

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: October 30, 2011

Fiscal (FY) 2011 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 Production 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 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

FY 2011 Accomplishments

- Modified silicalite/Zeolite Socony Mobil (ZSM)-5 bilayer membrane synthesized on the yttria-stabilized zirconia (YSZ)-coated alumina porous supports for H_2/CO_2 separation factor improvement.
- MFI (zeolite structure code) membranes have negligible water vapor permeance with $\text{H}_2/\text{H}_2\text{O}$ selectivity of about 100, and the presence of water vapor has minimum effect on H_2 permeance and H_2/CO_2 selectivity.
- High H_2/CO_2 separation factor (25) and considerable H_2 permeance ($1.26 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$) were obtained on the modified silicalite/ZSM-5 bilayer membrane.
- Developed alumina tubular porous supports coated with YSZ barrier layer for stability improvement of tubular MFI zeolite membranes.
- Conducted WGS reactions in the modified disk MFI zeolite membrane reactor at pressures up to 6 atm to enhance the CO-conversion and hydrogen recovery.
- Developed and characterized the most effective catalysts for high-temperature (HT) WGS in the presence of 400 ppm H_2S .



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 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 (a zeolite structure code) 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 chemical vapor deposition 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

In order to obtain modified MFI zeolite membrane with high H₂/CO₂ separation factor, considerable H₂ permeance and high chemical and thermal stability, a silicalite/ZSM-5 bilayer membrane consisting of a ZSM-5 top thin layer and a silicalite bottom thick layer was synthesized on an alumina support coated with a YSZ intermediate barrier layer. The YSZ barrier layer was used to prevent the diffusion of Al³⁺ from the alumina porous support into zeolite membrane to improve the stability of the zeolite membrane. The synthesized silicalite/ZSM-5 membrane was modified through catalytic cracking deposition of methyl-diethoxy silane (MDES) carried by equimolar H₂/CO₂ mixture gas at 450°C to improve the H₂/CO₂ separation factor of the membrane.

Figure 1 shows the variations of H₂, CO₂ permeance and H₂/CO₂ separation factor during the on-stream catalytic cracking deposition (CCD) modification of the silicalite/ZSM-5 bilayer membrane at 450°C under H₂/CO₂ reducing environment. The H₂/CO₂ separation factor of the membrane was improved from 4.95 to 25.3 after CCD modification for one hour and got stabilized, indicating that the CCD modification process was fast which is consistent with the previous observation on modification of MFI zeolite disk membranes. The H₂ permeance decreased from 1.85 × 10⁻⁷ mol·m⁻²·s⁻¹·Pa to 1.26 × 10⁻⁷ mol·m⁻²·s⁻¹·Pa with only a reduction rate of 31.9%. The significant improvement of H₂/CO₂ factor with only modest reduction in H₂ permeance is ascribed to the unique structure of the silicalite/ZSM-5 bilayer membrane. Because CCD of MDES precursor only occurred in the ZSM-5 top thin layer instead of the entire

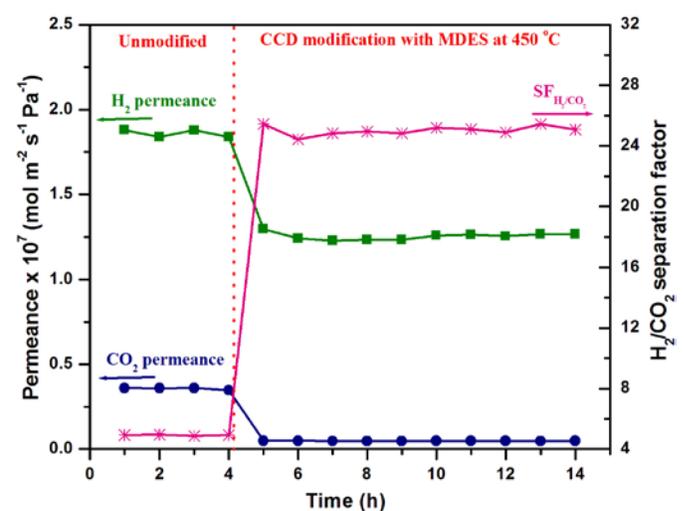


FIGURE 1. On-stream CCD modification of the stability improved silicalite/ZSM-5 bilayer membrane on YSZ coated alumina porous support.

