous Materials, edited by T.J. Pinnavaia and M.F. Thorpe (Plenum Press, New York, 1995), pp. 123-139; and references therein.

<sup>2</sup> For example, R.M. de Vos and H. Verweij, *J. Mem. Sci.*, **143**, 37-51 (1998); and references therein.

<sup>3</sup> Report No. DOE/ER/80591-14, “A Ceramic Membrane for Gas Separations: SBIR Phase II Final Report,” submitted to U.S.D.O.E. by CeraMem Corporation, Waltham, MA, May, 1993.

compared to alternatives include ease of processing, lower cost and poison-resistance (compared to palladium membranes), high permeance (compared to most silica-based membranes prepared via CVD approaches), and good selectivity for hydrogen and helium over other permanent gases (compared to zeolites, for instance). A weakness of these membranes, however, has been a documented lack of stability during long-term exposure to even low concentrations of water vapor. Furthermore, the long-term thermal stability properties of these membranes have not been demonstrated.

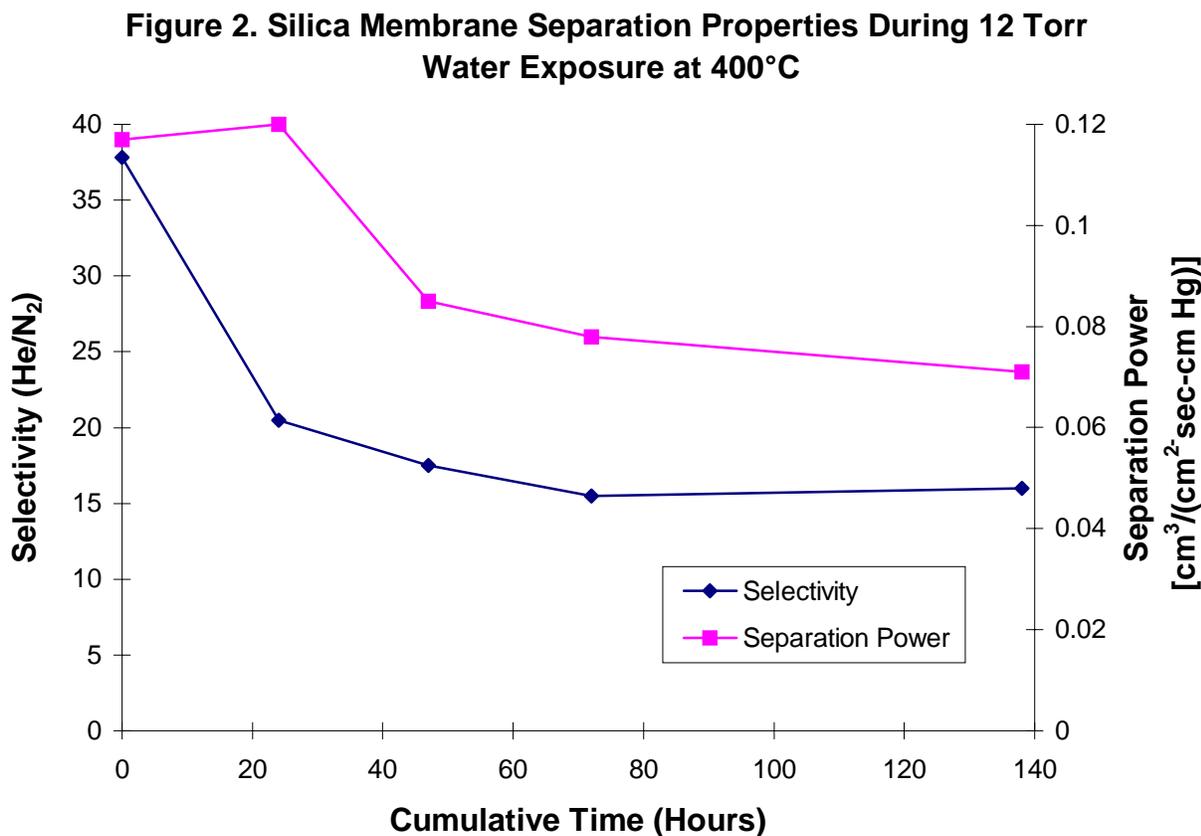
In this program, both pure silica and modified membrane chemistries are being developed and applied upon commercially available alumina ultrafiltration tubes (Membralox®, U.S. Filter Corp., Warrendale, PA) with a characteristic pore size of 4 nm. The ultrafiltration supports are initially modified by application of a thin  $\gamma$ -alumina layer with a characteristic pore size of 2 nm, which serves to improve the capability to produce defect-free overlying silica-based gas separation membrane layers.<sup>4</sup> The membrane chemistries under development in this program involve incorporation of additive metal species into the silica-based amorphous membrane structure to attempt to enhance the thermal stability and chemical stability (in particular, with respect to water vapor present at up to 100 torr) of the membranes during long-term use, while maintaining desirable membrane separation properties. The selectivity and permeability properties of several silica-based membranes developed under this program during short-term tests using pure helium, hydrogen, and nitrogen feeds at 400°C are illustrated in Figure 1. As expected, there is a demonstrated trend of decreased permeance (pressure-normalized flux) for membranes as their selectivity increases. The data shown include membranes for which up to 33 mole percent of the metal cations in the amorphous structure have been replaced by more chemically refractory metals.



