II.C.8 Zeolite Membrane Based Shift Reactor

Jerry Y.S. Lin
Department of Chemical and Materials Engineering
University of Cincinnati and
Arizona State University
Tempe, AZ 85287
Phone: (480) 965-7769; Fax: (480) 965-0037
E-mail: 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: Carolyn Elam
Phone: (303) 275-4953; Fax: (303) 275-4788
E-mail: Carolyn.Elam@gd.doe.gov

Contract Number: DE-PS36-03GO93007

Subcontractors:
Arizona State University, Tempe, AZ
Ohio State University, Columbus, OH
New Mexico Tech, Socorro, NM

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

Objectives

- Synthesize chemically and thermally stable silicalite membranes with hydrogen permeance and H₂/CO₂ selectivity of larger than 5 x 10⁷ mol/m²·s·Pa and 50 at 500°C.
- Fabricate tubular silicalite membranes and a membrane reactor module suitable for membrane reactor applications.
- 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 CO₂ stream with 97% purity.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section (3.1.4.2.3) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(L) Durability
(M) Impurities
(O) Selectivity
(P) Operating Temperature

Technical Targets

The overarching goal of this project is to develop low-cost, high-efficiency technology for distributed and central hydrogen production. Microporous membranes with high hydrogen flux and selectivity and good thermal and chemical stability are critical in developing advanced separation technology (i.e., membrane reactor) to achieve the goal. The technical targets to achieve the performance criteria with zeolite membranes are listed in the table below.

<table>
<thead>
<tr>
<th>Criteria</th>
<th>2006</th>
<th>Project goal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flux [mol/m²·s·Pa]</td>
<td>&gt;1x10⁻⁷</td>
<td>&gt;5x10⁻⁷</td>
</tr>
<tr>
<td>H₂/CO selectivity [-]</td>
<td>10</td>
<td>50</td>
</tr>
<tr>
<td>Cost [$/kg]</td>
<td>–</td>
<td>0.40</td>
</tr>
</tbody>
</table>

Accomplishments

Developed and studied methods and techniques for

- Synthesis of disk-shaped supports with intermediate zirconia and silicalite layers (improvement of thermal and chemical stability).
- Synthesis of high-quality silicalite membranes with molecular sieving properties (H₂ permeance: >1x10⁻⁷ mol/m²·s·Pa, H₂/CO₂ permselectivity: 5).
- Development of the cost-effective microwave method to synthesize the silicalite membranes (shorter time and less energy consumption).
- Fabrication of tubular silicalite membranes and a membrane reactor module suitable for membrane reactor applications.
- Development of catalysts for the WGS membrane reactor application.

Introduction

Gasification of biomass, coal or heavy feedstock to produce hydrogen fuel gas using current technology includes partial oxidation to produce syngas, water-gas-shift 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. Commericially, WGS is normally conducted in two or more reactor stages with inter-cooling to maximize conversion for a given catalyst volume. Complete conversion of carbon monoxide 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 study of the synthesis of a new hydrogen permeable and thermally/chemically stable zeolite membrane, and its use in the membrane reactor for 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 micro pores 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 a cost-effective microwave method to synthesize the silicalite 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 an experimental and modeling study 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 below $0.40/kg.**

**Approach**

The project approach is to study issues related to synthesis of high-quality, stable zeolite membranes and membrane reactor for the WGS reaction and hydrogen separation. The **work being conducted in this project is to (1) develop disk-shaped and tubular supports with desired intermediate layers and silicalite membranes with a template-free hydrothermal synthesis method, (2) optimize the hydrothermal synthesis conditions and perform thorough permeation and separation characterization of silicalite membranes, (3) develop a microwave synthesis approach to more efficiently and cost-effectively synthesize high-quality silicalite membranes, (4) obtain a new WGS catalyst with activity and selectivity comparable to the best available commercial catalysts with improved chemical stability for SO₂ and H₂S containing reaction streams, and (5) develop methods to fabricate tubular membrane supports with desired intermediate layers and a membrane module and sealing system for the tubular membrane reactor that can be operated in WGS conditions.

**Results**

The work conducted during this reporting period was focused on testing the reproducibility of preparation of silicalite membranes with the zirconia intermediate layer. The morphology and thickness of the supported membranes were characterized by using scanning electron microscopy (SEM) and x-ray diffraction (XRD). The optimization of hydrothermal synthesis conditions (dip coating times, hydrothermal synthesis time) was examined by p-, o-xylene pervaporation separation at room temperature. H₂ permeation characteristics and thermal stability of this type of membrane were also examined.

SEM images of the cross section of the silicalite membranes after secondary growth (180°C, 4 h) can be seen in Figure 1. **As shown in these micrographs and results of XRD analysis, crack-free continuous silicalite film could be formed on the zirconia intermediate layer by the template-free secondary growth method.** The thickness of the secondary growth silicalite membrane is around 3 μm in both membranes, while the thickness of the zirconia intermediate layer is around 4 μm and 7 μm for 1 time and 2 times dip coating, respectively. The reproducibility of preparation of silicalite membranes was confirmed, and membrane thickness could be controlled by the dip coating times with the stable suspension.