diffusion channel along the membrane thickness direction, the resistance for the gas diffusion through the modified silicalite/ZSM-5 bilayer membrane is much smaller when compared to the membrane with the entire diffusion channel modified with MDES precursor. As a result, the H_2/CO_2 separation factor of the modified bilayer membrane was improved significantly with only modest reduction in H_2 permeance. The silicalite/ZSM-5 bilayer membrane is being shifted to the tubular porous supports with a YSZ intermediate barrier layer for stability improvement.

Understanding the effects of water vapor on gas permeation and separation properties of MFI zeolite membranes was important to the use of the zeolite membranes in WGS. The effects of water vapor on H_2 and CO_2 permeation and separation properties of ZSM-5 (Si/Al~80) zeolite and aluminum-free silicalite membranes were studied by comparing permeation properties of H_2 and CO_2 with the feed of equimolar H_2/CO_2 binary and $H_2/CO_2/H_2O$ ternary mixtures in 300°C-550°C. For both membranes, water vapor permeance was very low, with H_2/H_2O selectivity about 100. The presence of water vapor lowers H_2 and CO_2 permeance to the same extent, resulting in negligible effect on the H_2/CO_2 separation factor. The suppression effect of water vapor on H_2 and CO_2 permeation is larger for the less hydrophobic ZSM-5 zeolite membrane than for the hydrophobic silicalite membrane, and, for both membranes, is stronger at lower temperatures and higher water vapor partial pressures.

The modified silicalite/ZSM-5 bilayer membrane with improved H_2/CO_2 separation property was packed with a catalyst under WGS reaction conditions to examine the long-term stability of the membrane. Figure 2 presents the variations of CO-conversion and H_2 recovery of the modified disk membrane reactor during the long-term stability testing under WGS reaction conditions. The

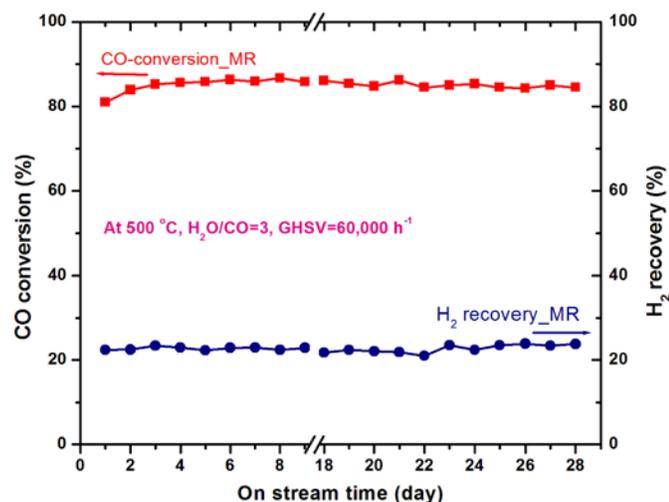


FIGURE 2. Results of stability tests (CO-conversion and H_2 recovery) of the modified silicalite/ZSM-5 bilayer/YSZ membrane disk under water gas shift reaction conditions, (at 500°C, $H_2O/CO=3$, $GHSV=60,000 h^{-1}$).

stability testing was conducted at 500°C, gas hourly space velocity ($GHSV$)=60,000, and $H_2O/CO=3$. As can be seen from this figure, the CO-conversion increased from 81% to 85% for the first a few days because the catalyst was not fully activated initially. After that, the CO-conversion kept constant at a value of 85% over the entire long-term stability testing period, indicating that the activity of the catalyst was very stable at high temperature under WGS reaction conditions. The H_2 recovery increased from 22.6% to 23.5% with an increase rate of only 3.9% over the stability testing for 28 days. These results also reveal that the modified silicalite/ZSM-5 bilayer membrane reactor with an YSZ intermediate barrier layer was very stable under WGS reaction conditions.

