

II.A.8 Zeolite Membrane Reactor for Water-Gas-Shift Reaction for Hydrogen Production

Jerry Y.S. Lin

Department of Chemical Engineering
PO Box 876006
Arizona State University
Tempe, AZ 85287
Phone: (480) 965-7769; Fax: (480) 965-0037
E-mail: Jerry.Lin@asu.edu

DOE Technology Development Manager:

Sara Dillich

Phone: (202) 586-7925; Fax: (202) 586-2373
E-mail: Sara.Dillich@ee.doe.gov

DOE Project Officer: Jill Sims

Phone: (303) 275-4961; Fax: (303) 275-4788
E-mail: Jill.Sims@go.doe.gov

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Objectives

- To synthesize chemically and thermally stable silicalite membranes with hydrogen permeance $>5 \times 10^{-7} \text{ mol/m}^2\cdot\text{s}\cdot\text{Pa}$ and H_2/CO_2 selectivity >50 .
- To fabricate tubular silicalite membranes and membrane reactor module suitable for membrane reactor applications.
- To identify experimental conditions for the water-gas-shift (WGS) reaction in the zeolite membrane reactor that will produce a hydrogen stream with at least 94% purity and a CO_2 stream with 97% purity.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Reformer Capital Costs
- (C) Operation and Maintenance (O&M)
- (K) Durability

(N) Hydrogen Selectivity

(P) Flux

Technical Targets

This project is focused on fundamental studies of zeolite membrane reactor for WGS reaction for hydrogen production. Insights gained from these studies will be applied towards the development of low cost, high efficiency technology for distributed and central hydrogen production that meet the following DOE 2010 hydrogen storage targets:

- Cost: \$0.4/kg
- Flux rate: 200 scfh/ft²
- Hydrogen recovery: $>80\%$
- Hydrogen quality: 99.5%
- Operating capability: 400 psi
- Durability: 26,280 hr

Accomplishments

- Improved understanding of gas transport, permeation and separation in microporous zeolite membranes at high temperatures.
- Developed a method to improve membranes designed using MFI (a zeolite structure code) (H_2 permeance: $> 0.8 \times 10^{-7} \text{ mol/m}^2\cdot\text{s}\cdot\text{Pa}$, H_2/CO_2 separation selectivity: >35).
- Improved understanding of the mechanism of chemical vapor deposition (CVD) modification by using methyl-diethoxy silane (MDES) as the silicon source.
- Developed methods to fabricate tubular silicalite membranes and membrane reactor module suitable for membrane reactor applications.
- Developed membrane supports by colloidal casting.
- Developed catalysts for the WGS membrane reactor application.



Introduction

Gasification of biomass or heavy feedstock to produce hydrogen fuel gas using current technology includes partial oxidation to produce syngas, the WGS reaction to convert carbon monoxide with water to hydrogen, separation of hydrogen from the product stream, and removal of water vapor and other impurities

(such as H₂S) from the CO₂ containing stream. Commercially, WGS is normally conducted in two or more reactor stages with inter-cooling to maximize conversion for a given catalyst volume. Complete conversion of WGS is possible in a single membrane reactor at high temperatures (~400°C). The membrane removes product hydrogen from the reactor, facilitating higher conversion at a given temperature.

This project is focused on experimental and theoretical studies of the synthesis of a new hydrogen permselective and thermally/chemically stable zeolite membrane and its use in the membrane reactor for the WGS reaction to produce hydrogen and CO₂ rich streams. The membrane reactor system is designed for operation with feeds containing sulfur or other biomass residual contaminants. The zeolite membrane consists of a continuous thin (1-3 μm), aluminum-free silicalite film without intercrystalline micropores on a support with macroporous zirconia and mesoporous silicalite intermediate layers. These composite silicalite membranes in disk and tubular geometries were prepared by a unique technique that combines several synthesis methods including a template-free secondary growth step. Research efforts were also directed towards development of the cost-effective microwave method to synthesize the MFI zeolite (silicalite and high Si/Al ratio ZSM-5) membranes in disk and tubular geometries.

