**Mixed-Matrix Membranes for $CO_2$ and $H_2$ Separations Using Metal-Organic Frameworks and Mesoporous Hybrid Silicas**

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## OBJECTIVES

The objectives of this project are to explore the use of metal-organic frameworks (MOF) and mesoporous hybrid silicas in polymer-based mixed-matrix membranes for $CO_2$ and/or $H_2$ gas separations. A goal is to exploit the high surface areas, adsorption capacities and selectivities of these nanoporous additives to achieve unprecedented transport of gases critical to energy conservation and emerging clean energy technology. Matrimid® was chosen as the polymer because of its excellent separation performance, and good chemical and mechanical properties. In this report, we report on four kinds of materials: MOF-5 ($H_2$ sorption), periodic mesoporous organosilicas (PMO) (hydrophobic frameworks that change the solubility of certain gases), ZSM-5/MCM-48 (mesoporous material with crystalline ZSM-5 pore wall), and carbon aerogel (both micropores and mesopores). The mentioned materials were synthesized and incorporated into Matrimid® to form mixed-matrix membranes. The manufactured membranes were fully characterized by SEM, XRD, IR, TGA, DSC, DMA, and gas permeation studies.

## ACCOMPLISHMENTS

*1) Polymer-based mixed-matrix membranes incorporating metal-organic frameworks.*

Sorption studies have shown that some microporous metal-organic frameworks have high $H_2$ sorption capacities due in part to their high surface areas (2500 – 3000 $m^2/g$). Specific examples include MOF-5, IRMOF-6, and IRMOF-8, which have $H_2$ sorption capacities of 1, 2, and 4 weight percent at room temperature and 20 bar, respectively. The incorporation of MOFs into polymeric membranes could potentially enhance the selectivity and permeability properties of mixed-matrix membranes for $H_2$ separation.

Microporous MOF-5 crystals (pore size 0.6 nm) were synthesized using published procedures. One procedure yielded crystals with sizes on the order of several micrometers (Figure 1). A second procedure yielded nano-sized crystals (Figure 1). Both procedures depended on the amount of water that the zinc nitrate hexahydrate salt absorbed from the ambient. To make the synthesis more reproducible, the second procedure was modified to include a step in which molecular sieves, activated at 400 °C, were introduced in the system to remove water.

Matrimid® membranes containing the nano-sized MOF-5 particles were prepared using the solvent N-methyl-2-pyrrolidone (NMP). SEM images of a 30% loading in Matrimid® showed that the MOF-5 crystals were evenly dispersed in the polymeric matrix (Figure 2). Permeation studies showed that the MOF-5 nano-crystals increased the permeability of the mixed-matrix membranes without significant degradation or loss of ideal selectivity as the loadings of MOF-5 increased from 10 to 30%. Compared to Matrimid cast from NMP ($H_2$ = 13.4, $N_2$ = 0.10, $O_2$ = 0.90, $CH_4$ = 0.08, and $CO_2$ = 4.1 Barrers), a maximum increase in permeability of 250% was achieved at 30% MOF-5 loading ($H_2$ = 41, $N_2$ = 0.34, $O_2$ = 2.9, $CH_4$ = 0.35, and $CO_2$ = 14.2 Barrers). The enhanced performance of the MOF-5/Matrimid membranes put them above the Robeson bound for the separation of $O_2/N_2$ ($P_{O_2}$ = 2.9 Barrers, $\alpha$ = 8.7) and on the bound for $H_2/N_2$ ($P_{H_2}$ = 41 Barrers, $\alpha$ = 120), which represents an improvement over pure Matrimid membranes. Similarly, at $P_{H_2}$ = 41 Barrers, ideal selectivities of membranes cast from NMP increased for a 30% MOF-5 loading ($H_2/CO_2$ = 3.0, $H_2/O_2$ = 14.0, and $H_2/CH_4$ = 120) compared to pure Matrimid ($P_{H_2}$ = 17.5 Barrers, $H_2/CO_2$ = 2.4, $H_2/O_2$ = 11.9, and $H_2/CH_4$ = 83.3) cast from 1,1,2,2-tetrachloroethane. Subsequent thermogravimetric and sorption analysis showed, however, that the pores of the as-synthesized MOF-5 nano-crystals were still occupied by the synthesis solvent that lowered its surface area from 2500 to 600 $m^2/g$. Current work is focused on increasing the surface area of MOF-5 nano-crystals by solvent exchange, which will be reflected in an increase in the amount of active sorption sites; initial results show an increase in the surface area from 600 to 2200 $m^2/g$.