To make good quality $\alpha-Al_2O_3$ tubular supports with YSZ barrier layer for stability improvement of tubular MFI zeolite membranes, the deposition of YSZ support layers was investigated with commercial tubular $\alpha-Al_2O_3$ carriers from Pall Corporation. The carrier tubes have inner and outer diameters of 7 and 10 mm, respectively, and a specified nominal pore size of 800 nm. A 10 wt% YSZ dispersion was first prepared by dispersing 8 mol% yttria YSZ (TZ-8Y, Tosoh Co.) in an aqueous suspension adjusted to pH 2 with HNO_3 . The dispersion was then ultrasonically mixed with a Branson Digital sonifier (Branson Ultrasonics Corp.) for approximately 20 min and screened with 20 μm nylon mesh to remove any agglomerates and external contaminants. A polyvinyl alcohol (PVA) solution was prepared by mixing 3 wt% PVA (Celvol® 125, Celanese Chemicals) with pH 2 HNO_3 . The YSZ dispersion was then mixed with the PVA solution in a 3:2 volume ratio and flow coated onto the tubular carriers with an actuator speed of 10 mm/s and residence time of 30 s. The coating procedure was repeated a second time after waiting 30 s. The coated tubes were allowed to dry overnight at room temperature and calcined at 1,000°C for 3 hr with heating and cooling rates of 1.67°C/min.

Scanning electron microscopy (SEM) cross-sections of the YSZ-coated Pall carriers are shown in Figure 3. Figure 3 (a) illustrates the multilayer structure of the modified Pall carriers. A single continuous YSZ coating is observed on top of the two layer $\alpha-Al_2O_3$ substrate (with an 18 μm thick top layer). From the high magnification SEM cross-section in Figure 3(b), the thickness of the YSZ coating is estimated to be approximately 3 μm . After performing a surface analysis of the coated Pall carrier (Figure 3(c)), the YSZ coating was found to have a much smoother surface than the uncoated carrier (Figure 3(d)). The YSZ-coated tubular alumina porous supports have good quality for MFI zeolite membrane synthesis.

During the reporting period, the work on catalysts was focused on screening the best catalysts for HTWGS reactions in the presence of 400 ppm H_2S . Several different kinds of ferrite-based HTWGS catalysts were synthesized according to the procedure reported in the previous annual report. The best HTWGS catalysts that can be used at

