II.C.1 Zeolite Membrane Reactor for Water-Gas Shift Reaction for Hydrogen Production

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Contract Number: DE-PS36-05GO15043

Subcontractors:
- University of Cincinnati, Cincinnati, OH
- Arizona State University, Tempe, AZ
- Ohio State University, Columbus, OH

Start Date: July 1, 2005
Projected End Date: June 30, 2009

Objectives

- To synthesize chemically and thermally stable silicalite membranes with hydrogen permeance $>5x10^{-7}$ mol/m^2·s·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 (3.1) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Reforming Capital Costs for Distributed Hydrogen Production

(C) Operation and Maintenance Cost of Distributed Hydrogen Production

(K) Membrane Durability for Hydrogen Separation

(N) Membrane Hydrogen Selectivity

(P) Membrane Hydrogen Flux

Technical Targets

This project is focused on fundamental studies of zeolite membrane reactor for water-gas shift 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 meets the following DOE 2010 hydrogen storage targets:

- Cost: $0.4/kg
- Flux rate: 200 scfh/ft^2
- Hydrogen recovery: >80%
- Hydrogen quality: 99.5%
- Operating capability: 400 psi
- Durability: 26,280 hrs

Accomplishments

- Improved reproducibility of silicalite seed layers and membranes.
- Improved the performance of chemical vapor deposition (CVD)-modified MFI (a zeolite structure code) zeolite membranes (H_2 permeance: $>1.35\times10^{-7}$ mol/m^2·s·Pa, H_2/CO_2 separation selectivity: >60).
- Understood fundamentally the mechanism of CVD modification by using methyl-diethoxy silane (MDES) as the silicon source.
- Conducted CVD modification on tubular MFI membranes.
- Conducted WGS reaction in a tubular membrane packed with developed catalyst.
- Developed tubular membrane supports with smoother inner surface by optimizing the dispersion chemistry and deposition of mesoporous intermediate layers on the supports.
- Developed ternary spinel-based catalysts for sulfur-tolerant WGS reaction.

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Introduction

Gasification of biomass or heavy feedstocks 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 H_2S) from the CO_2 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 CO_2 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 H_2 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 SO_2 and H_2S 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 reporting period was focused on CVD modification to repair the intercrystalline pores using tetra-ethoxy silane (TEOS) and narrow MFI zeolite pores using MDES to further improve the H_2/CO_2 separation selectivity of MFI zeolite membranes. Investigation of CVD modification mechanism and reproducibility study of zeolite membrane synthesis were also conducted during this year.

MFI zeolite membranes were synthesized by template-free secondary growth of zeolite crystals on silicalite seeded porous supports. High quality and reproducibility silicalite seed layers were obtained by dip-coating of silicalite suspension with optimized concentration on smooth alumina porous supports. Single gas permeation experiments were performed on as-synthesized and CVD modified membranes. After CVD modification, the permselectivity of H_2/CO_2 increased from 0.6 to 44.3 at 297 K, and 4.2 to 146.9 at 673 K. A CVD-modified membrane was tested by separation of H_2/CO_2 (50:50) gas mixtures and the results are shown in Figure 1. After CVD modification with TEOS, the H_2 permeance decreased by ~33% but the H_2/CO_2 selectivity only increased from 3.4 to 5.2 because the large TEOS molecules ($d_k = 0.96$ nm) are unable to enter the intracrystalline pores but can access and modify the nanometer-scale intercrystalline pores. After switching the precursor from TEOS to MDES, the H_2/CO_2 selectivity dramatically increased to 22.6 with

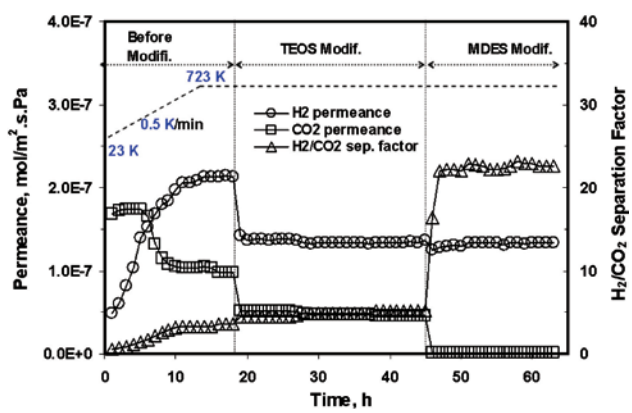

FIGURE 1. H_2/CO_2 separation results during the CVD modification of a disk membrane using TEOS and MDES.

only an additional ~5% decrease in H_2 permeance. The results indicate that there was no silica film deposited on the TEOS-modified membrane surface to block the pore entrances for MDES molecules.