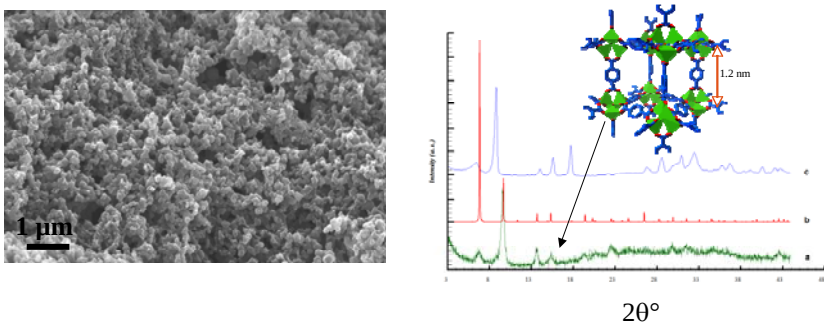


Figure 1. SEM image and powder XRD pattern of MOF-5 nano-crystals synthesized according to modified published procedure.

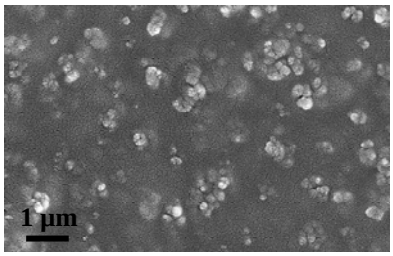


Figure 2. SEM image of surface of 30% MOF-5/Matrimid® membrane.

*2) Polymer-based mixed-matrix membranes incorporating periodic mesoporous organosilicas.*

Periodic mesoporous organosilica (PMO), which has pores defined by bridging organosilane groups, was used as the additive in Matrimid® membranes. The PMOs include mesoporous benzene-silica (MBS), an ordered benzene–silica hybrid material, as well as ethane, ethene, and methane silicas. The pore sizes of these PMOs are between 2.7 and 3.0 nm, and the BET surface areas are between 600 and 900 $m^2/g$, which were determined by $N_2$ adsorption. Pure gas permeation tests show that permeability increases as the loading increases while the selectivity does not decrease. When the MBS loading is 10%, $O_2/N_2$, $H_2/N_2$, $CO_2/CH_4$ and $H_2/CH_4$ selectivities are 8.1, 104.1, 58.6 and 137.3, respectively, all higher than the pure Matrimid® membrane. This can be attributed to the good contact between the PMO and polymer phase and the hydrophobic nature of the PMO framework. Compared with methane silica, other PMO membranes show higher selectivity towards $O_2/N_2$, $H_2/N_2$, and $CO_2/CH_4$. $CO_2/CH_4$ selectivity for methane silica was not improved which might be attributed to its less hydrophobic framework.

*3) Microporous mesoporous materials (MMM) in polymer membranes.*

MMM can be prepared by using preformed zeolite seeds as framework building units which results in a material that has both mesopores and micropores. Matrimid® membranes were prepared containing mesoporous MCM-48 nano-particles with crystalline pore walls composed of ZSM-5. ZSM-5 is a medium pore zeolite that can provide size and shape selectivity, while the MCM-48 is a three-dimensional mesoporous material into which the polymer chains can penetrate to give good interfacial contact. SEM cross-section images show there are no voids between the polymer and ZSM-5/MCM-48 particles. The increment in glass transition temperature and Young's modulus of mixed-matrix membranes suggests that the polymer chains penetrate into the mesopores of ZSM-5/MCM-48 particles, which provides for better interface contact. The selectivity of $H_2/N_2$ increased from 79.6 (pure Matrimid®) to 143 (10% loading), the selectivity of $O_2/N_2$ increased from 6.6 (pure Matrimid®) to 10.4 (20% loading), and $H_2/CH_4$ increased from 83.3 to 169 (20% loading). The results show that the mesopores of ZSM-5/MCM-48 can provide good contact between the ZSM-5/MCM-48 particles and the polymer.

*4) Carbon aerogel/Matrimid® membranes.*

A carbon aerogel with both micropores (0.53 nm) and mesopores (2.14 nm) was made by pyrolyzing Resorcinol-Formaldehyde polymer gel. The carbon aerogel was incorporated into Matrimid® membranes successfully. SEM cross section images show there are no visible defects between the polymer and carbon aerogel particles. The increase in Young's moduli for mixed-matrix membranes suggests better contact between the two phases. Pure gas permeation tests show higher selectivity toward $O_2/N_2$ (9.4), $H_2/N_2$ (115.8), $CO_2/CH_4$ (47.8) and $H_2/CH_4$ (123.6) at 10% loading. The result suggests that the polymer chains can penetrate into the mesopores, which provides for better contact. The presence of micropores can provide size and shape selectivity. The low cost of carbon aerogel is especially promising for industrial applications.