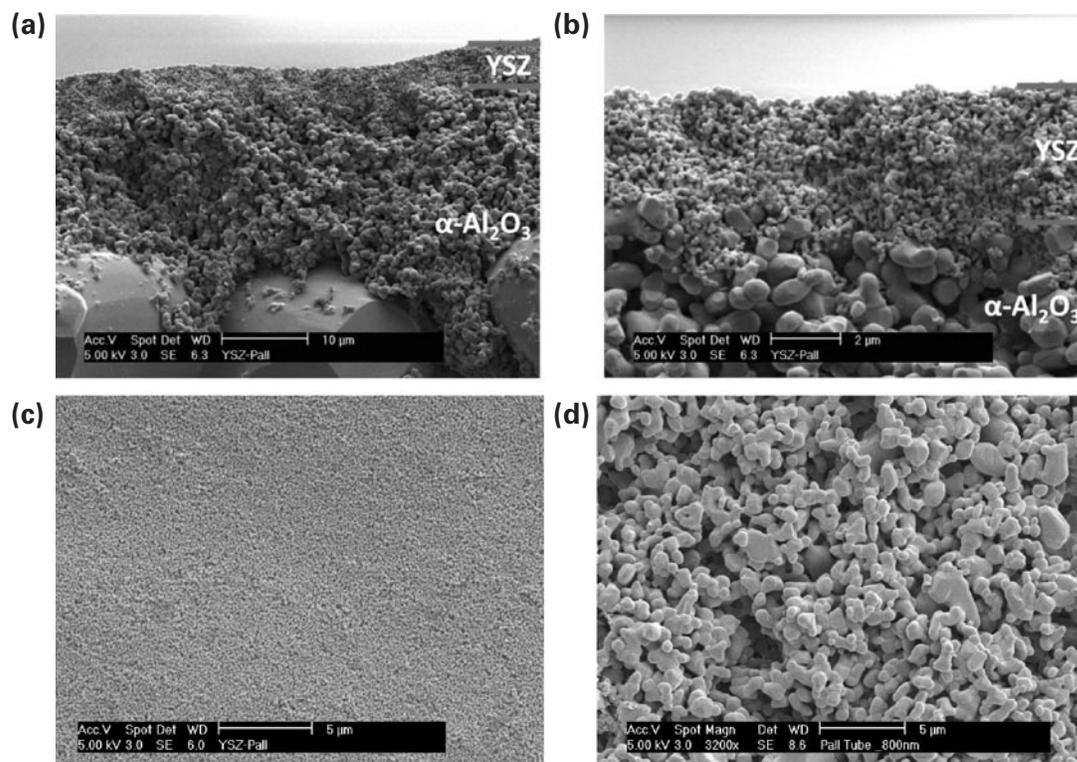


FIGURE 3. Microstructure of the YSZ coated and uncoated alumina tubular support. (a) SEM cross-section of an YSZ coating on a Pall tubular α - Al_2O_3 carrier, (b) High magnification SEM cross-section of YSZ coating on a Pall tubular carrier, (c) SEM surface image of an YSZ coating on a Pall tubular carrier, and (d) SEM surface image of an uncoated Pall tubular carrier.

relatively low and high $\text{H}_2\text{O}/\text{CO}$ ratios in the presence of H_2S were selected and tested, respectively.

HTWGS reaction has been carried out over the catalysts at temperature 500°C and compared with commercial catalyst. WGS reaction was performed at low steam to CO ratio ($\text{H}_2\text{O}/\text{CO}=1.5$) in the presence of 400 ppm of sulfur. A relatively high space velocity of $60,000 \text{ h}^{-1}$ was maintained in all the experiments. On the whole, the WGS operating conditions were chosen to mimic conditions found in a membrane reactor. Before the reaction, all the ferrite catalysts are activated in the presence of process gas at 400°C for 4 h. The activation process was described in our previous reports. WGS activity profile of Fe/Ce/Cr and commercial catalysts for 30 days time on stream experiment is presented in Figure 4(a) at steam to CO ratio of 1.5 and 400 ppm of H_2S . Remarkably, Fe/Ce/Cr catalyst exhibited excellent stability for 30 days. There is no decrease in CO conversion within the permissible error during the 30 days of reaction. On the other hand commercial catalyst started to deactivate from the 4th day onwards. The deactivation continued up to the 13th day and the catalyst became stable. Hence, our shift activity results show that our Fe/Ce/Cr catalyst exhibits better stability compared to the commercial catalyst at specific activation and reaction conditions. The excellent stability of Fe/Ce/Cr is due to the promotional effect of ceria and stabilization effect of chromium.