A new catalyst was developed for the WGS reaction under membrane reactor conditions. The final research task is to perform experimental and modeling studies on the performance of the WGS reaction in the membrane reactors with the silicalite membranes and the catalyst developed in this project. The results obtained in this project will enable development of a large-scale one step membrane reactor process for the WGS reaction for cost-effective production of hydrogen to below \$0.40/kg.

Approach

The approach used in this project is to study fundamental issues related to synthesis of high quality, stable zeolite membranes and a membrane reactor for WGS reaction and hydrogen separation. The details of project are to (1) synthesize disk-shaped and tubular supports with desired intermediate layers and silicalite membranes with a template-free hydrothermal synthesis method, (2) optimize the hydrothermal synthesis condition and perform thorough permeation and separation characterization of silicalite and ZSM-5 membranes, (3) perform CVD for improvement of H₂ permselectivity, (4) develop a microwave synthesis approach to more efficiently and cost-effectively synthesize high quality silicalite membranes, (5) obtain a new WGS catalyst with activity and selectivity comparable to the best available commercial catalyst with improved chemical stability for SO₂ and H₂S containing WGS reaction stream, and (6) develop

methods to fabricate a tubular membrane support with desired intermediate layers and a membrane module and sealing system for a tubular membrane reactor that can be operated in WGS conditions.

Results

The work conducted on zeolite membranes during this year was focused on the permeation and diffusion performance of hydrogen, helium, carbon dioxide and carbon monoxide in MFI- and DDR-type zeolite membranes. CVD modification was conducted to repair the intracrystalline pores and to reduce MFI-type zeolite pores to improve the H₂/CO₂ separation selectivity of MFI membranes.

The intermediate pore MFI-type zeolite membranes were prepared by the template-free secondary growth method followed by on-stream counter-diffusion or one-side CVD modification to eliminate the intercrystalline pores. Gas permeation and separation experiments were conducted on the un-modified and modified membranes at 25-500°C. For the un-modified MFI-type zeolite membranes, the single gas permeation of H₂, He, CO and CO₂ exhibits characteristic of Knudsen diffusion up to 500°C, and adsorption of CO₂ on MFI zeolite has a strong effect on ternary gas separation (H₂, CO and CO₂) below 300°C. Counter-diffusion CVD modification is an effective method to seal the intercrystalline gaps in order to produce defect-free MFI-type zeolite membranes. Permeance of the non-adsorbing gases (He, H₂ and CO) through the counter-diffusion CVD modified zeolite membranes can be described by the following equation based on the gas translational diffusion model:

$$F_i = \frac{\phi \alpha}{L z} \left(\frac{8}{\pi M_i RT} \right)^{1/2} \exp\left(\frac{-E_{d(i)}}{RT}\right) \quad (1)$$

where ϕ , α and z are parameter related to membrane and zeolite pore structure, L the membrane thickness, M_i and $E_{d(i)}$ the activation energy for diffusion for the permeating gas. The permeation exhibits Knudsen diffusion characteristics with very small activation energy for diffusion, approximately 0.1-3 kJ·mol⁻¹. Additionally, the gas permeance (diffusivity) and molecular weight appear to be inversely proportional.

The small pore DDR-type zeolite membranes were prepared by the templated secondary growth method on porous α -alumina disks, followed by on-stream counter diffusion chemical vapor deposition modification to eliminate the intercrystalline micropores. Single gas permeation of He, H₂, CO₂ and CO through this zeolite membrane was measured before and after CVD modification at 25-500°C. Intracrystalline diffusivities for these four gases in DDR-type zeolite were obtained from the permeation data above 300°C to examine the effects of the size and molecular weight of permeating gases on diffusion and permeation rate

for this zeolite membrane. For the un-modified DDR-type zeolite membrane with presence of a small amount intercrystalline micropores the diffusivity (or permeance) with a low activation energy depends on both the size and molecular weight of permeating gases. For the CVD modified DDR-type zeolite membrane with intercrystalline micropores eliminated, the activation energy for diffusion and diffusivity increases with increasing molecular size of the permeating gases. Their permeance can be also described by eq.(1).