On-going tests include extended-term exposure of membranes at elevated temperature to feed gases containing modest quantities of water vapor, to confirm that the chemically modified membranes have improved stability compared to pure silica membranes. The deterioration in membrane

<sup>4</sup> C.J. Brinker et al., "Sol-Gel Processing of Inorganic Membranes for Natural Gas Purification," Proceedings of U.S.D.O.E. Natural Gas Conference, March 24-27, 1997. (Available on World Wide Web at URL: [http://www.fetc.doe.gov/publications/proceedings/97ng/ng\\_pro.html](http://www.fetc.doe.gov/publications/proceedings/97ng/ng_pro.html))

selectivity and membrane separation power (defined as the product of selectivity and permeance for the more permeable of a chosen gas pair, in this case He and N<sub>2</sub>) for a pure silica membrane continuously permeating a nitrogen feed stream containing about 12 torr water at 400°C is shown in Figure 2. Similar tests, continuing to over 1,000 hours permeation time, are in progress for modified membranes.



## B. Evaluation of “Catalytic” Membranes for Hydrogen Separation Applications

Among the types of modified microporous silica membranes developed earlier in this program are those with precious metals added to the membrane. It was posited that such membranes might display enhanced transport of hydrogen due to the following mechanism. Hydrogen molecules in the feed gas might dissociate to atomic species upon contact with the precious metal (e.g., platinum or palladium) atoms within the membrane. Hydrogen atoms would subsequently diffuse through the oxide membrane via a spillover mechanism, and recombine at the underside of the microporous layer, thereby providing an alternate hydrogen-selective transport mechanism through the membrane. To test this theory, silica-based membranes containing up to 10 wt% platinum and palladium were fabricated. The best of these membranes exhibited separation properties equivalent to those of other silica-based membranes (e.g., as displayed in Figure 1).

Measurement of pure hydrogen, pure helium, pure nitrogen, and mixed hydrogen/nitrogen permeation rates through the modified membranes demonstrated that the presence of platinum or palladium in the microporous membranes did not result in measurable increases in hydrogen fluxes as compared to pure silica membranes. (Most notably, hydrogen/helium selectivities were essentially

the same for doped and non-doped membranes.) Subsequent calculations utilizing known surface concentrations and diffusivities for hydrogen atoms on oxide surfaces involved in spillover processes demonstrated that the predicted flux of atomic hydrogen through the doped membranes would be no more than 10% that of molecular hydrogen, principally due to the low effective surface saturation values for atomic hydrogen on oxide surfaces.<sup>5</sup> In these tests, however, it was determined that platinum and palladium incorporation in the silica membranes performed by a specific procedure generally improved the selectivity of membranes, did not appreciably decrease membrane permeance, and increased the thermal stability of the membrane separation properties. This discovery led to the further membrane chemistry development efforts described in the previous section.