However, at high steam to CO ratio ($\text{H}_2\text{O}/\text{CO}=3.5$), the Fe/Ce catalyst exhibited the best long-term stability with/without the presence of 400 ppm H_2S in the gas stream. WGS activity profile of the Fe/Ce catalyst for 30 days time on stream experiment is presented in Figure 4(b) at a steam to CO ratio 3.5. Remarkably, the Fe/Ce catalyst exhibited excellent stability for 30 days. The CO conversion is decreased only from 84 to 80% during the 30 days of reaction. The excellent stability of Fe/Ce is because both iron and ceria undergo a facile charge transfer reaction between $\text{Fe}^{\text{III}} \leftrightarrow \text{Fe}^{\text{II}}$ and $\text{Ce}^{\text{IV}} \leftrightarrow \text{Ce}^{\text{III}}$ redox couples, respectively; the synergism between the two couples could be responsible for the improved WGS activity. Additionally, at higher temperatures, the rapid transformation of oxygen exchange between $\text{Ce}^{3+}/\text{Ce}^{4+}$ redox couple, as well as the improvement in the oxygen storage capacity of ceria will help the magnetite to keep its shift stability from CO poisoning. The experiments were also carried out in the presence of 400 ppm of sulfur to check the resistance of Fe/Ce towards sulfur. Interestingly, Fe/Ce catalyst exhibited excellent stability towards sulfur for 30 days as shown in Figure 4(c). The Fe/Ce catalysts in the presence of sulfur exhibited same activity as Fe/Ce catalyst in the absence of sulfur. Here also, the CO conversion is decreased only from 83 to 79% during 30 days of reaction. These results reveal that sulfur has no effect on the structure of Fe/Ce catalyst for the WGS reaction.

