

II.C.3 Zeolite Membrane Reactor for Water-Gas Shift Reaction for Hydrogen Production

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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 Section 3.1 Hydrogen Production of the Fuel Cell 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 the 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 meets 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

- Optimized the template-free secondary growth for MFI (a zeolite structure code) zeolite membrane synthesis.
- Improved MFI zeolite membrane stability by applying a yttrium-stabilized zirconia (YSZ) barrier layer between the α -alumina porous support and MFI zeolite membrane.
- Conducted the WGS reaction in chemical vapor deposition (CVD)-modified tubular MFI membrane reactors at different conditions and the optimal operating conditions were obtained.
- Modeled WGS reactions in CVD-modified MFI tubular membrane reactors with different catalyst packing configurations.
- Optimized the process for centrifugal casting of tubular supports with reduced resistance for gas flow.
- Developed and characterized the most effective catalysts for high-temperature water-gas shift (HTWGS).



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 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 ($\sim 400^\circ\text{C}$). 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 $\$0.40/\text{kg}$.

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 MFI zeolite membranes during the reporting period was focused on the experiments and simulations of HTWGS reactions in CVD-modified zeolite membrane reactors. Several different kinds of ferrite-based WGS catalysts were developed and tested in this research. The best catalyst was packed in central composite design-modified tubular membrane reactors for WGS reactions. The feasibility of applying a YSZ barrier layer between the α -alumina porous support and zeolite membrane to improve the stability of MFI membranes was demonstrated successfully on the disk membranes. This technique will be transferred onto the tubular membrane to improve the stability of modified tubular membrane reactor during WGS reactions.

In this research, tubular zeolite membranes for WGS reaction were synthesized and CVD-modified according to the procedure reported in the previous annual reports. The CVD-modified tubular zeolite membrane reactor was packed with the best catalyst that was synthesized in the project. Extensive tests of HTWGS reactions have been conducted in the modified tubular MFI zeolite membrane reactor and a traditional reactor as a function of H_2/CO ratio (H_2/CO ratio=1~3.5) at a fixed weight-hourly-space-velocity (WHSV) ($60,000 \text{ h}^{-1}$) and temperature. The results showed that the highest CO conversion and hydrogen recovery were obtained at $\text{H}_2/\text{CO}=3.5$ in both the modified MFI tubular membrane reactor and traditional reactor (Figure 1). The results also showed that the CO-conversion in the modified membrane reactor is higher than that in the traditional reactor due to the on-stream separation of H_2 from the membrane reactor.

Based on these experimental results, the WGS reaction was further tested at different temperatures and different WHSVs while keeping H_2/CO at 3.5 to obtain the optimum operating conditions. Figure 2 shows the experimental $\chi_{\text{CO,e}}$ (CO-conversion) and R_{H_2} (H_2 -recovery) for WGS reactions in a zeolite membrane reactor and packed-bed traditional reactor, as a function of WHSV. As can be seen from this figure, The χ_{CO} in both membrane and traditional reactors increased with decreasing WHSV because of the prolonged residence time for WGS reaction and H_2 transport. The enhancement of χ_{CO} by reducing WHSV was more pronounced at low temperatures where kinetic and mass transport limits are severe. The gas permeation and separation performance of the modified membrane before and after WGS reactions was also studied. The HTWGS reactions lasted about 300 h in the modified MFI zeolite membrane reactor. It was found that the