CVD modification was also conducted on a tubular zeolite membrane and the results are shown in Figure 2. The surface of the zeolite membrane layer was exposed to MDES at 450°C in the first round of the CVD modification. The separation factor of H_2 to CO_2 increased from 3.0 to 28.5 with the H_2 permeance decreasing from 3.32×10^{-7} mol/m^{-2}·s·Pa to 1.63×10^{-7} mol/m^{-2}·s·Pa. The membrane was modified for the second round for 8 hours at the same modifying conditions (at 450°C, no pressure difference, with sweeping gas). The separation factor of hydrogen to CO_2 further increased from 28.5 to 60.2 with the H_2 permeance decreased from 1.63×10^{-7} mol/m^{-2}·s·Pa to 1.35×10^{-7} mol/m^{-2}·s·Pa. Primary experiments have shown that a small amount of H_2S (0.5 mol%) in the feed stock has little effect on the separation performance. No H_2S was detected in the permeate stream indicating a high H_2/H_2S selectivity.

The modification mechanism of MFI membrane with MDES was studied during the past year to gain better understanding of CVD modification process and to optimize the CVD modification procedure. Fourier transform infrared (FTIR) spectroscopy was used to investigate the CVD modification of zeolite sample by MDES and the results are shown in Figure 3. After adsorbing MDES vapor at 423 K, the peaks of Si-OC_2H_5 (~2,990 cm^{-1}), Si-H (~2,160 cm^{-1}), and Si-CH_3 (~1,405 cm^{-1}) appeared as a result of chemical and physical adsorption of MDES. In the sample treated at 573 K, the peaks of Si-H, and Si-CH_3 disappeared and the Si-OC_2H_5 peak remained strong. When the modification temperature increased to 723 K, the Si-OC_2H_5 peak also disappeared with strong silanol peak remaining at ~3,740 cm^{-1}. This result suggests the final deposits are likely to be $(OH)_3Si[O\text{-}Si\equiv]_{framework}$ in the H_2/CO_2 carrier gas.

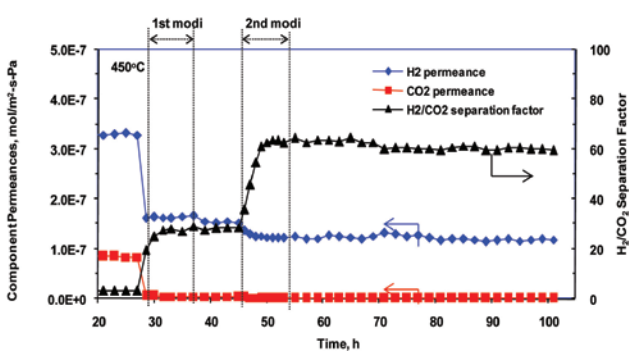

FIGURE 2. Separation performance of the tubular membrane after modification (29-37 hr for the first round; 46-54 hr for the second round).

To obtain tubular membrane supports with a smoother inner surface appropriate for zeolite membrane growth, flow coating was performed on tubular supports made from AA3 powder (Sumitomo Chemical Corp.) which have a slightly smaller pore size (approximately 1 µm) and a smoother surface when compared to the Pall tabular α-Al_2O_3 supports. The chemistry of the AKP30 dispersion was optimized by adjusting the AKP30 solid load, additive content and composition. An additional vacuum treatment step was also performed to remove any microbubbles after mixing of the dispersion to ensure high quality of the AKP30 coating on AA3 supports. This process involved a brief sonification treatment in an ultrasonic bath for approximately 30 sec, followed by evacuation inside of a pressure-controlled vacuum chamber for about 15 min. After drying, the coated tubular supports were fired at 950°C for 3 hrs. To further improve the quality of AKP30-AA3 supports, a γ-Al_2O_3 mesoporous intermediate layer was deposited on AKP30 modified AA3 supports. The γ-Al_2O_3 precursor dispersion was prepared by mixing Boehmite [AlO(OH)] sol and 3 wt% polyvinyl. The dip dispersion was screened with 20 µm nylon mesh, sonicated in an ultrasonic bath, and then evacuated for about 20 min to remove microbubbles. The γ-Al_2O_3 coated tubular supports were fired at 600°C for 3 hrs. Scanning electron microscopy observation of the surface and cross-section of the γ-Al_2O_3 deposited AKP30-AA3 supports was performed and compared with the microstructure of AKP30-AA3 supports. The

