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

Inga H. Musselman, Kenneth J. Balkus, Jr., John P. Ferraris
Department of Chemistry, BE 26
University of Texas at Dallas, P.O. Box 830688
Richardson, TX 75083-0688
(972) 883-2706 Telephone Number
(972) 883-2925 Fax Number
imusselm@utdallas.edu
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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. During this past performance period, we have investigated MOF-5 (H_2 selective), MOF-177 (CO_2 selective), ZIF-8 (H_2 selective), a carbon aerogel-zeolite composite (combination of micropores and mesopores), single-walled carbon nanotubes (H_2 selective), and two Cu-MOFs (strong affinity toward CH_4). 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

The successful synthesis of activated microporous MOF-5 nano-crystals (high surface area of 3,000 m^2/g) allowed us to fabricate activated-MOF-5/Matrimid® mixed-matrix membranes for gas separations, specifically H_2 separation, which demonstrated enhanced permeability (up to 2 fold increase in permeability for H_2 and other gases) at 30% (w/w) loading. The membranes presented high thermal stability (up to 300 °C before decomposition) and high mechanical resistance to breakage upon folding. Additionally, the protocol developed for the synthesis and activation of MOF-5, as well as for its storage, was extended to the other MOFs (IRMOF-8, MOF-177, ZIF-8, and Cu-MOFs). This protocol proved to be very effective in enhancing the gas transport/storage properties of these materials.

MOF-177, which is reported to have a high capacity for CO_2 storage, consists of 1,3,5-benzenetribenzoate (BTB) linked to an octahedral unit of zinc(II) carboxylate clusters. The resulting pores are 1.1 nm in diameter and a surface area as high as 4,500 m^2/g has been reported for this MOF. This high surface area results in a CO_2 capacity of 33.5 mmol/g as evidenced by the CO_2 adsorption isotherms. Also, MOF-177 has one of the highest CO_2 storage capacities ever reported at room temperature. This MOF could be used to purify H_2 from a mixture with low CO_2 content. A reflux synthesis procedure has been used to prepare MOF-177. Conditions for the synthesis are currently being optimized to obtain a material with the desired surface area.

ZIF-8 (zeolitic imidazolate framework) is a material that is promising for H_2 separation. ZIF-8 is a new class of metal-organic framework that is isostructural with several zeolite phases. It uses imidazolate ligands to bind to tetrahedral Zn(II) ions that results in bond angles quite similar to those found for Si-O-Si in many zeolites. The five-membered imidazolate ring creates a framework by bridging the Zn(II) centers to the N atoms in the 1,3-positions of the ring. This MOF has been reported to readily adsorb H_2 because of its pore size, which is 0.34 nm in diameter. Another interesting feature of this MOF is the apparent thermal stability to nearly 500 °C as determined by thermogravimetric analysis. Preliminary results of ZIF-8 mixed-matrix membranes showed increases in the permeabilities of the gases, whereas the selectivities of the gases remained the same.

Carbon aerogels with both micropores (0.53 nm) and mesopores (2.14 nm) were prepared by pyrolyzing a Resorcinol-Formaldehyde polymer gel. Nano-zeolite A and zeolite Y crystals were then grown in the mesopores of the carbon aerogel. The carbon aerogel-zeolite A and zeolite Y composites were incorporated into Matrimid® membranes successfully. SEM images of membrane cross-sections showed that 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. Compared to the pure polymer, pure gas permeation tests of 10% (w/w) carbon aerogel-zeolite A/Matrimid® membranes show higher selectivity toward O_2/N_2 (9.3), H_2/N_2 (120.6), CO_2/CH_4 (71.5) and H_2/CH_4 (171.9). The carbon aerogel-zeolite Y/Matrimid® membranes provided similar results. The results suggest that the polymer chains can penetrate into the mesopores, which provides for better contact. The presence of micropores (from both carbon aerogel and zeolites) can provide size and shape selectivity for gas separation. The low cost of carbon aerogels is especially promising for industrial applications.

Three types of SWNTs were examined in this project, raw SWNTs, SWNT-COOH (functionalized with carboxylic acid groups), and SWNT-short (short carbon nanotubes functionalized with carboxylic acid groups). Although it is very difficult to disperse raw SWNTs in any solvent, functionalized SWNTs can be dispersed easily in NMP. From the SEM images of the mixed-matrix membrane cross-sections, a good dispersion of SWNTs and contact between the SWNTs and the polymer were obtained. Compared with pure Matrimid®, there is no apparent change in selectivity, but the permeability of all gases increase by about 30%, which can be attributed to fast diffusion of gas molecules in the SWNTs.