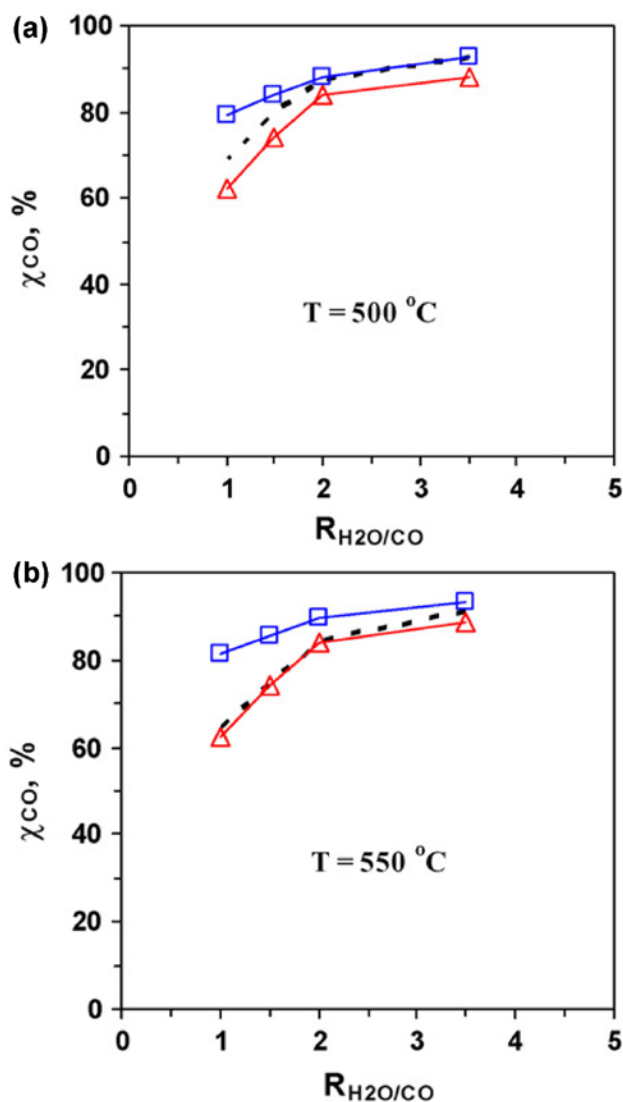


FIGURE 1. Effect of steam-to-CO ratio on the CO-conversion at $WHSV = 60,000 \text{ h}^{-1}$ and temperatures of (a) $500^\circ C$ and (b) $550^\circ C$: (---) $\chi_{CO,MR}$; (\square) χ_{CO} in MR; (Δ) χ_{CO} in a traditional reactor.

H_2/CO_2 separation factor of modified membrane reactor reduced by about 18.7%, while the H_2 permeance reduced by 17.7% due to the degradation of the modified zeolite membrane during the WGS process.

In order to improve the stability of the modified tubular zeolite membrane reactors for WGS reactions for H_2 production, a YSZ barrier layer will be coated onto the surface of the α -alumina porous supports. After that, MFI zeolite membranes will grow on the silicalite seed layer coated on the YSZ barrier layer. The feasibility of applying a YSZ barrier layer between the α -alumina porous support and the MFI zeolite membrane was demonstrated successfully on disk membranes. Figure 3 shows the scanning electron microscope (SEM) micrographs of the YSZ layer coated on the α -alumina porous support (Figure 3(a)),

silicalite seed layer on the YSZ coated porous support (Figure 3(b)), and the MFI zeolite membrane grown on a YSZ coated porous support (Figure 3 (c)). Similarly, a YSZ will be applied between the tubular porous support and zeolite membrane to improve the stability MFI tubular zeolite membrane reactor during WGS reactions. To accomplish it, a YSZ will be coated onto the inner surface of the α -alumina tubular supports through centrifugal casting of YSZ slurry.

WGS reactions in the modified membrane reactor have also been modeled at different conditions with more attention focused on studying the effect of different membrane reactor configurations on the CO-conversion and H_2 recovery of a membrane reactor. The schematic diagrams of the MFI tubular membrane reactors with different catalyst packing configurations for WGS reactions are shown in Figure 4(a): (1) the catalyst particles are packed in part of the membrane permeation zone, (2) the catalyst particles are packed in the whole membrane permeation zone, and (3) the catalyst particles are packed in both the membrane permeation zone and non-permeation zone. The non-permeation zone was glazed with dense glass. Note that the mass of the active catalyst and the particles packing density for these cases are assumed to be the same. Figure 4(b) and (c) show that the reactor configuration has some effect on the performance of the MFI membrane reactor. The final CO conversions of these cases are in the order of: case 3 > case 2 > case 1 > conventional fixed-bed reactor, and the order of H_2 recovery in these membrane reactor configurations is: case 1 > case 3 > case 2 at different temperatures. At a fixed contact time and feeding conditions, the performance of the membrane reactor is mainly determined by the permeation of a gas species through the membrane, while the permeation is determined by both the driving force and the effective permeation area. As expected, the CO conversions of these three cases are all higher than those of the conventional fixed-bed reactor due to the on-stream removal of the product H_2 . In particular, the equilibrium of the WGS reaction can be overcome by the MFI membranes reactors, as shown in Figure 4(b).