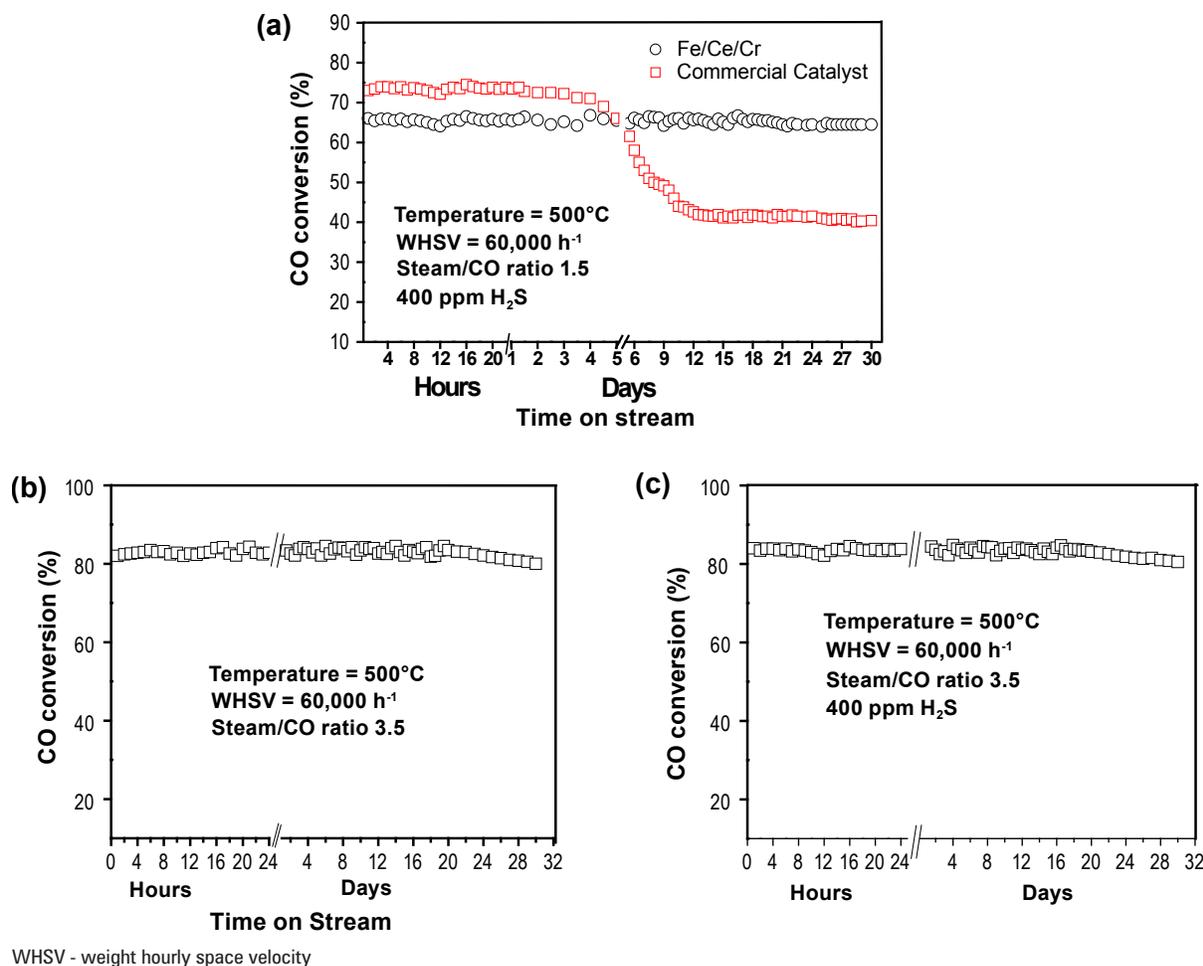


FIGURE 4. (a) Long-term stability of Fe/Ce/Cr and commercial catalysts at steam to CO ratio of 1.5 and 400 ppm of H₂S, (b) long term stability of the Fe/Ce catalyst at steam to CO ratio of 3.5 in the absence of H₂S, and (c) long term stability of the Fe/Ce catalyst for at steam to CO of 3.5 in the presence of 400 ppm of H₂S.

The work conducted on zeolite membrane reactor during the reporting period was focused on WGS reactions in the modified zeolite disk membrane reactor at different pressures (2~6 atm) with fixed GHSV and H₂O/CO ratios. MFI zeolite membranes were synthesized on the alumina porous supports with a YSZ barrier layer for stability improvement. The synthesized membranes were modified through catalytic cracking deposition of MDES precursor for H₂/CO₂ separation factor improvement. HTWGS reaction catalysts that can be used at relatively high and low H₂O/CO ratios were synthesized, respectively. The long-term stability of the catalysts was tested with/without the presence of 400 ppm H₂S in a fixed bed reactor.

The WGS reaction was performed at various feed pressures (2~6 atm) and different temperatures (400-550°C) in a modified disk MFI zeolite membrane. The permeate side pressure was kept at 1 atm. Figure 5 presents the CO conversion in the disk zeolite membrane reactor (MR) at a fixed GHSV of 7,500 h⁻¹ as a function of pressure

in comparison with the traditional reactor (TR) and the previous results obtained from a tube MR (H₂/CO₂ separation factor ~40). At all temperatures, the CO conversion in the disk MR was increased when feed pressure increased from 2 to 6 atm (constant permeate pressure of 1 atm) because high feed pressure increases ΔP_{H_2} , the driving force for H₂ permeation that in turn increases H₂ removal from the catalyst bed. In the TR, the dependence of the CO conversion on the reaction pressure was not significant, with a slight increase in CO conversion of <2%. The CO conversion in disk zeolite MR was higher than that in TR and also higher than the equilibrium CO conversions at 500°C and 550°C, indicating that faster reaction rate and higher H₂ permeance under higher temperature facilitated the WGS reaction to overcome the equilibrium CO conversion. As temperature increased, the CO conversion in disk MR increased gradually to the level of CO conversion in tube MR which has better quality than disk membrane. This suggests that the membrane quality becomes less influential on the MR performance when temperature is sufficiently high.