Platinum-doped and palladium-doped membranes were also tested as catalytic membranes for dehydrogenation of propane, a commercially important reaction. These membranes were tested versus pure silica microporous membranes on modules into which a pelletized catalyst (either 5 weight percent Pt on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> or Cr<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> (chromia-alumina)) was packed, as shown schematically in Figure 3. In these tests, an inert sweep gas flow was employed to maintain a driving force for hydrogen permeation from the modules. Most tests were performed using a sweep gas flow to feed gas flow ratio of eight at a temperature (500°C) chosen as a compromise between attainment of reasonable catalyst activity and maintenance of catalyst and membrane stability. Space velocity values employed in the tests were generally fixed at 2 h<sup>-1</sup> WHSV, a value representative of commercial non-membrane production processes for propylene.<sup>6</sup>

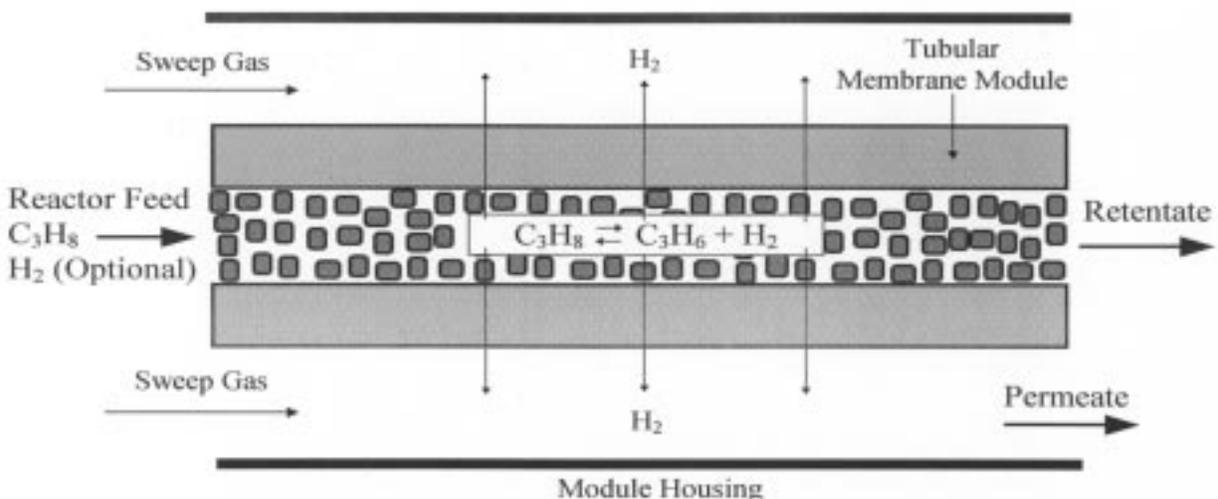


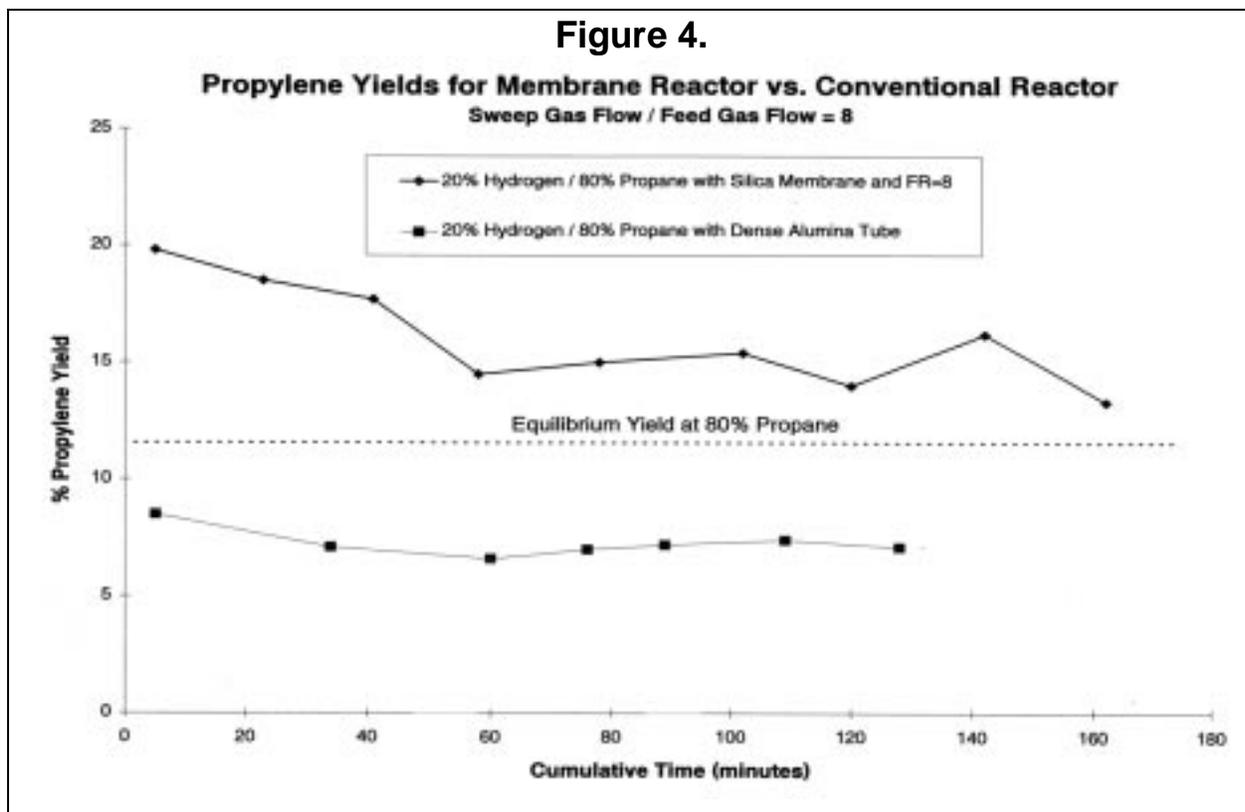
Figure 3. Cross section of a packed-bed membrane reactor for the catalytic dehydrogenation of propane to propylene