During the reporting period, the work on catalysts was focused on screening the best catalysts for HTWGS reactions. Several different kinds of ferrite-based WGS catalysts were synthesized according to the procedure reported in the previous annual report. The activity of the synthesized catalysts was tested at different conditions (temperature, steam/CO ratio, and WHSV) in a fixed-bed traditional reactor. The results showed that Fe/Cr and Fe/Ce catalysts with various Fe/Cr and Fe/Ce ratios are the best catalysts for HTWGS reactions. Figure 5 shows the WGS activity results of Fe/Cr- and Fe/Ce-based catalysts with various Fe/Cr and Fe/Ce atomic ratios. In this study, WGS reactions were performed at a constant steam to CO ratio of 3.5 and at temperatures $400^\circ C$ and $500^\circ C$. A relatively

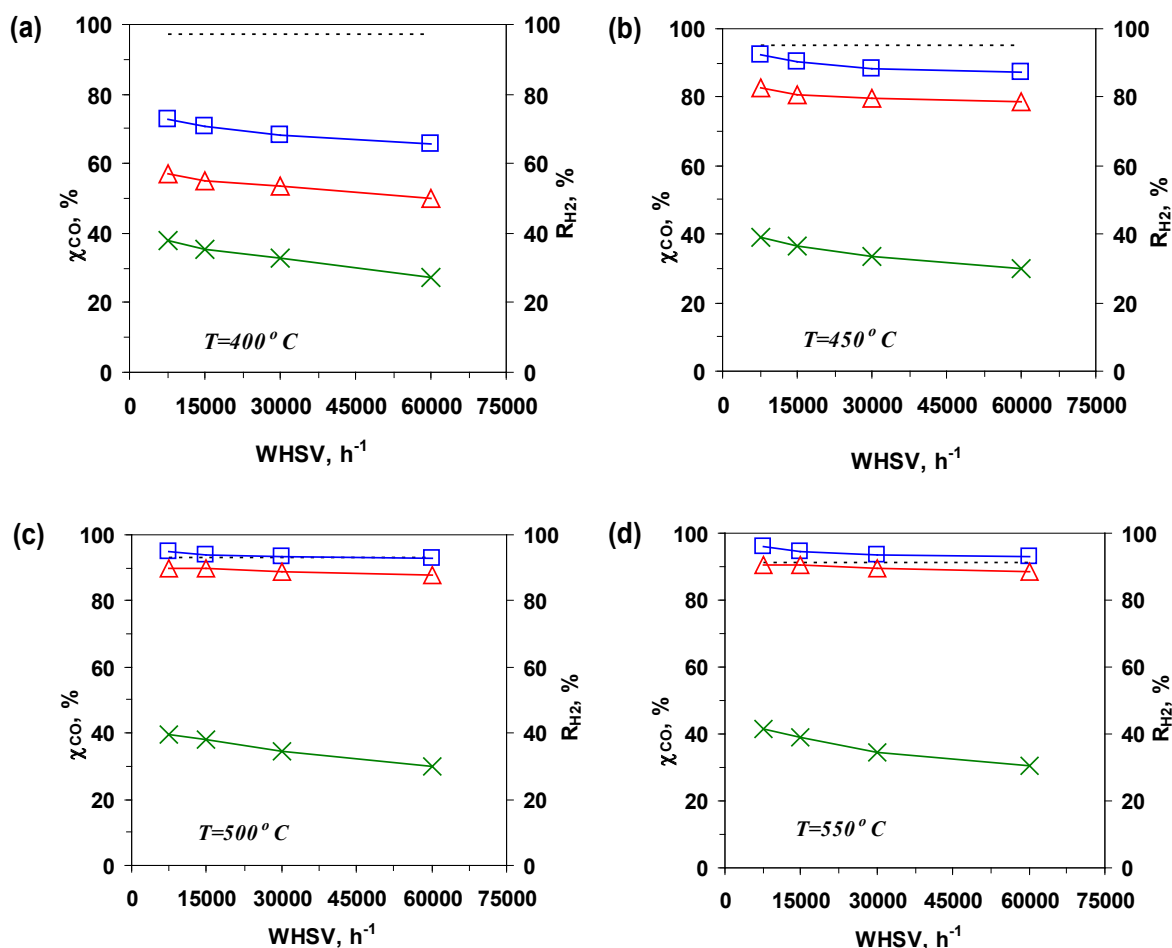


FIGURE 2. Effect of WHSV on CO-conversion for a fixed R_{H₂O}/CO of 3.5: (---) χ_{CO,e_r}; (□) χ_{CO} in a membrane reactor; (Δ) χ_{CO} in traditional reactor; (×) H₂-recovery.