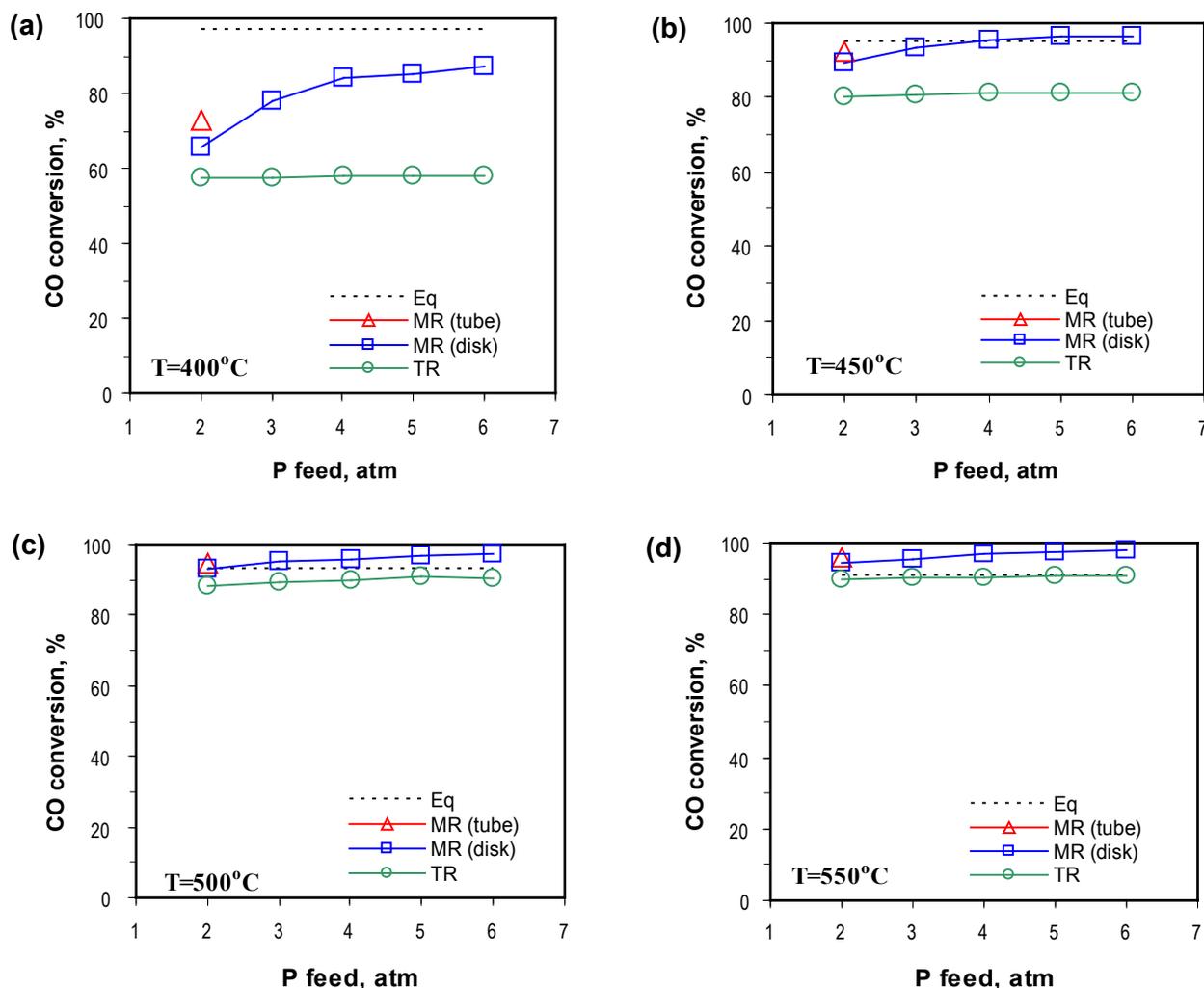


FIGURE 5. CO conversion for a fixed GHSV=7,500 h⁻¹ and various temperature of (a) 400°C, (b) 450°C, (c) 500°C and (d) 550°C: (---) equilibrium CO conversion; (▲) CO conversion under feed pressure 1.5atm in tube MR of previous work; (■) CO conversion in disk MR; (○) CO conversion in TR.

Conclusions and Future Directions

Conclusions

- Silicalite/ZSM-5 bilayer membrane consisting of a silicalite bottom thick layer and a ZSM-5 top thin layer was synthesized on the alumina porous supports coated with YSZ barrier layer for stability improvement.
- The modified silicalite/ZSM-5 bilayer membrane exhibited high H₂/CO₂ separation factor and considerable H₂ permeance.
- Alumina tubular porous supports with YSZ barrier layer for stability improvement were obtained through optimization of a flow coating procedure.
- Several different kinds of ferrite-based catalysts were synthesized and tested in a fixed-bed reactor. The long-term stability of the best sulfur-tolerant HTWGS catalyst was tested in the presence of 400 ppm H₂S.

- WGS reactions were conducted in a modified disk membrane at pressures up to 6 atm to obtain higher CO-conversion and hydrogen recovery.

