II.D.1 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 address: Jerry.Lin@asu.edu

DOE Technology Development Manager: Arlene Anderson  
Phone: (202) 586-3818; Fax: (202) 586-9811  
E-mail: Arlene.Anderson@ee.doe.gov

DOE Project Officer: Jill Gruber  
Phone: (303) 275-4961; Fax: (303) 275-4753  
E-mail: Jill.Gruber@go.doe.gov

Contract Number: DE-PS36-03GO93007

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

(N) Hydrogen Selectivity  
(P) Flux

Technical Targets

This project is conducting fundamental studies of zeolite membrane reactors to perform WGS for hydrogen production. Insights gained from these studies will be applied toward 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 hrs

Accomplishments

Developed and studied methods and techniques for:

- Synthesis of disk-shaped supports with intermediate zirconia and silicalite layers (improvement of thermal stability).
- Improved understanding of gas transport, permeation and separation in microporous zeolite membranes at high temperatures.
- Development of silicalite membranes modified by thermal cracking method (H₂ permeance: >1×10⁻⁷ mol/m²s Pa, H₂/CO₂ permselectivity: 20, H₂/CO₂ separation selectivity: 13).
- Development of the cost-effective microwave method to synthesize the silicalite membranes (shorter time and less energy consumption).
- Fabrication of tubular silicalite membranes and membrane reactor module suitable for membrane reactor applications.
- Development of membrane support by colloidal casting.
- Development of 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 (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 (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 during this reporting period was focused on testing the hydrogen separation performance of silicalite zeolite membranes in a wide temperature range. Decomposition CVD (or thermal cracking) was applied to modify silicalite membranes to improve the H₂ separation performance at high temperatures. The hydrothermal stability of the modified membranes was also examined. The morphology and thickness of the supported membranes were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD).

H₂ separation performance for a silicalite membrane at dry conditions can be seen in Figure 1. The permeances (H₂, CO, CO₂) that are obtained by ternary-component gas separation are quite similar to those for single gas permeation above 400°C. However, a clear difference between these permeances was observed below 300°C. The permeances of H₂ and CO for ternary-component gas separation decrease drastically with decreasing temperature, lowering the H₂ permselectivity.

**FIGURE 1.** Temperature dependency of gas permeances for MFI-type zeolite membrane (closed symbols on solid line: gas permeances for single permeation, open symbols on broken line: those for multi-component gas separation), feed composition (H₂:CO:CO₂ = 1:1:1, P_gas = 0.3 MPa, P_permeate = 0.1 MPa).
On the other hand, CO₂ permeance for ternary-component gas separation is similar to that for single gas permeation. It is expected that CO₂ preferential adsorption on zeolitic pores should occur due to much stronger affinity between CO₂ and zeolitic pores than that between H₂ or CO and zeolitic pores. Since CO₂ adsorption on zeolitic pores decreases with increasing temperature, it can be considered that H₂ separation performance for ternary-component gas separation coincides well with that for single gas permeation at high temperature (>400°C). On the other hand, at low temperature, the zeolitic pores are blocked by the adsorbed CO₂ molecules that make H₂ and CO molecules unable to permeate through these pores in the membrane.

An MFI-type zeolite membrane was modified by decomposition CVD (thermal cracking of methyl-diethoxy silane, MDES) in a reducing atmosphere. The surface of the zeolite layer was exposed to MDES at 450°C. MDES appeared to diffuse into zeolite pores and decompose to cause deposition of carbon or silicon in the pores. The zeolite membrane before modification was first tested by p/o-xylene vapor separation at 300°C. The membrane exhibited p/o-xylene a vapor separation factor of approximately nine before modification. After modification, the membrane became non-selective for p/o-xylene and the xylene permeance decreased by two orders of magnitude. This indicates that the zeolite pore size/structure was successfully reduced/modified, and became inaccessible to the both p- and o-xylene molecules.

The modified membrane was then tested by separation of H₂/CO₂ (50:50) gas mixtures. The results show that the zeolite pore modification by the decomposition CVD dramatically enhanced the separation of H₂/CO₂ with a moderate decrease of the H₂ permeance. Figure 2 shows the separation of a H₂/CO₂ 50/50 mixture with 11% and 28% of water vapor in the feed stream. The membrane exhibits a H₂/CO₂ selectivity of 13 at 450°C. This result also indicates that the modified membrane is stable at humid operation conditions.