**FUTURE WORK**

Additional metal-organic frameworks and mesoporous hybrid silicas will be synthesized, characterized, and tested for $CO_2$ and $H_2$ gas separations.

**CONFERENCE PRESENTATIONS**

"Gas Permeability Properties of Copper(II) Biphenyl Dicarboxylate-Triethylenediamine in Rubbery Mixed-Matrix Membranes", Carlos Bárcena, Hadi Yehia, Thomas J. Pisklak, John P. Ferraris, Kenneth J. Balkus, Jr., Inga H. Musselman, 10th Annual Chemistry-Biology Symposium, University of Texas at Dallas, Richardson, TX, March 29, 2005.

"Metal-Organic Framework 5 (MOF-5) Mixed-Matrix Membranes for Hydrogen Adsorption/Separation", Edson Perez, Kenneth J. Balkus, Jr., John P Ferraris, Inga H. Musselman, 10th Annual Chemistry-Biology Symposium, University of Texas at Dallas, Richardson, TX, March 29, 2005.

"Gas Permeability Properties of Matrimid Membranes Containing the Mesoporous Benzene Silica", Yanfeng Zhang, Inga H. Musselman, Kenneth J. Balkus, Jr., John P. Ferraris, 10th Annual Chemistry-Biology Symposium, University of Texas at Dallas, Richardson, TX, March 29, 2005.

"Gas Permeability Properties of Matrimid Membranes Containing the ZSM-5/MCM-48 Composite Material", Yanfeng Zhang, Inga H. Musselman, Kenneth J. Balkus, Jr., John P. Ferraris, 10th Annual Chemistry-Biology Symposium, University of Texas at Dallas, Richardson, TX, March 29, 2005.

"Novel Mixed-Matrix Membranes Based on Mesoporous Molecular Sieves and Hybrid Frameworks", Kenneth R. Balkus, Jr., Yanfeng Zhang, Inga H. Musselman, John P. Ferraris, 16th Annual Conference of the North American Membrane Society (NAMS 2005), Providence, RI, June 11 - 15, 2005.

"Gas Permeability Properties of Matrimid Membranes Containing Material with Both Micropores and Mesopores", Yanfeng Zhang, Kenneth J. Balkus, Jr., Inga H. Musselman, John P. Ferraris, 16th Annual Conference of the North American Membrane Society (NAMS 2005), Providence, RI, June 11 - 15, 2005.

"Mixed Matrix Membranes Composed of Matrimid and Carbon Aerogel-Zeolite Composite Nanoparticles", Yanfeng Zhang, Kenneth J. Balkus, Jr., Inga H. Musselman, John P. Ferraris, 11th Annual Chemistry-Biology Symposium, University of Texas at Dallas, Richardson, TX, March 31, 2006.

"Mixed-Matrix Membranes for $H_2$ Separation Using Metal-Organic Frameworks", Edson Perez, Kenneth J. Balkus, Jr., John P. Ferraris, Inga H. Musselman, 11th Annual Chemistry-Biology Symposium, University of Texas at Dallas, Richardson, TX, March 31, 2006.

"Mixed-Matrix Membranes for Gas Separations Using Metal-Organic Frameworks", Edson V. Perez, Kenneth J. Balkus, Jr., John P. Ferraris, Inga H. Musselman, 2006 Meeting-in-Miniature of the DFW Section of the American Chemical Society, Texas Woman's University, Denton, TX, April 29, 2006.

"Hybrid Framework Materials for Mixed-Matrix Membranes", Kenneth J. Balkus, Jr., UOP, Des Plaines, IL, October 2005.

"Mixed-Matrix Membranes Composed of Matrimid and Carbon Aerogel-Zeolite Composite Nanoparticles", Yanfeng Zhang, Kenneth J. Balkus, Jr., Inga H. Musselman, John P. Ferraris, 2006 Meeting-in-Miniature of the DFW Section of the American Chemical Society, Texas Woman's University, Denton, TX, April 29, 2006.

"Mixed Matrix Membranes Composed of Matrimid and Carbon Aerogel – Zeolite Composite Nanoparticles", Yangfeng Zhang, Kenneth Balkus, Inga Musselman, John Ferraris, 17th Annual Conference of the North American Membrane Society (NAMS 2006), Chicago, IL, May 12 – 17, 2006.

"Mixed-Matrix Membranes for $H_2$ Separation Using Metal-Organic Frameworks", Edson V. Perez, Kenneth J. Balkus, Jr., John P. Ferraris, Inga H. Musselman, 17th Annual Conference of the North American Membrane Society (NAMS 2006), Chicago, IL, May 12 – 17, 2006.

**STUDENTS SUPPORTED UNDER THIS GRANT**

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