Typical results obtained in tests involving catalytic membrane reactors with pure silica membranes and platinum-on-alumina catalyst pellets packed within the reactor are shown in Figure 4. This figure shows the propylene yields obtained or predicted for a feed stream composed of 80 mole percent propylene, diluted with 20 mole percent hydrogen in order to mitigate catalyst coking, for

<sup>5</sup> Report No. DOE/ER/82140-1, "Catalytic Membrane for High Temperature Hydrogen Separations: SBIR Phase I Final Report," submitted to U.S.D.O.E. by CeraMem Corporation, Waltham, MA, 1997.

<sup>6</sup> Ward, T.L., Hagan, G.P., and Udovich, C. pp. 335-44 in Proceedings of the Third International Conference on Inorganic Membranes, July 1994, Worcester Polytechnic Institute, Worcester, MA.

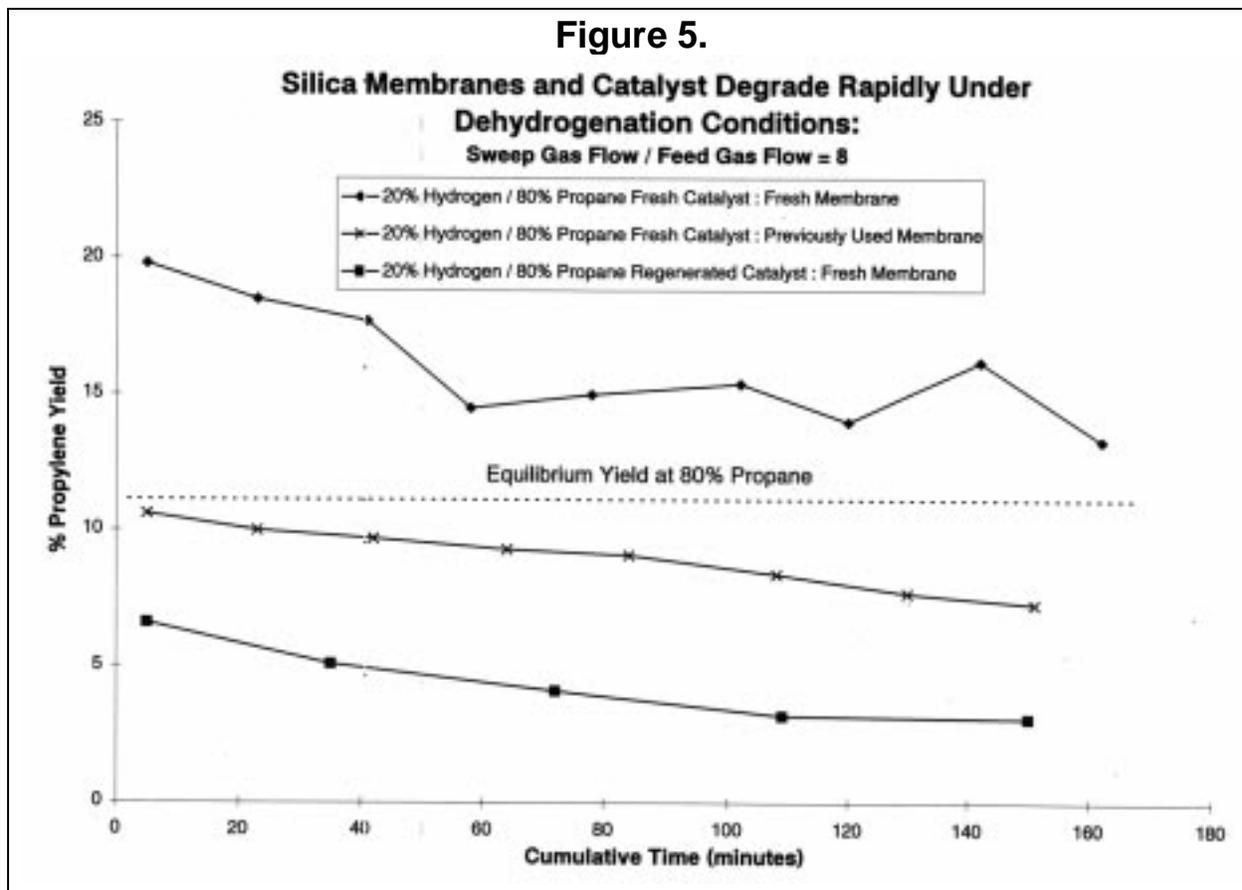
three separate cases: (a) predicted yield based on thermodynamic equilibrium considerations; (b) experimentally observed yields obtained with the catalyst packed into a dense tube (a non-membrane or conventional reactor); and (c) experimentally observed yields for the silica membrane reactor. These results show that, while sub-equilibrium yields are obtained in the non-membrane reactor (due to kinetic limitations), use of the hydrogen-selective membrane reactor provided moderate increases in propylene yield above equilibrium levels. Of note, when analogous tests were conducted using microporous silica membranes containing platinum or palladium within the microporous membrane layer, negligible conversion of propane to propylene was detected. This was considered to be due to poor contact between the catalyst and propane molecules, since no catalyst was present within the tube lumen where bulk propane flow occurred.