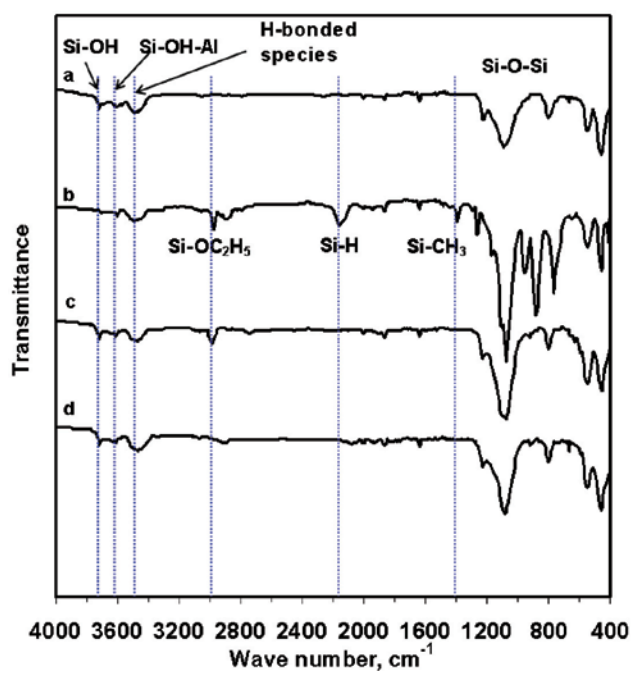

FIGURE 3. FTIR spectra of MFI zeolite samples: (a) before modification, (b) MDES adsorbed at 423 K, (c) MDES adsorbed at 573 K, and (d) modified by MDES at 723 K.