The activation energy for these gases through MFI and DDR-type zeolite membranes can be correlated to the ratio (λ) of the kinetic diameter (d_m) to the pore size of the zeolite membranes (d_p), as shown in Figure 1. As shown in Figure 1(a), the activation energy is essentially equal to zero with λ smaller than 0.5, and increases with further increase in λ . From Figure 1(a) and the known molecular size, the permselectivity of H_2 to CO_2 can be estimated as a function of the membrane pore size using eq.(1) and based on the fact that at high temperature permselectivity of the mixture is the same as the ideal gas separation factor. The results are given in Figure 1(b). It is shown that the maximum selectivity for the small pore zeolite membranes is about 12. Thus, to further improve H_2 to CO_2 selectivity the MFI type pores should be narrowed.

MFI-type zeolite membranes were modified by decomposition CVD (thermal cracking of MDES) in a reducing atmosphere. The surface of the zeolite layer was exposed to MDES at 450°C. Figure 2 shows on-stream modification and permeation results of a MFI zeolite, prepared by in situ synthesis for 4 hr with microwave heating. The diameter of MDES is about 0.4 nm smaller than the pore size of MFI zeolite, so it can be used to modify both the inter-crystalline and zeolite pores. The membrane exhibits a separation factor of ~ 25 for H_2/CO_2 equimolar mixture during first modification at 450°C. The separation factor increased to ~ 60 during second modification at 450°C, and stabilized at ~ 35 after second modification. The experimental results showed that the separation performance was improved apparently when the second modification was employed. However, the permeance of H_2 decreased from 2.7×10^{-7} to 0.8×10^{-7} mol.m⁻².s⁻¹.Pa⁻¹. The effects of modification conditions on the separation performance of the membranes are being investigated.

The modification mechanism of MFI membrane with MDES was also studied during the past year to further improve the CVD procedure. Thermogravimetric analysis was used to investigate the modification of MFI zeolites (powder) by MDES and tetra-ethoxy silane. The results indicated that (i) MDES can modify the MFI pore size by catalytic cracking and deposition inside the pores, but TEOS can not due to its molecular size is too large to enter the zeolitic channels; (ii) chemisorption of MDES starts from $\sim 100^\circ C$ and the catalytic thermal

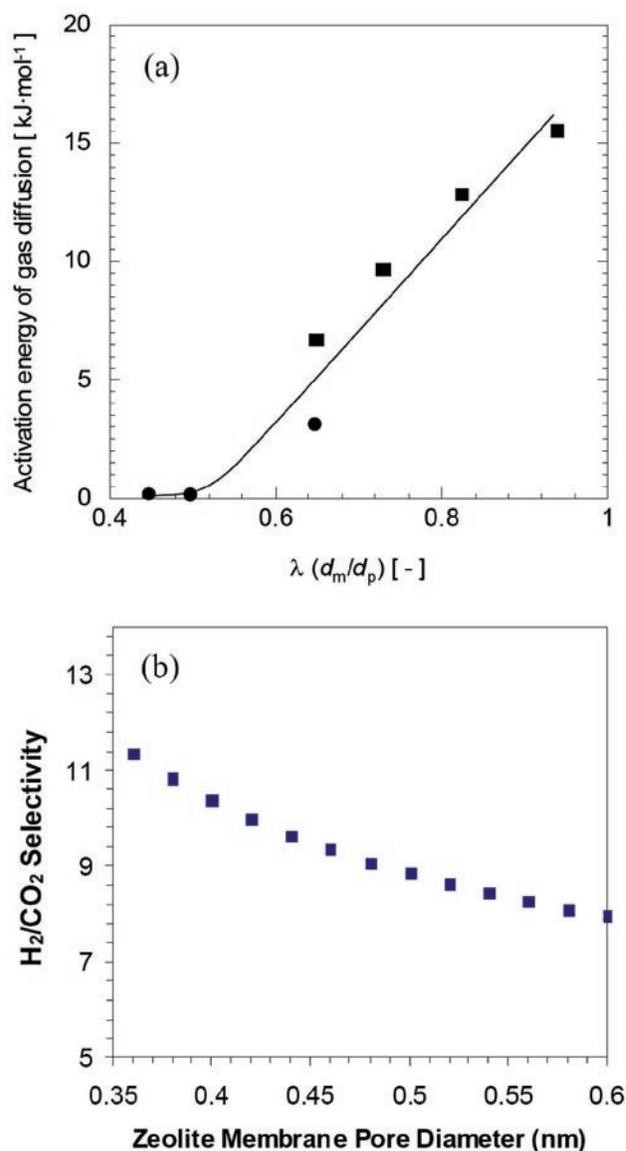


FIGURE 1. Activation energy for diffusion for small gases in MFI and DDR-type zeolite membranes (a), and estimated H_2 to CO_2 perm-selectivity (at 400°C) for zeolite membranes with various pore diameter (b).