Continuing efforts in developing the microwave heating synthesis method, MFI-type zeolite membranes were synthesized on high quality seed layers with seed crystallite size of 60~120 nm. Template-free synthesis precursors were used for secondary growth to form continuous zeolite membranes, which were successfully obtained from precursors with and without aluminum contents by microwave heating. It was found that 3-4 hours of hydrothermal reaction were sufficient for the secondary growth process under microwave heating, while a 10 to 20-hour reaction time was necessary in conventional heating. It has been also confirmed that aluminum components in the synthesis precursor facilitate secondary growth and a high concentration of SiO₂ is needed for membrane formation in an aluminum-free precursor.

Membrane reactor modules have been assembled incorporating commercially available, custom porous tube (CoorsTek Inc., Golden, CO, USA) with dimension (O.D × I.D×length) of 12×10×100 mm. In this reporting period the surrounding framework for the membrane reactor has been put into place including control systems for gas handling, back pressure, temperature, and process characterization. The membrane reactor and its accompanying control systems have been assembled within a rack mount with a centralized computer, which monitors and implements the control systems on a LABView™ 7.1.1 platform.

A schematic diagram of the membrane reactors control components is shown in Figure 3. The steady-state flow rates for the H₂/CO₂ gaseous feed and N₂ sweep are maintained by mass flow controllers (Brooks Instruments, The Netherlands) with a mild back pressure preserved by combining down stream pressure flow controllers (Brooks Instruments) and

![FIGURE 2. Separation of H₂/CO₂ (50/50) (with Steam Added) for the Modified Membrane](image)

![FIGURE 3. A Schematic Diagram of the Membrane Reactor Control Components](image)
precision pressure transducers (MKS, USA). The membrane reactor is heated to temperature by a coiled resistive Kanthal heating element with the internal and element temperature monitored with dedicated type S thermocouples. The membrane reactors temperature control system is the multi-zone furnace. The composition of the membrane reactors retentate and permeate streams is examined by gas chromatography (Dual channel CP-4900 Micro-GC, Varian Inc.) where the 10 m, 5 Å moliseve and 10 m poraplot Q column allow accurate determination of CO, CO₂ and H₂.

The work on catalysis was focused on preparation of a new family of ternary spinel-based catalysts for sulfur-tolerant WGS reaction. The WGS reaction was performed at a low steam-to-CO ratio (S/CO = 1) to study the influence of a steam deficient environment on the activity of the catalysts. Figure 4 shows WGS activity performance over various ferrite-based catalysts at different steam-to-CO ratios. The WGS reaction was performed in the temperature range of 350 to 550°C using a designated amount of steam and CO. In general with increase in temperature from 350 to 550°C, the WGS activity was found to increase. Also the WGS activity was found to increase as the steam-to-CO ratio was increased, particularly from S/CO = 1 to S/CO = 3.5. However, the WGS activity went down slightly for S/CO = 7.0 when compared to S/CO = 3.5 in the case of Fe/Cr catalysts.

**Conclusions and Future Directions**

- Tested hydrogen separation performance for silicalite membranes in a wide temperature range (25-500°C).
- Developed modified silicalite membranes with high hydrothermal stability (H₃PO₄ permeance: >1×10⁻⁷ mol/ m² s Pa, H₂/CO₂ permselectivity: 20, H₂/CO₂ separation selectivity: 15).
- Identified the optimum conditions of microwave synthesis for silicalite membranes.
- Designed and realized membrane reactor system.
- Developed membrane support by colloidal casting.
- Developed ternary spinel-based catalysts for sulfur-tolerant WGS reaction.

Future work will include the following tasks.

- Improve H₂ separation performance for silicalite membranes by CVD modification.
- Test hydrogen separation and chemical/hydrothermal stability of silicalite membranes under syngas conditions.
• Develop and design intermediate layer/tube leak/flow testing membrane module.
• Test the performance of sulfur-tolerant hybrid WGS catalyst developed by simulating SO₂ and H₂S in the feed stream.

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Journal Papers

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