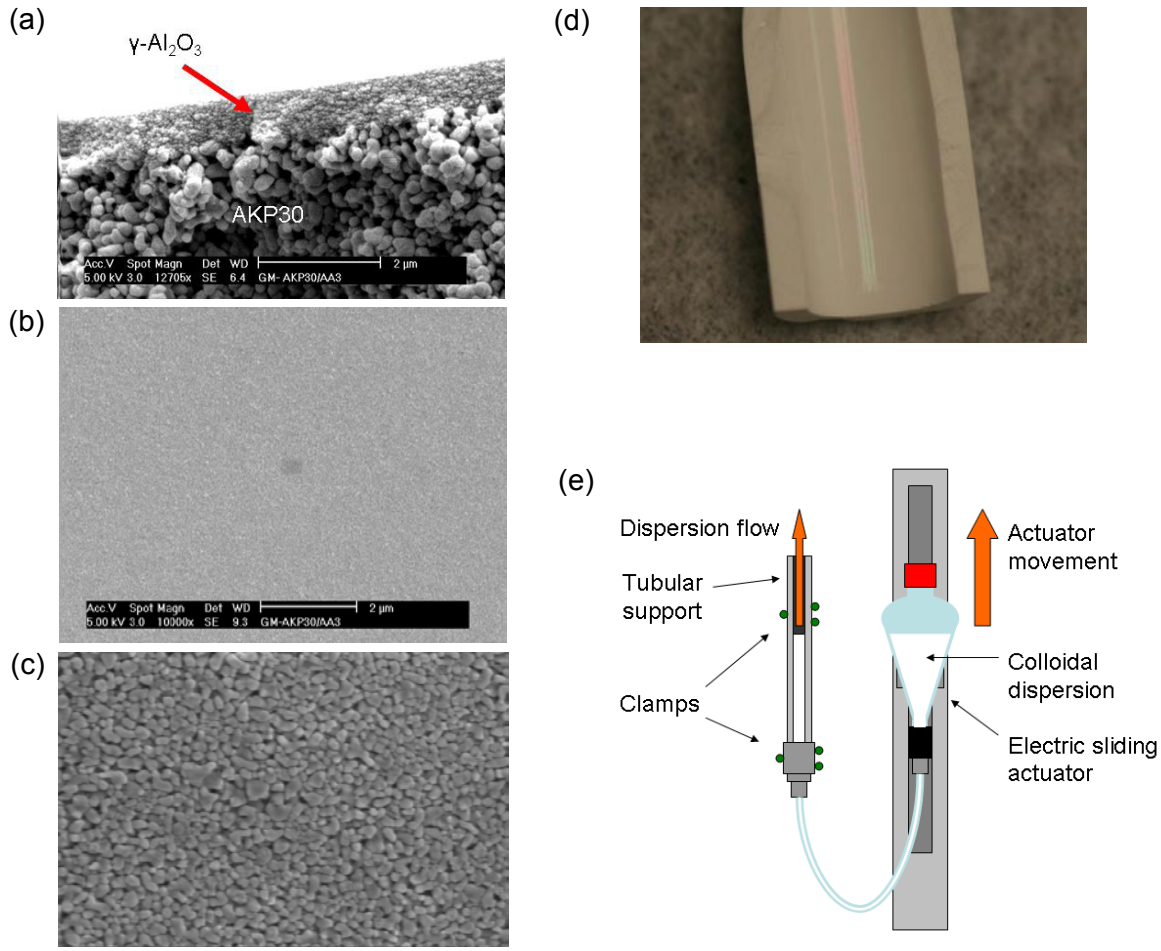

FIGURE 4. (a) Cross section of a γ-Al2O3 membrane on an AKP30-AA3 tubular support; (b) Surface of a γ-Al_2O_3 membrane on an AKP30-AA3 tubular support; (c) Surface of an AKP30 coated AA3 tubular support; (d) γ-Al_2O_3 membrane on the inner surface of an AKP30-AA3 tubular support; (e) Flow coating apparatus.

results shown in Figure 4 indicate that the γ-Al_2O_3 layer results in a surface that is smoother than that of the AKP30-AA3 support and the γ-Al_2O_3 layer appears to be defect-free.

The work on catalysis was focused on optimizing the atomic ratio between Fe to M (M=Ce, Cr). The chosen Fe/M ratios were 10:1, 10:0.5 and 10:2. Ammonia assisted co-precipitation route was explored for high-yield preparations of various modified spinels Fe/M (M = Ce, Cr) at different iron to metal ratio. Iron nitrate, chromium nitrate and cerium nitrate was chosen as precursors. In a typical preparation, the calculated amounts of nitrates were dissolved separately in deionized water and mixed together. Dilute aqueous ammonia was added gradually drop wise to the aforementioned mixture solutions, with vigorous stirring, until precipitation was complete (pH 8.5). The obtained precipitates were filtered off, dried at 80°C for 12 hrs and finally calcined at 500°C for 3 hrs in N_2 environment. The previous results indicated that copper acted as a promoter for the Fe/Cr catalyst, while it acted as an inhibitor for the Fe/Ce catalyst. To study the role of copper on modified ferrites, copper-doped ferrite-based ternary catalysts Fe/Cu/M (atomic ratio 10:1:0.25) (M=Co, Ni, Mn, Zn, Ce, Cr) were synthesized. The preparation process is similar to that of Fe/M (M=Ce, Cr) as described above except that a portion of the precipitated gels were subjected to ultra-sonic treatment for 30 min to improve the textural and thermal stability of the prepared catalysts. The catalytic properties of the synthesized catalysts will be tested and the optimal catalyst WGS reaction will be screened.

Preliminary WGS reaction was performed on the zeolite membrane reactor to test the feasibility of the zeolite membrane reactor for WGS. Figure 5(a) shows experimental setup for the WGS membrane reactor. The membrane was fixed in a stainless steel cell with the silicalite membrane facing opposite to the feed side, and was sealed by graphite rings. The WGS Fe/Cr catalyst described above, with particle size of about 150 μm, was filled in the chamber in the feed/retentate side (or α-Al_2O_3 side) of the zeolite membrane.