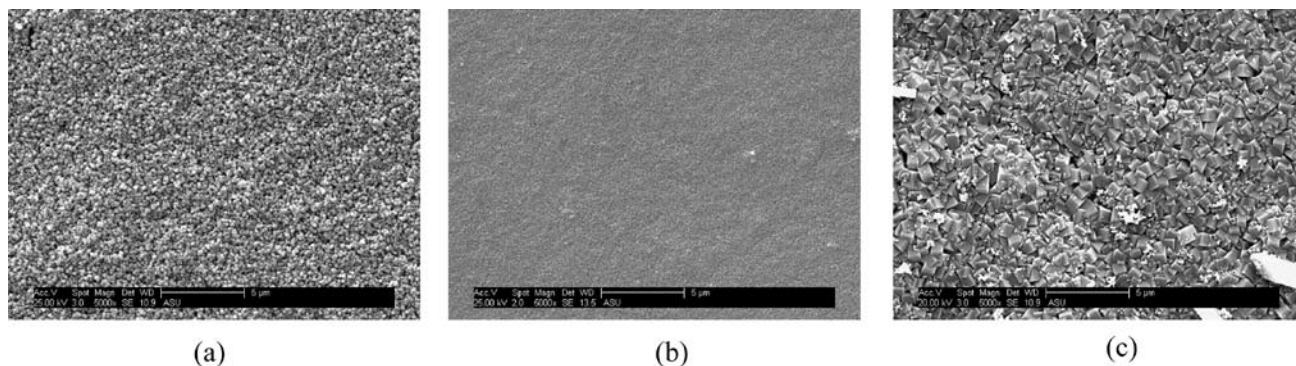


FIGURE 3. SEM micrographs: (a) YSZ barrier layer on an α-alumina porous support, (b) silicalite seed layer on the YSZ barrier layer, and (c) MFI zeolite membrane.

high space velocity of 60,000 h⁻¹ was maintained in all experiments. Figure 5 (a) shows the activity results of Fe/Ce catalysts with different atomic ratios. The order of WGS activity for the Fe/Ce catalysts is Fe₂O₃ < Fe/Ce (10:0.5) < Fe/Ce (10:1) < Fe/Ce (10:2) > Fe/Ce (10:2.5).

The rapid increase in WGS activity with increase in reaction temperature from 400°C to 500°C is due to the improvement in the oxygen storage capacity of ceria at higher reaction temperatures.