cracking of chemisorbed MDES starts at $>450^\circ C$. NH_3 temperature programmed desorption experiments showed that the samples modified by MDES following calcination exhibited a significant decrease in the number of acid sites as compared with the fresh sample, indicating that silicon compounds were deposited in the channels of the zeolites. The number of acid sites of the modified samples decreases with the modifying temperature increasing because of more deposition of silicon on the samples at higher temperatures. The samples treated by MDES vapor continuously from 23°C to 450°C showed the biggest loss of acidic sites. The above result means that the acid sites in zeolitic

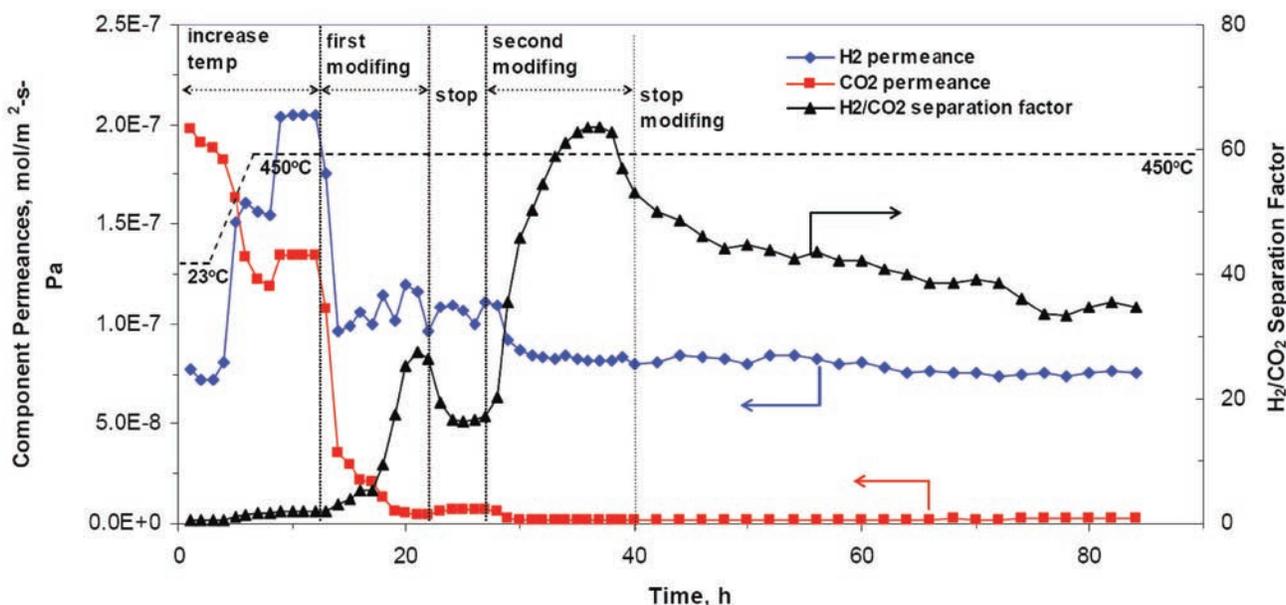


FIGURE 2. Time dependency of gas permeances for one side CVD modification of MFI-type zeolite membrane at 450°C.

channels are the activated sites of the catalytic crack of MDES and the CVD modification should operate at 450°C.