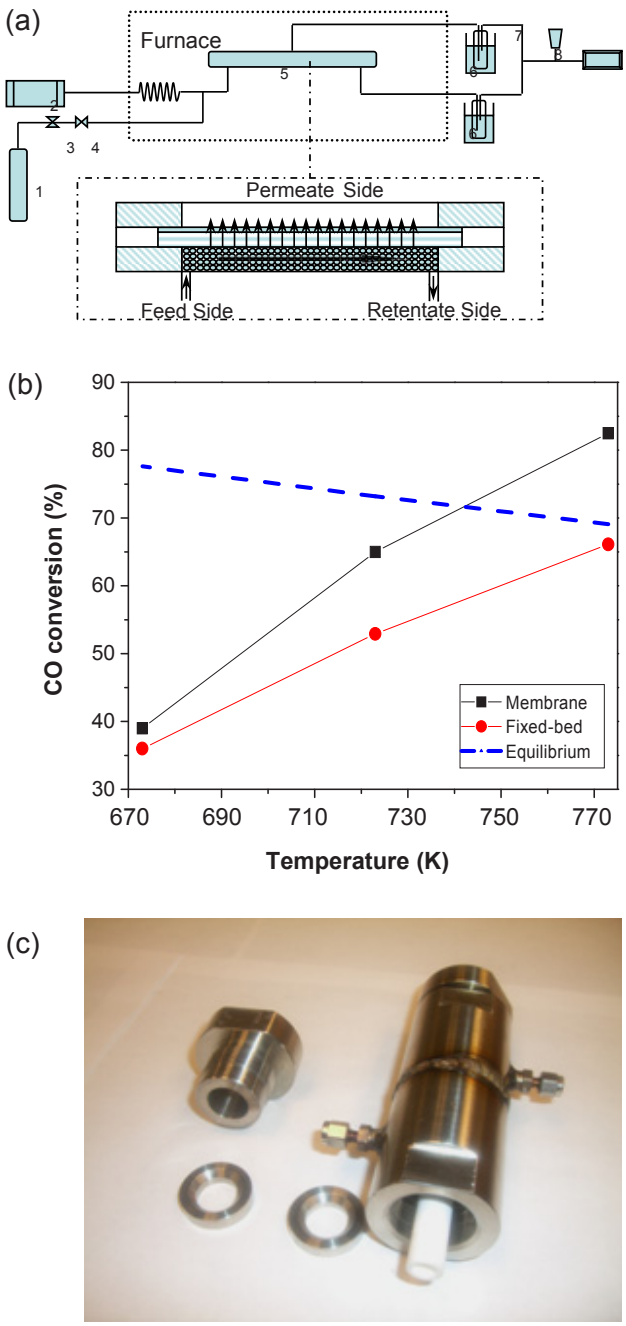

FIGURE 5. (a) Schematic of membrane reactor setup for WGS reaction, (b) CO conversion for WGS reaction under H_2O/CO ratio of 1 and space velocity of 3,500 h^{-1} in the disk-shaped silicalite membrane reactor with Fe/Cr WGS catalyst, fixed-bed reactor, (c) Tubular WGS membrane reactor.

Permeation and reaction experiments were conducted in 573-773 K with a heating/cooling rate of 30 K/h without purging gas in all experiments. The upstream pressure was regulated by a needle valve at the retentate side while keeping the permeate side atmospheric. The flow rates and compositions of the retentate/permeate were respectively measured or analyzed by bubble flow meters and gas chromatography with a thermal conductivity detector (5973 Agilent gas chromatograph/mass spectrometer system with stainless-steel column; HAYESEP DB [ALLTECH]). Simulated fixed bed reactor was carried out by closing the permeate side and only gas mixtures from the retentate side were analyzed by gas chromatograph.

Figure 5(b) shows the effect of reaction temperature on CO conversion for membrane and simulated fixed-bed reactor with H_2O/CO=1 and gas hourly space velocity = 3,500 h^{-1}. CO conversion increases with temperature for both kinds of reactors, which is opposite to the trend of thermodynamic variation. Moreover, CO conversion difference between these two operating reactors increases with the increase of temperature. At 773 K, CO conversion for the membrane reactor reaches 82.5%, which exceeds thermodynamic equilibrium conversion (69.1%). The results clearly show advantages of using the zeolite membrane reactor for WGS reaction. A tubular zeolite membrane reactor, including high temperature seals, has been fabricated, as shown in Figure 5(c). Research next year will be focused on WGS reaction experiments on the tubular silicalite membrane reactor using higher quality silicalite membrane.