The results obtained in short-duration (< 30 h.) tests using catalyst-packed silica microporous membrane reactors were similar to recently published results of similar experiments performed by other research groups<sup>7</sup> with one exception. Unlike these other studies, in this work it was found that the performance of membrane reactors degraded rapidly. Initially, it was not clear whether this occurred due to microstructural changes in the silica membranes during use or due to catalyst coking. Figure 5 shows propylene yields obtained in the membrane reactor experiment described above (in Figure 4) along with analogous experiments in which (a) fresh catalyst was replaced with a previously used (but regenerated) catalyst, and (b) a membrane used in a previous membrane reactor experiment was re-used. These results show clearly that inadequate catalyst regeneration (platinum-

<sup>7</sup> J.P. Collins et al., *Ind. Eng. Chem. Res.*, **35**, 4398-4405 (1996); H. Weyten et al., *AIChE Journal*, **43** [7], 1819-1827 (1997).

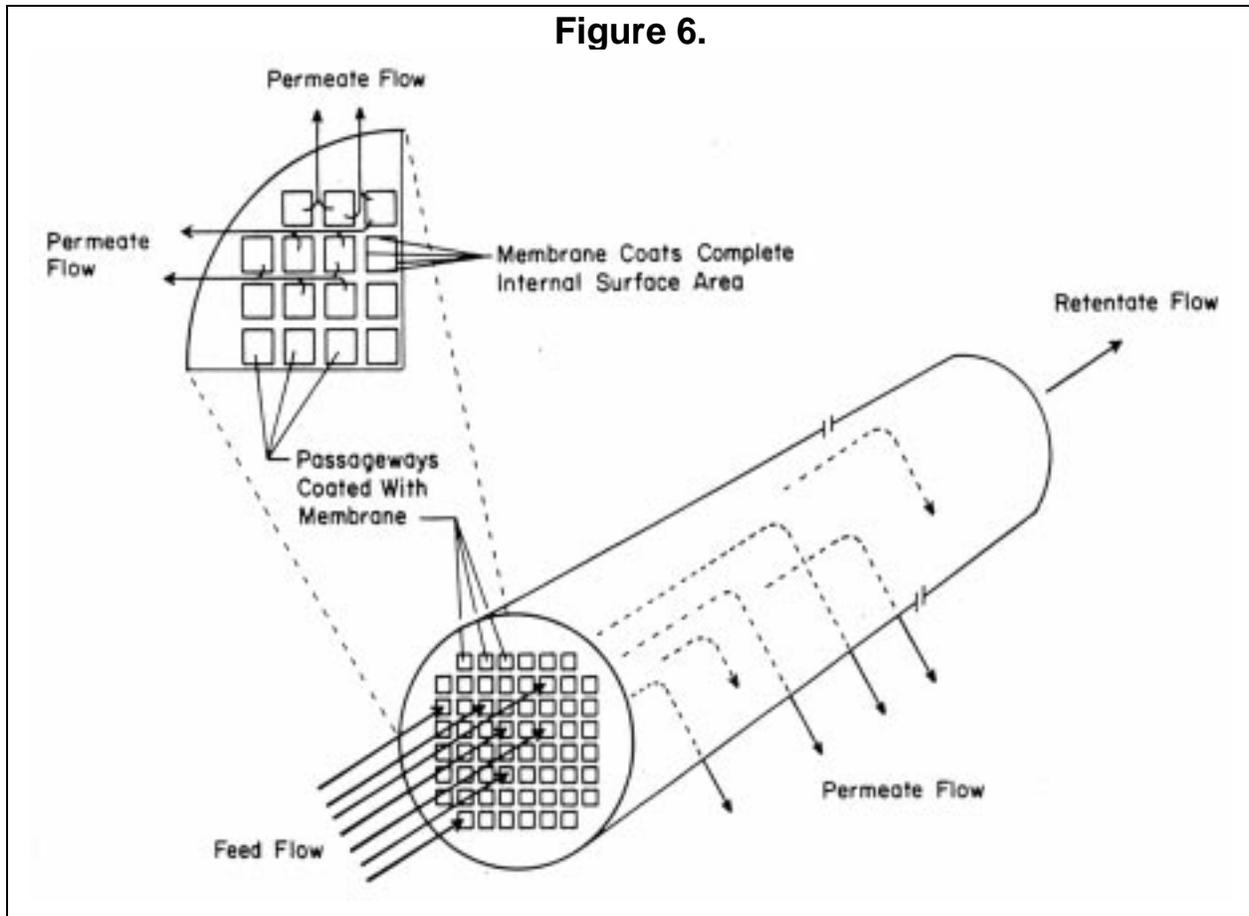
on-alumina catalyst was used in all these experiments) was the primary reason for rapid degradation in membrane reactor performance, although silica membrane degradation also contributed appreciably. Several regeneration methods (both ex-situ and in-situ) were investigated for both types of catalysts used in these experiments, but none was determined to provide complete regeneration of coked catalyst.



### C. Development of Low-Cost High-Temperature Gas Separation Membrane Modules

In order for inorganic membranes for high temperature hydrogen separations to become commercially viable, they must be successfully manufactured as part of a modular design that combines high membrane packing density (membrane area per unit volume of module) and low cost per unit membrane area. Small single-lumen ceramic tubes cannot provide these requirements. CeraMem is developing low-cost high-temperature gas separation membrane modules based on low-cost extruded cordierite honeycomb monoliths as membrane supports. Relatively small modules with dimensions of 2.5 cm diameter, 30 cm length having a membrane area of 0.12 m<sup>2</sup> are being developed in this program. (This compares with the ca. 50 cm<sup>2</sup> membrane area of the tubular ultrafiltration supports employed in the membrane development efforts described above.) The geometry and gas flow configuration of these modules is shown in Figure 6.