A colloidal casting technique was developed to produce tubular supports with a high quality inner surface. A stabilized dispersion was first produced using AKP30 α - Al_2O_3 powder (Sumitomo Chemical Corp.). The dispersion was ultrasonically treated for approximately five minutes to mix the contents and to break up agglomerated particles. A Delrin[®] mold was filled with the dispersion and placed in a high speed centrifuge (Carl Padberg Zentrifugenbau GmbH). After centrifuging for 10 minutes at 20,000 rpm, the mold liquid was drained. The as-cast tube was dried in air for two days. Initial tests were performed without a release agent on the mold walls; as a result removal of the green tube was difficult. Future tests will be performed with a release agent consisting of petroleum jelly in petroleum ether. Pieces recovered from the mold were sintered at 950°C for 10 hr. As shown by Figure 3(a), an inner tube surface with an optically smooth surface was obtained. Scanning electron microscopy analysis was performed on a fractured cross section. Figure 3(b) shows a fairly homogenous packing of particles with regions of agglomerated particles. As shown by Figure 3(c), the inner surface of the tube consists of fine particles which contribute to the surface smoothness. There are also indications of particle segregation, which can be eliminated with optimization of dispersion technology.

The work on catalysis was focused on preparation of H_2S tolerant catalysts for high temperature (HT)-WGS reaction. Studies were performed in the presence of 100 ppm H_2S in feed stream at 400 and 500°C operation temperature. Prior to evaluating shift

activity, the catalysts were activated and pre-sulfided in a stream of process gas mixture (CO , CO_2 , H_2O and steam) containing 100 ppm H_2S at 400°C for 4 hr. The corresponding results obtained are presented in Figures 4, for the two temperatures 400 and 500°C selected, respectively. It is clear that, the use of Cu as promoter for $\text{Fe}_{3-x}\text{Cr}_x\text{O}_4$ has resulted in improved activity at 400°C with the activity decreasing in this order: $\text{Fe}_{3-(x+y)}\text{Cr}_x\text{Cu}_y\text{O}_4 \geq \text{Commercial} > \text{Fe}_{3-x}\text{Ce}_x\text{O}_4 > \text{Fe}_{3-x}\text{Cr}_x\text{O}_4$. Interestingly, as the operating temperature was raised to 500°C, the order of activity followed the order $\text{Fe}_{3-x}\text{Ce}_x\text{O}_4 > \text{Commercial} > \text{Fe}_{3-(x+y)}\text{Cr}_x\text{Cu}_y\text{O}_4 > \text{Fe}_{3-x}\text{Cr}_x\text{O}_4$. From the present studies, it is evident that the iron-chromium-copper and iron-cerium formulations, act as an excellent sulfur-tolerant HT-WGS catalysts at 400 and 500°C, respectively. More specifically, iron-cerium based modified ferrite can be employed as an alternative to the conventional industrial iron-chrome HT-WGS catalyst formulation at temperatures $\geq 500^\circ\text{C}$ and under extreme conditions of operation (as typically encountered in a membrane reactor).

Conclusions and Future Directions

Conclusions

- Improved understanding of the diffusion of small molecule gases in MFI zeolite membranes.
- Improving the CVD modification procedure and obtain high H_2/CO_2 separation selectivity (>35) and considerable H_2 permeance ($0.8 \times 10^{-7} \text{ mol/m}^2\cdot\text{s}\cdot\text{Pa}$).
- Investigated the CVD modification mechanism when MDES is used as silicon source.

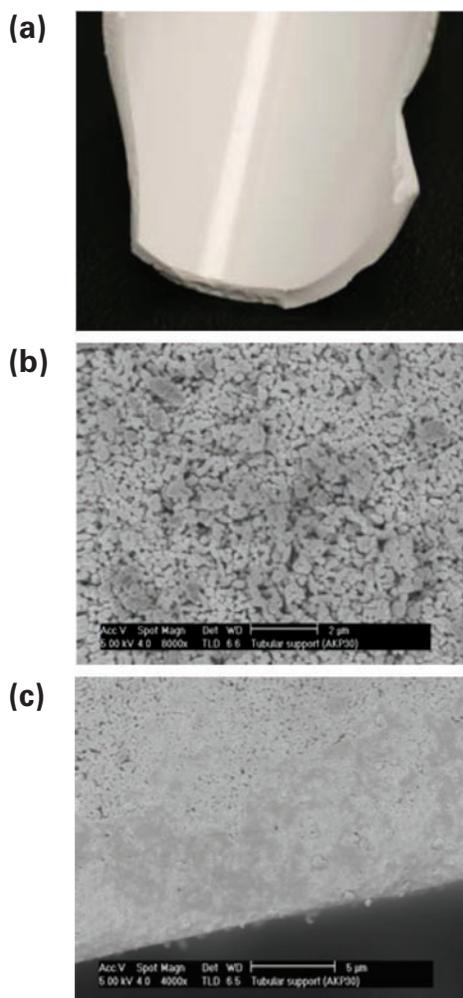


FIGURE 3. Pictures of a centrifugally cast AKP30 tubular support (a) inner surface, (b) cross section, (c) cross section of the inner support surface.