An interesting Cu(II) based metal-organic framework (Cu-DHBC-BPY) is based on 2,5-dihydroxybenzoic acid (DHCB) and 4,4'-bipyridine linkers. In this case, the DHBC forms a 2D net linked by the bipyridine ligands. The resulting 1D pores are only 0.36 x 0.42 nm and exhibit selective adsorption of gases depending upon the pressure. As the pressure increases, the interaction of gas and the flexible MOF changes the crystal structure. The onset pressure for adsorption is termed the gate opening pressure, which for nitrogen, oxygen, methane and carbon dioxide is 50, 35, 8 and 0.4 atm, respectively, while the gate closing pressures are 30, 25, 2 and 0.2 atm, respectively. The Cu-DHBC-BPY crystals were prepared and incorporated into Matrimid® to form mixed-matrix membranes. Cu-DHBC-BPY shows thin plate morphology. The surface area is 750 m^2/g and the pore size is 0.82 nm, determined by nitrogen adsorption. The TGA data demonstrate that the DMF can be removed by solvent exchange. Pure gas permeation studies show that the Cu-DHBC-BPY has affinity toward CH_4. Higher CH_4/N_2 selectivity and lower CO_2/CH_4 selectivity were obtained. We are working on the separation of gas mixtures.

A Cu(II)-based MOF synthesized from copper hexafluorosilicate (HFS) and 4,4'-bipyridine (BPY) was reported. The structure of Cu-BPY-HFS involves a square net of copper bipyridyl complexes that are pillared by the SiF_6^{2-} ions. The largest pores are 0.8 x 0.8 nm in diameter. This MOF was reported to be insensitive to water and exhibits a high methane uptake, 145.6 cm^3(STP)/g at 298 K and 3.6 MPa. The Cu-BPY-HFS (Cu^{2+}-bipyridine-hexafluorosilicate) crystals were prepared and incorporated into Matrimid® to form mixed-matrix membranes. Nitrogen adsorption shows that this MOF has a high surface area, nearly 2,000 m^2/g and a pore size of 0.78 nm. The crystal size is approximately 300 nm. Pure gas permeation data reveals that the membrane is selective towards CH_4, while pure Matrimid® is more selective towards N_2. The highest CH_4/N_2 selectivity is 1.2. Compared to the pure polymer, the CO_2/CH_4 selectivity decreases from 35 to 25, which suggests that the presence of Cu-BPY-HFS increases the CH_4 permeability. Mixture separations show the same trend. The 20 wt% Cu-BPY-HFS-Matrimid® membrane exhibits a CH_4/N_2 selectivity of 2.1 and a CO_2/CH_4 selectivity of 14.1. The results suggest that the Cu-BPY-HFS crystal has strong affinity for CH_4 and has the potential to be used for CH_4/N_2 separation.

FUTURE WORK

Additional metal-organic frameworks and mesoporous hybrid silicas will be synthesized, characterized, and tested for CO_2 and H_2 gas separations. Future experiments will also include the permeability measurements of mixed-matrix membranes using *gas mixtures* in addition to single gases. Finally, we are summarizing our results in manuscripts that will soon be submitted for publication.

LIST OF PAPERS PUBLISHED
"Mixed Matrix Membranes Composed of Matrimid and Carbon Aerogel and Carbon Aerogel+Zeolite Composite Nanoparticles", Yangeng Zhang, Kenneth J. Balkus, Jr., Inga H. Musselman, John P. Ferraris, *PMSE Preprints* **95**, 812-814 (2006).

"Mixed-Matrix Membranes for Gas Separation Using Metal-Organic Frameworks", Edson V. Perez, Kenneth J. Balkus, Jr., John P. Ferraris, Inga H. Musselman, *PMSE Preprints* **95**, 815-816 (2006).

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", Yanfeng 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.

“Mixed-Matrix Membranes for Gas Separation Using Metal-Organic Frameworks”, Edson V. Perez, Kenneth J. Balkus, Jr., John P. Ferraris, Inga H. Musselman, 232nd American Chemical Society National Meeting, San Francisco, CA, September 10 – 14, 2006.

“Mixed Matrix Membranes Composed of Matrimid and Carbon Aerogel and Carbon Aerogel+Zeolite Composite Nanoparticles”, Yanfeng Zhang, Kenneth J. Balkus, Jr., Inga H. Musselman, John P. Ferraris, 232nd American Chemical Society National Meeting, San Francisco, CA, September 10 – 14, 2006.

“Mixed Matrix Membranes Composed of Matrimid and Single-walled Carbon Nanotubes”,
Yanfeng Zhang, Kenneth J. Balkus, Jr., Inga H. Musselman, John P. Ferraris, 62nd Southwest Regional Meeting of the American Chemical Society, Houston, TX, October 19 – 22, 2006.

“Mixed-Matrix Membranes for Gas Separation Using Metal-Organic Frameworks”, Edson V. Perez, Kenneth J. Balkus, Jr., John P. Ferraris, Inga H. Musselman, 62nd Southwest Regional Meeting of the American Chemical Society, Houston, TX, October 19 – 22, 2006.

“Gas Permeability Properties of Matrimid Membranes Containing Metal-Organic Frameworks”, Yanfeng Zhang, Kenneth J. Balkus, Jr., Inga H. Musselman, John P. Ferraris, 12th Annual Chemistry-Biology Symposium, University of Texas at Dallas, Richardson, TX, March 20, 2007.

“Mixed-Matrix Membranes for Gas Separation Using Metal-Organic Frameworks”, Edson V. Perez, Kenneth J. Balkus, Jr., John P. Ferraris, Inga H. Musselman, 12th Annual Chemistry-Biology Symposium, University of Texas at Dallas, Richardson, TX, March 20, 2007.

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