**Figure 6.**



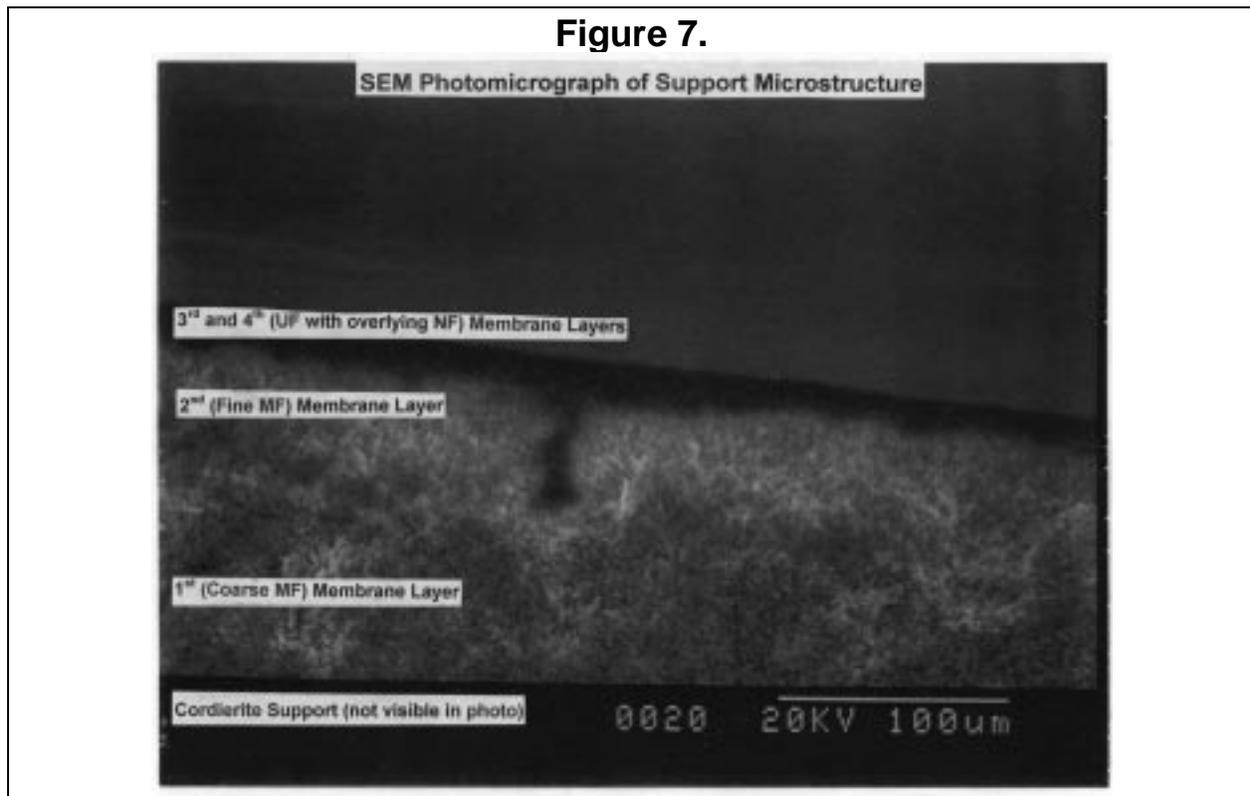
Cordierite supports for larger analogues of these modules that are 14 cm in diameter and 85 cm long, containing 11 m<sup>2</sup> membrane area, are commercially available at relatively low cost. Such modules would be very similar to analogous modules that CeraMem has previously commercialized for industrial-scale liquids separations.<sup>8</sup> Preliminary calculations confirm that the cost for such industrial-scale gas separation membrane modules per unit membrane area would be about \$100 per m<sup>2</sup>.

In order to fabricate modules with appropriate properties to support ca. 100-nm thickness, defect-free inorganic gas separation membranes, the internal surfaces of the cordierite supports, which have an average pore size of about 8 μm, must be coated with several porous membrane layers of sequentially decreasing pore size and thickness. Each of these layers must be suitably defect-free. These individual supporting membrane layers, which form an asymmetric structure, are:

1. Initial “coarse” microfiltration (MF) membrane layer (ca. 0.5 μm pore size)
2. Second “fine” MF membrane layer (ca. 0.1 μm pore size)
3. Ultrafiltration (UF) membrane layer (ca. 0.02 μm pore size)
4. Nanofiltration (NF) membrane layer (0.002 μm pore size)

<sup>8</sup> Further information on such modules is available at URL:<http://www.ceramem.com>.

Experimental work utilizing these supports has involved development of well-controlled processing approaches for each membrane layer, followed by evaluation of the resulting supports via bubble point tests, scanning electron microscopic (SEM) observations, and liquid filtration tests using polymeric and oligomeric compounds of narrow molecular weight in aqueous solutions. An SEM photomicrograph of the cross-section of an NF membrane structure applied on a monolithic support is shown in Figure 7. At this low magnification, the thin (ca. 0.5  $\mu\text{m}$  thickness) NF membrane layer cannot be differentiated from the underlying UF membrane layer.