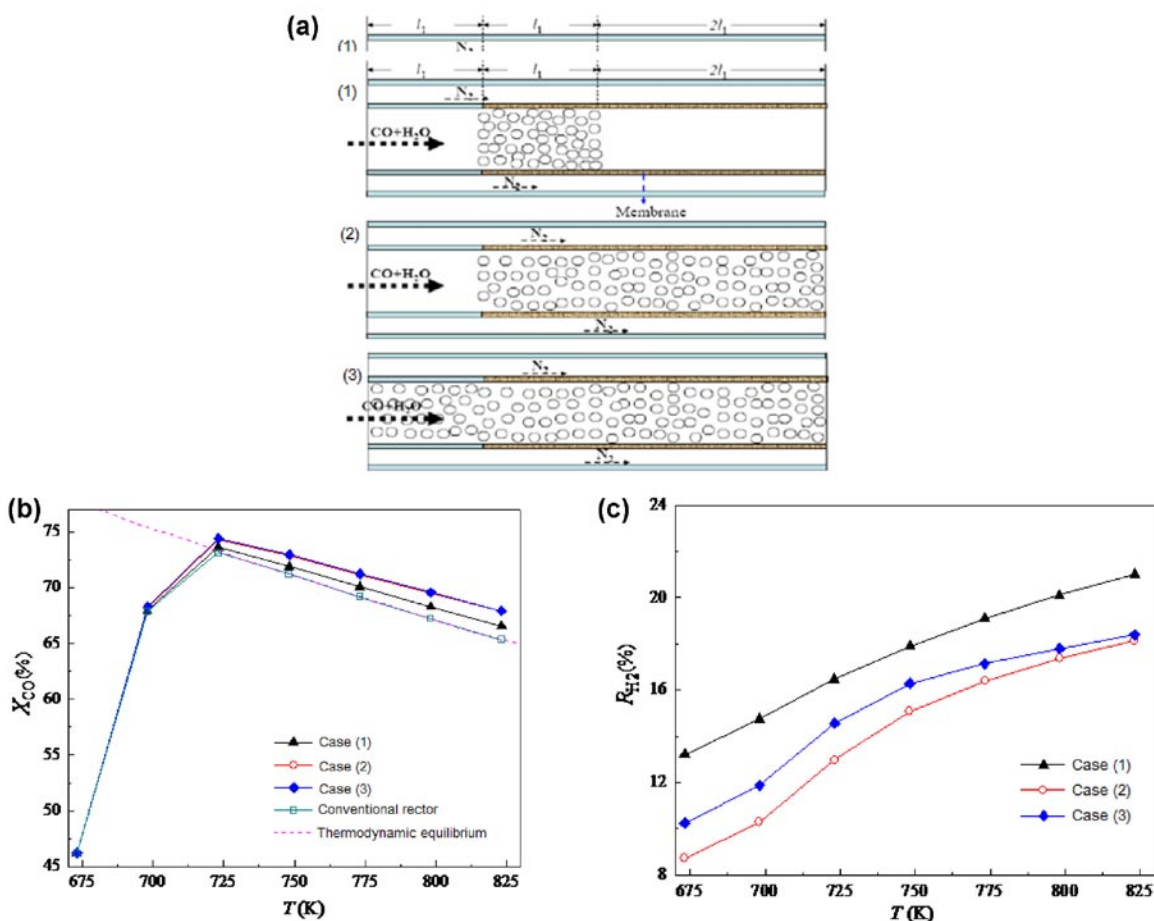


FIGURE 4. Modeling of WGS Reactions in a Membrane Reactor (a) schematic diagrams of the tubular MFI membrane reactor with different catalyst packing configurations (1-3); (b) effect of temperature on the CO conversion in different catalyst packing configurations; and (c) effect of the temperature on the hydrogen recovery in different catalyst packing configurations.

Among the various Fe/Cr catalysts, Fe/Cr (10:0.5) shows better WGS activity compared to the other catalysts as shown in Figure 5(b). X-ray diffraction and crystallite size measurements suggest that the addition of Cr decreases the crystallite size of hematite up to the Fe/Cr (10:0.5) atomic ratio and further increase in the amount of chromium increases the crystallite size slightly. Mossbauer spectroscopic results inferred that in the pure magnetite, structural rearrangements of Fe^{2+} and Fe^{3+} ions take place during the WGS reaction which leads to the lower WGS activity. These rearrangements continue to happen in Fe/Cr (10:0.2) catalyst as well. On the other hand, in the other Fe/Cr catalysts with the atomic ratios 10:0.5, 10:1, 10:2, chromium stabilizes the magnetite phase during the WGS reaction and thus leads to a higher WGS activity. A slight decrease in the WGS activity for Fe/Cr (10:1) and Fe/Cr (10:2) catalysts compared to Fe/Cr (10:0.5) might be due to the smaller Brunauer-Emmett-Teller surface area as well as larger crystallite size.