- Developed colloidal casting technique for preparation of tubular supports with a high quality inner surface.
- Developed iron-chromium-copper and iron-cerium catalysts for sulfur-tolerant WGS reaction.

Future Work

- Improve H₂ separation performance for MFI membranes by CVD modification.
- Improve the understanding of the mechanism of CVD modification.
- Test the WGS reaction in the CVD modified disk-type MFI membranes, and investigate the performance of zeolite membrane reactor.
- Investigate the CVD modification of tubular MFI membranes.

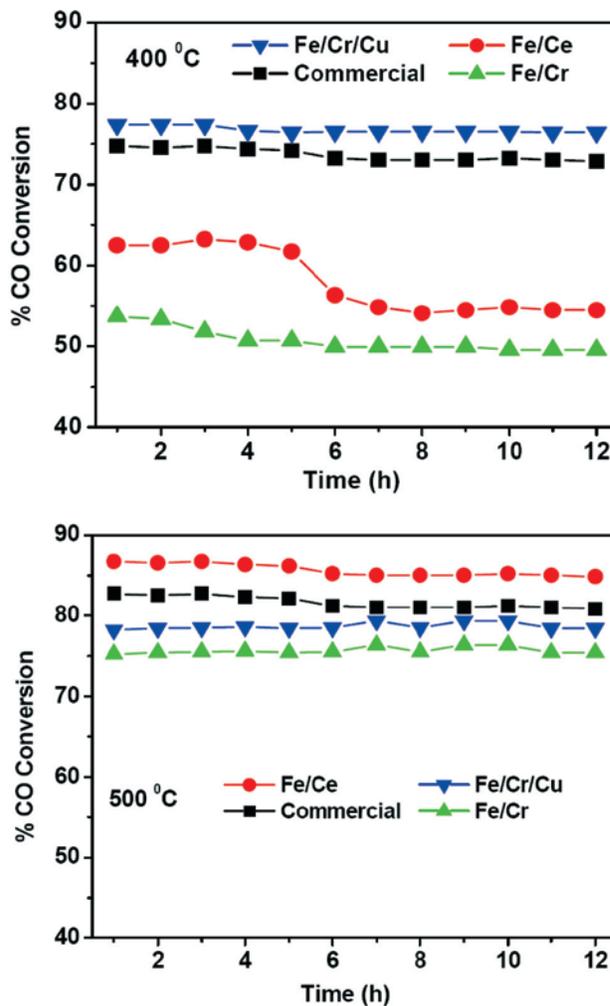


FIGURE 4. HT-WGS stability studies at 400 and 500°C, gas hour space velocity = 10,000 h⁻¹ in presence of 100 ppm H₂S with a H₂O/CO=3.5.

- Optimize the dispersion chemistry and improve the casting procedure of the centrifugal casting technique.
- Investigate the influence of operation conditions on the developed sulfur-tolerant WGS catalyst.

FY 2008 Publications/Presentations

Journal Papers

1. M. Kanezashi, J. O'Brien and Y.S. Lin, "Thermal stability improvement of MFI-type zeolite membranes: Effect of YSZ intermediate layer", *Micropor. Mesopor. Mater.*, **103**, 302-308 (2007).
2. J. O'Brien-Abraham, M. Kanezashi and Y.S. Lin, "A comparative study on permeation and mechanical properties of random and oriented MFI-type zeolite membranes", *Micropor. Mesopor. Mater.*, **105**, 140-148 (2007).