Conclusions and Future Directions

Conclusions

- Improved the reproducibility of silicalite seed layers by dip-coating of silicalite suspension with optimized concentration on smooth alumina porous substrates.
- Improved the CVD modification procedure and obtained high H_2/CO_2 separation selectivity (>60) and considerable H_2 permeance (1.35×10^{-7} mol/m^2·s·Pa).
- Investigated fundamentally the CVD modification mechanism when MDES is used as a silicon source.
- Conducted CVD modification on tubular MFI membranes and improved significantly the performance of the modified tubular membranes.
- Conducted WGS reaction in a tubular membrane reactor packed with a catalyst developed in this project.
- Developed tubular membrane supports with high quality inner surface by optimizing the dispersion chemistry and deposition of mesoporous γ-Al_2O_3 intermediate layers on the AKP30 modified supports.
- Developed and optimized ternary spinel-based catalysts for sulfur-tolerant WGS reaction.

Future Work

- Synthesize high quality membranes and optimize the CVD modification procedure to further improve the membrane performance (i.e. with a higher H_2 selectivity and flux).
- Perform the WGS reaction in the CVD-modified MFI tubular membranes, and investigate the performance of the zeolite membrane reactor.
- Modeling the WGS reaction on the silicalite membrane reactor.
- Optimize the dispersion chemistry and improve the deposition of mesoporous intermediate layers on the tubular supports.
- Perform full optimization of the WGS catalysts in conjunction to the WGS membrane reactor, characterize and develop the most effective catalysts.
- Economic evaluation of the project results to validate the scale-up and operation in an industrial scale.

FY 2009 Publications/Presentations

Journal Papers

1. J. Dong, Y.S. Lin, M. Kanezashi, Z. Tang, "Microporous Inorganic Membranes for High Temperature Hydrogen Purification", *J. Appl. Phys.* **104**, 121301-121318 (2008).

2. J.C. White, P.K. Dutta, K. Shqau, H. Verweij, "Synthesis of Controlled Thickness Zeolite L Membranes", *Micropor. Mesopor. Mater.*, **115**, 389-398 (2008).

3. Z. Tang, S-J. Kim, X. Gu, J. Dong, "Microwave Synthesis of MFI-Type Zeolite Membranes by Seeded Secondary Growth Using Pure Inorganic Precursor Solutions", *Micropor. Mesopor. Mat.,* **118**, 224-231(2009).

4. M. Kanezashi and Y.S. Lin, "Gas Permeation and Diffusion Characteristics of MFI-type Zeolite Membranes at High Temperatures", *J. Chem. Phys. C.* **113**, 3767-3774 (2009).

5. L. Zhang, I.S. Park, K. Shqau, W.S. Ho and H. Verweij, "Supported inorganic membranes: promises and challenges," *JOM - J. Met.*, **61**(4) 61-71 (2009).

6. Z. Tang, T.M. Nenoff, J. Dong, "Internal Surface Modification of MFI-Type Zeolite Membranes for High Selectivity and High Flux for Hydrogen", *Langmuir*, **25**(9), 4848-4852 (2009).

Conference Presentations

1. S-J. Kim, Z. Tang, J. Dong, Effect of Heating Sources and Template-Free Secondary Growth Synthesis on MFI-Type Zeolite Microstructure, *AIChE Annual Meeting*, Philadelphia, PA, USA, Nov. 10, 2008.

2. A. Khan and Panagiotis G. Smirniotis, "Ferrite-based High Temperature Water Gas Shift Catalysts" Presented at *14th International Congress on Catalysis*, Seoul, South Korea, July 13-18, 2008.

3. A. Khan and Panagiotis G. Smirniotis, "Contaminant Tolerant Catalysts for High Temperature Membrane WGS Reaction" To be presented at *100th AICHE Annual Meeting*, Philadelphia, PA, Nov 16-21, 2008.

4. Z. Tang, S.-J. Kim, J. Dong, Modification of Internal Surface in MFI-Type Zeolite Membranes for High Selectivity and High Flux Hydrogen Separation. *North American Membrane Society (NAMS) Annual Meeting*, June 20-24, 2009, Charleston, South Carolina USA.

5. T.M. Nenoff, Z. Tang, J. Dong, Surface Modified Zeolite Membranes for High Selectivity and High Flux of Hydrogen from Biofuels. *238th ACS National Meeting*, Washington, DC, August 16-20, 2009.