Previously, centrifugal casting of membrane supports has been performed with AKP30 $\alpha\text{-Al}_2\text{O}_3$

powder (300 nm particle size, Sumitomo Chemical Corp.) which resulted in an optically smooth inner tube surface. To reduce gas flow resistance, centrifugal casting is currently being performed with AA3 $\alpha\text{-Al}_2\text{O}_3$ powder (Sumitomo Chemical Corp.) with a particle size of $\sim 3 \mu\text{m}$. Due to the increased particle size of the AA3 particles, colloidal stabilization with pH 2 HNO_3 is not sufficient to prevent particle sedimentation. To produce AA3 $\alpha\text{-Al}_2\text{O}_3$ (Sumitomo Chemical Corp.) tubular supports with sufficient green strength for removal after centrifugal casting, cross-linking of polyvinyl alcohol (PVA) is being investigated. The cross-linker that was selected is 2,5-dimethoxy-2,5-dihydrofuran (DMDF) which is reported to increase the green strength of gel-cast parts. It was found that gelation of $\sim 3 \text{ mL}$ dispersion/solution of 79.82 wt% AA3, 0.76 wt% PVA, 0.55 wt% HNO_3 , and 0.26 wt% DMDF, resulted in a rigid body in about 10 min. at 65°C . First, the mold was filled with the above AA3 dispersion and placed in a preheated oven at 80°C for approximately 15 min. Then, the mold was removed from the oven and allowed to cool at room temperature. After drying

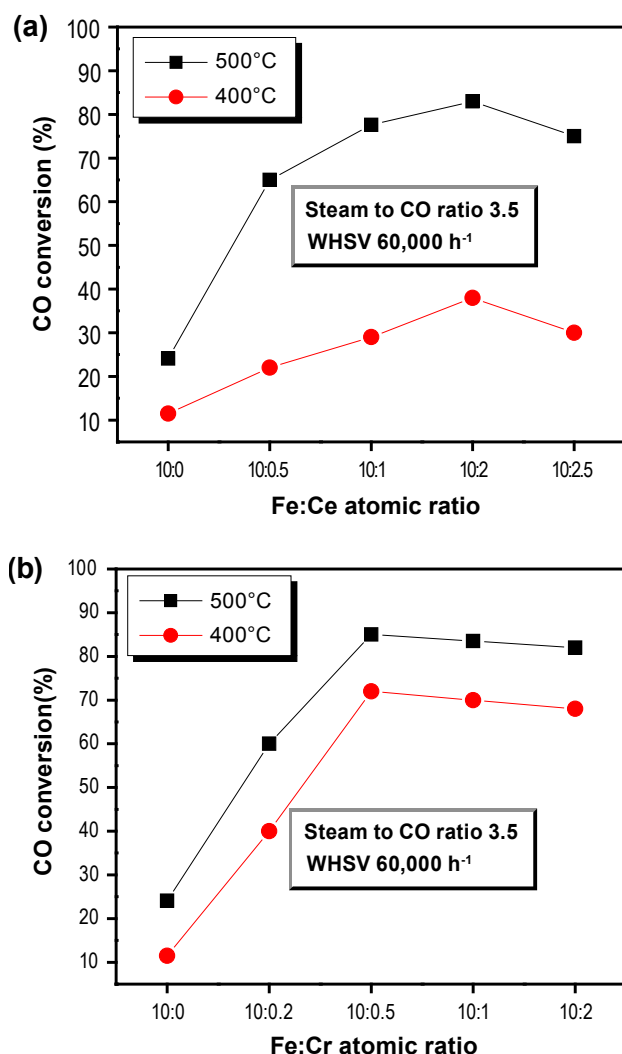


FIGURE 5. (a) Schematic WGS activity results of Fe/Cr catalysts at temperatures 400°C and 500°C (WHSV 60,000 h⁻¹, steam to CO ratio 3.5); (b) Activity results of Fe/Ce catalysts at temperatures 400°C and 500°C (WHSV =60,000 h⁻¹, steam to CO ratio 3.5).

at room temperature for ~48 h, the green tube with good property was extracted from the mold. A release agent will be applied in future studies to prevent the introduction of defects due to the removal of mold parts.

DMDF cross-linking of PVA was then applied to the colloidal centrifugal casting technique. An aqueous dispersion containing 50 wt% AA3 α -Al₂O₃ was prepared with 2 wt% PVA and 0.68 wt% DMDF. The dispersion was adjusted to pH 2 with HNO₃. A petroleum jelly/petroleum ether release agent was applied to the inner surface of a Delrin mold with an inner diameter of 25 mm. The mold was then filled with the dispersion and placed in a high speed centrifuge (Carl Padberg Zentrifugenbau GmbH) and centrifuged for 15 min. at 20,000 rpm. After completing of the centrifugation however, it was found that the α -Al₂O₃

particles did not form a cast and remained in dispersion. This is believed to be caused by excessive stability or viscosity of the dispersion. The dispersion chemistry will be adjusted in the future by reducing the binder and cross-linking agent content. Preheating of the Delrin mold to accelerate the rigidification of the cast tube will also be investigated.