Future Work

- Test the long-term stability of the modified silicalite/ZSM-5 bilayer membrane under WGS reaction conditions in the presence of 400 H₂S.
- Synthesize and modify the silicalite/ZSM-5 bilayer membrane on the alumina tubular porous supports coated with YSZ barrier layer.
- Conduct WGS reactions in the modified MFI zeolite membrane reactor at pressures up to 20 atm.
- Perform the atmospheric kinetics by using the best catalytic system Fe/Ce/Cr for HTWGS and determine kinetic parameters for that catalyst.
- Economic evaluation of the project results to validate the scale up and operation in an industrial scale.

FY 2011 Publications/Presentations

Journal Papers

1. M.C. Schillo, I.S. Park, W.V. Chiu and H. Verweij, "Rapid Thermal Processing of Inorganic Membranes," *J. Membrane Sci.*, **362**, 127–133 (2010).
2. X.F. Zhu, H.B. Wang, and Y.S. Lin, "Effect of the Membrane Quality on Gas Permeation and Chemical Vapor Deposition Modification of MFI-Type Zeolite Membranes", *Ind. Eng. Chem. Res.* **49**, 10026–10033 (2010).
3. G.K. Reddy, K. Gunasekara, P. Boolchand, and P.G. Smirniotis, "Cr - and Ce - Doped Ferrite Catalysts for the High Temperature Water-Gas Shift Reaction – TPR and Mossbauer Spectroscopic Study", *J. Phys. Chem. C*, **115**, 920–930 (2010).
4. Z. Tang, S.J. Kim, G.K. Reddy, J.H. Dong and P. Smirniotis, "Modified zeolite membrane reactor for high temperature water gas shift reaction", *J. Membr. Sci.*, **354**, 114-122 (2010).
5. H.B. Wang and Y.S. Lin, "Effects of Synthesis Conditions on MFI Zeolite Membrane Quality and Catalytic Cracking Deposition Results", *Microporous and Mesoporous Materials*, **142**, 481-488 (2010).
6. G.K. Reddy, and P.G. Smirniotis, "High Temperature WGS Reaction over Copper Doped Fe/Ce and Fe/Cr Catalysts", *Catalysis Letters* **141**, 27 (2011).
7. G.K. Reddy, K. Gunasekara, P. Boolchand, J. Dong and P.G. Smirniotis, "High temperature water gas shift reaction over nano crystalline copper co-doped modified ferrites". *J. Phys. Chem. C*, **115**, 7586–7595 (2011).
8. H.B. Wang and Y.S. Lin, "Effects of water vapor on gas permeation and separation properties of MFI zeolite membranes at high temperatures", *AIChE Journal*, 2011, DOI: 10.1002/aic.12622.

Conference Presentations

1. Y.S. Lin, "Zeolite membranes for high temperature gas separations", Plenary Lecture, 2010 Chemical Engineering Conference, Amman, Jordan, Oct.10–13, 2010.
2. H.B. Wang and Y.S. Lin, "Improving H₂/CO₂ separation factor of MFI zeolite membranes through catalytic cracking deposition of silane", Gordon Research Conference: Membrane Materials and Processes, (Poster) New London, NH, July 25, 30, 2010.
3. Y.S. Lin and H. B. Wang, "Effects of water vapor on gas separation properties of zeolite membranes", ACS National Meeting, Anaheim, CA, March 26-30, 2011.
4. H.B. Wang, Y.S. Lin, "Synthesis and catalytic cracking modification of silicalite/ZSM-5 bilayer membrane", NAMS Meeting, Las Vegas, NV, June 4–8, 2011.
5. S. Kim, J. Provenzano, Z. Xu, G. Reddy, P. Smirniotis, J. Dong, "High temperature water gas shift reaction in a modified zeolite membrane reactor: effect of operation pressure and long term stability", NAMS Meeting, Las Vegas, NV, June 4–8, 2011.
6. S. Kim, J. Provenzano, Z. Xu, G. Reddy, P. Smirniotis, J. Dong, "Water gas shift reaction of simulated syngas in a zeolite membrane reactor", NAMS Meeting, Las Vegas, NV, June 4–8, 2011.