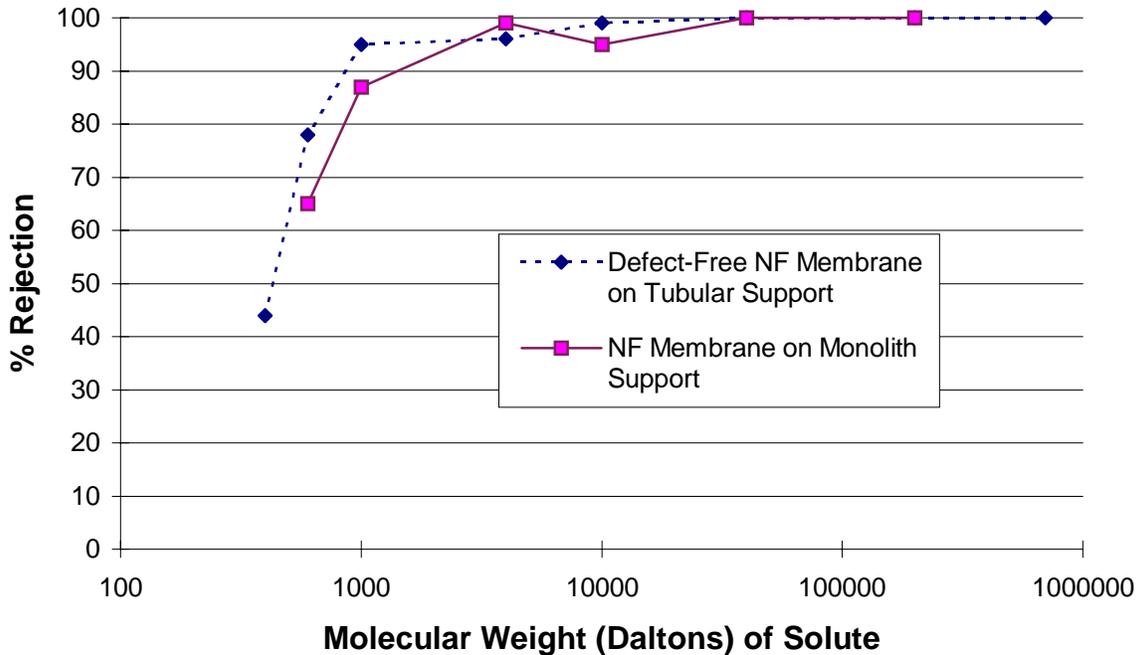


Bubble point tests<sup>9</sup> using water and isopropanol as wetting fluids are being employed to detect defects in prototype modules for characteristic defect sizes down to about 0.15  $\mu\text{m}$ . This is sufficient to detect pinholes and cracks that may form in the second and third membrane layers. To characterize NF membrane layers, the liquid filtration test method is predominantly employed. Figure 8 compares the polymer/oligomer rejection properties of a recently developed monolith-based NF membrane module with those of the same NF membrane applied to the commercial (Membralox®) tubular UF support employed in gas separation chemistry development. These results indicate that the rejection properties of the NF membranes on the two different supports are essentially identical, implying that such a monolithic NF membrane module may be suitable for support of thin, defect-free gas separation membrane layers.

Very recent work has demonstrated that the retention properties of the monolithic NF membrane modules can be readily reproduced from sample to sample. As of the date of this report, work on applying microporous silica-based gas separation membrane layers to these supports had been

<sup>9</sup> Goel et al., pp. 516-523 in Membrane Handbook, edited by W.S.W. Ho and K.K. Sirkar (Van Nostrand Reinhold, NY, 1992).

**Figure 8. Aqueous Solute Rejection of Four-Layer NF Support Structure on Monolith Supports vs. Tubular Supports**



initiated but no evaluations had been completed. This will be the major focus for continuing work on this project. Work is also on-going to develop chemically resistant glazing compounds and related application methods to seal the exposed end face surfaces of the membrane module channels, where an integral defect-free gas separation membrane layer cannot be formed.

### **Future Activities**

Since the ultimate purpose of this program is to initiate commercialization of devices for elevated temperature hydrogen separations, future work will focus on the most critical developmental areas towards this end. No further work is planned in the area of catalytic membrane reactors, since appreciable improvements in both membrane and catalyst stability, both outside of the scope of this program, are required for commercial feasibility. Further development and extended-duration permeation tests of chemically modified silica-based microporous membranes will be continued to attempt to develop membranes that have highly stable separation properties during exposure to elevated temperatures and modest concentrations of water vapor and other aggressive feed constituents. The primary thrust during the remainder of this program, however, will involve development and demonstration of such gas separation membranes as applied to the low-cost honeycomb monolith-based modules.

### **Contract Information and Acknowledgements**

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