Conclusions and Future Directions

Conclusions

- The stability of the MFI zeolite membranes was improved by applying a YSZ barrier layer between the α -alumina porous support and MFI zeolite membrane layer to avoid the diffusion of Al⁵⁺ from the porous support into the zeolite membrane.
- WGS reactions were conducted in CVD-modified MFI tubular membrane reactors at different WHSV, H₂O/CO ratio, and temperatures. Optimum WGS conditions were obtained.
- WGS reactions were modeled at different operating conditions and catalyst packing geometries to guide the WGS reaction experiments.
- α -Al₂O₃ tubular porous supports with reduced resistance for gas flow are prepared by centrifugal casting of α -Al₂O₃ powder with particle size of ~3 μ m. The dispersion chemistry of the slurry was optimized to obtain integral and robust porous supports.
- Several different kinds of ferrite-based catalysts were synthesized and tested in a fixed-bed traditional reactor, the best catalyst was selected for sulfur-tolerant HTWGS reactions.

Future Work

- Further optimization of MFI zeolite membrane synthesis and CVD modification for enhancement of the H₂/CO₂ separation factor of the modified membranes.
- Improve the stability of MFI tubular zeolite membrane reactor for WGS reactions by applying a YSZ barrier layer between the tubular porous support and zeolite membrane. The YSZ layer will be coated onto the inner surface of tubular supports by a centrifugal casting technique.
- Optimize the dispersion chemistry and improve the centrifugal casting process for fabrication of tubular porous supports with reduced resistance for gas flow.
- Perform high-pressure kinetics of two most effective WGS catalysts.
- Develop highly active and time stable (extensive up to time on stream: up to 2 months on stream)

catalysts for WGS reaction in the modified MFI zeolite tubular membrane reactor.

- Economic evaluation of the project results to validate the scale up and operation in an industrial scale.

FY 2010 Publications/Presentations

Journal Papers

1. 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).
2. 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)
3. 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).
4. 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).
5. Z. Tang, S.-J. Kim, K. Reddy, J. Dong, P. Smirniotis, “Modified Zeolite Membrane Reactor for High Temperature Water Gas Shift Reaction”, *Journal Membrane Science*, **354** (2010) 114 – 122.
6. J. O’Brien-Abraham and Y.S. Lin, “Effect of Isomorphous Metal Substitution in Zeolite Framework on Pervaporation Xylene-Separation Performance of MFI-type Zeolite Membranes”, *Ind. Eng. Chem. Res.*, **49**, 809-816 (2010).
7. J.C. White, P.K. Dutta, K. Shqau, H. Verweij, “Synthesis of thin zeolite Y membranes and their gas separation characteristics”, *Langmuir*, **226** (12), pp 10287–10293 (2010).

Conference Presentations

1. G.K. Reddy, Panagiotis G. Smirniotis, P. Boolchand “Relationship between Electron Hopping Capability and Activity of $\text{Fe}_2\text{O}_3/\text{M}_x\text{O}_y$ (M= Ce, Cr) Based Catalysts for WGS Reaction”, Presented at *AICHE Annual Meeting*, Nashville, TN, Nov 8–13, 2009.
2. Z. Tang, S. Kim, G.K. Reddy, Panagiotis G. Smirniotis, J. Dong “Development of Zeolite-Based Membrane Reactors for High Temperature Water Gas Shift Reaction”, Presented at *AICHE Annual Meeting*, Nashville, TN, Nov 8–13, 2009.
3. J. O’Brien-Abraham and Y.S. Lin, “Study of the Microstructure-Property Relationship for MFI-Type Zeolite Membranes for Separation,” *AICHE Annual Meeting*, Nashville, TN, Nov. 8–13, 2009.
4. Y.S. Lin, “Zeolite Membranes for Gas Separation - Relationship Between Structure and Gas Permeation Properties”, Keynote Lecture, *ACS National Meeting*, San Francisco, CA, March 18–24, 2010.