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4. H. Verweij, M.C. Schillo, J. Li, "Concept: Fast Mass Transport through Carbon Nanotube Membranes," *Small*, **3** [12] 1996-2004 (2007).
5. Khan, Panagiotis G. Smirniotis, "Relationship between Temperature Programmed Reduction Profile and Activity of Modified Ferrite-Based Catalysts for WGS Reaction," *Journal of Molecular Catalysis: Chemical* **280**, 43-51 (2007).
6. T.A. Kuzniatsova, Y.H. Kim, K. Shqau, P.K. Dutta, and H. Verweij, "Zeta potential measurements of zeolite Y: application in homogeneous deposition of particle coatings," *Micropor. Mesopor. Mater.*, **103**, 102-107 (2008).
7. X. Gu, Z. Tang, J. Dong, "On-stream modification of MFI zeolite membranes for enhancing gas separation at high temperature," *Mesopor. Micropor. Mater.*, **111**, 441-448, (2008).
8. M.L. Mottern, K. Shqau and H. Verweij, "Permeation porometry: Effect of probe diffusion in the condensate," *J. Membrane Sci.*, **313**, 2-8, (2008).
9. M.L. Mottern, W.V. Chiu, Z.T. Warchol, K. Shqau and H. Verweij, "High-performance membrane supports: A colloidal approach to the consolidation of coarse particles," *J. Hydrogen. Tech.*, **accepted** (2008).
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11. M. Kanezashi, J. O'Brien- Abraham, Y.S. Lin and K. Suzuki, "Gas permeation through DDR-type zeolite membranes at high temperatures," *AIChE J.*, **accepted** (2008).
12. T.A. Kuzniatsova, M.L. Mottern, W.V. Chiu, Y.G. Kim, P.K. Dutta, and H. Verweij, "Novel synthesis of thin, oriented zeolite A membrane," *Adv. Funct. Mater.*, **18**, 952-958, (2008).
13. J. O'Brien-Abraham, M. Kanezashi and Y.S. Lin, "Effects of Adsorption Induced Microstructural Changes on Separation of Xylene Isomers through MFI-Type Zeolite Membranes," *J. Membrane Sci.*, **accepted** (2008).

Proceedings/Book Chapters

1. M.L. Mottern, J.Y. Shi, K. Shqau, D. Yu, and H. Verweij, "Micro-structural optimization of thin supported inorganic membranes for gas and water purification," in *Membranes: Manufacturing and Applications*, Norman N. Li, Anthony G. Fane, W.S. Winston Ho, and Takeshi Matsuura, eds., John Wiley & Sons, New York, (in press) (2007).
2. Y.S. Lin and M. Kanezashi, "Gas permeation and diffusion in small and intermediate pore zeolite membranes," *Studies in Surface Science and Catalysis*, **170**, 347-854 (2007).
3. J. L. O'Brien-Abraham, M. Kanezashi, Y.S. Lin, "Effect of microstructure of MFI-type zeolite membranes on separation of xylene isomers," *Proc. 15th International Zeolite Conf.*, in press (2007).

Conference Presentations

1. T.A. Kuzniatsova, M.L. Mottern. M.C. Schillo, K. Shqau, D. Yu, and H. Verweij, "Application of inorganic membranes in energy conversion technology," TMS 135th Annual Meeting, Orlando FL, March 12-16, 2007.
2. Y.S. Lin and M. Kanezashi, "Gas permeation and diffusion in small and intermediate pore zeolite membranes," *Keynote Lecture*, 15th International Zeolite Conference, Beijing, China, Aug.12-17 (2007).
3. J.L. O'Brien Y.S. Lin and M. Kanezashi, "Effect of microstructure of MFI-type zeolite membranes on separation of xylene isomers", 15th International Zeolite Conference, Beijing, China, Aug.12-17 (2007).
4. Khan and P.G. Smirniotis, "Design of modified Ferrite-based shift catalysts for ultra high temperature membrane reactor applications" 20th North American Meeting (NAMS), Houston, Texas Jun 11-17, 2007.
5. Z. Tang, X. Gu, J. Dong, Mechanism of MFI Zeolite Membrane Modification by In Situ Catalytic Thermal Cracking of Silane in Reducing Atmosphere, Submitted to 10th International Conferences on Inorganic Membranes.
6. Khan and Panagiotis G. Smirniotis, "Investigation into the role of various dopant ions on the High Temperature Water Gas Shift activity of Modified Ferrites", AIChE Annual Meeting, Salt Lake City, Utah, Nov 4-9, 2007.