**FIGURE 1.** SEM Images of the Cross Section of the Zeolite Membranes after Secondary Growth (180°C, 4 h) (a) 1 Time Dip Coating (YSZ), (b) 2 Times Dip Coating (YSZ)
From the results of pervaporation, it was found that (1) the membrane quality could be substantially improved on supports with a good quality seed-layer prepared by the dip-coating method, and (2) annealing prior to the temperate removal step can prevent defects and/or cracks in the zirconia intermediate layer, resulting in the ability to form a high-quality silicalite seed layer.

Thermal stability of silicalite membranes with zirconia intermediate layers was examined by observing the temperature dependency of gas permeance below 300°C before and after the membranes were heat-treated in air at 500°C for 50 hours. Temperature dependence of gas permeances for silicalite membranes with ZrO₂ layers is shown in Figure 2. The permeance of He, H₂, CO and CO₂ for a fresh silicalite membrane slightly increases with decreasing temperature and is similar to the trend observed for Knudsen diffusion. This membrane shows relatively large H₂ permeance above 10⁻⁷ mol/m²-s·Pa with selectivity of around 30-40 (He/SF₆). This is approximately 6 times higher than Knudsen selectivity (6.04). The permeability of H₂/CO, H₂/CO₂ at 300°C is similar to the Knudsen selectivity. These types of membranes were thermally stable at 500°C.

After heat treatment, the Si/Al ratio for silicalite membranes without a zirconia intermediate layer decreased from 34.6 to 17.8, while membranes with zirconia intermediate layers (1 time, 2 times dip coating) showed little change in the Si/Al ratio. It can be considered that the zirconia intermediate layer is effective in eliminating interaction between alumina and the silicalite coated on the surface of the zirconia layer.

Research efforts were also directed towards the synthesis of nano-sized MFI zeolite particles (50-100 nm) by microwave heating and dispersion of the synthesized nano-particles in aqueous solutions. The zeolite nanoparticles were characterized by XRD, SEM, transmission electron microscopy and the Bruner, Emmett and Teller surface area analysis method. Silicalite nanoparticles (size 40-100 nm) were obtained by two-step microwave synthesis processes with a 1st step temperature of 40-90°C and a 2nd step temperature of 120°C, and a total synthesis time of 5-8 hours. The particle size was controlled by varying the 1st step temperature. For example, MFI particles with sizes of 50-60 nm were obtained by microwave heating at 50°C for 6 hours and 120°C for 1 hour. This synthesis time is significantly shorter compared to that required by conventional heating (65°C for 360 hours).

In situ MFI tubular membranes were synthesized and characterized by vapor (not pervaporation) separation of xylene isomers. The membranes exhibit a separation factor of >50 for a p/o-xylene (1:1) vapor mixture at 250°C and ~1 kPa feed vapor pressure.

Membrane reactor modules have been assembled incorporating commercially available porous ceramic tubes with dimensions of 12×10-100 mm (outside diameter×inside diameter×length). The specifications for the porous ceramic tubes include an average pore diameter of <0.5 μm and an apparent porosity of 23%. The assembled membrane module is shown in Figure 3. Cooling water has successfully been incorporated into
the stainless steel caps on both ends of the modules, allowing for incorporation of Viton® type o-ring seals (maximum operating temperature 170°C). Consol Multi-physics finite element analysis (FEA) has been applied to the modules’ design in order to estimate temperature distributions within the modules. The FEA modeling for the module predicted a uniform temperature gradient along the length of the tube with sufficiently low temperatures at the o-ring seals. The latter depends on the extent of the heating coils. Temperature control of the membrane modules is currently being incorporated for device verification and testing.

WGS catalytic activity was tested as a function of operating temperature between 400 and 550°C. Tests were performed in H₂ lean conditions to mimic membrane reactor conditions. The reactor was placed vertically inside a programmable tubular furnace (Lindberg). Parameters pertaining to pretreatment conditions were optimized. In order to investigate the influence of steam/dry gas ratio on the progress of the WGS reaction, different steam/dry gas ratios ranging from 3.5 to 7 were employed, as shown in Figure 4. Interestingly, maximum activity is observed at 550°C. The highest WGS activity (% CO conversion) of 94-97% is observed in a single pass. UCM-7 (primarily Fe₂O₃/CeO₂) catalyst is found to be very promising; its activity results are encouraging for possible commercialization. The ultrasonic treated catalysts are found to be less active for WGS reaction than their untreated counterparts.

Conclusions and Future Directions

- Synthesis of high-quality silicalite membranes with high thermal stability (500°C) was achieved (H₂ permeance: > 1x10⁻⁷ mol/m²-s-Pa, H₂/CO₂ permselectivity: 5).
- Developed cost-effective microwave method.
- Designed and realized two types of membrane modules.
- Developed high-activity catalyst for the WGS reaction (CO conversion: 94-97%).
- Tested separation and hydrothermal stability of silicalite membranes under syngas conditions.
- Established the microwave synthesis system for a tubular membrane.

Future work will include the following tasks:
- Develop and design intermediate layer/tube leak/flow testing membrane module.
- Test the performance of a sulfur-tolerant hybrid WGS catalyst developed by simulating SO₂ and H₂S in the feed stream.

FY 2006 Publications/Presentations