DOE/ER/83206-1

REACTIVE SEPARATIONS VIA A HYDROTHERMALLY STABLE HYDROGEN SELECTIVE MEMBRANE

Final Report

08/27/01 – 02/26/02

Rich J. Ciora, Jr. and Paul KT Liu

Media & Process Technology Inc.

Pittsburgh, PA 15238

DOE Patent Clearance Granted
MP Dvorscak
Mark P Dvorscak
(630) 252-2393
E-mail: mark.dvorscak@ch.doe.gov
Office of Intellectual Property Law
DOE Chicago Operations Office

2/24/04
Date

October 29, 2002

Prepared for

THE U.S DEPARTMENT OF ENERGY
Under Award No. DE-FG02-01ER83206

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Abstract

In this SBIR Phase I program, we have successfully completed the fabrication of SiC-based hydrogen selective membranes suitable for use as a membrane reactor for steam-methane reforming applications. Hydrothermal stability was performed to demonstrate the stability of the membrane for ~50 hours under the proposed reforming condition. In addition, several mechanistic study was conducted to elucidate the SiC membrane formation mechanism. This understanding will facilitate membrane optimization work to be proposed for the Phase II study. The reaction study was postponed to Phase II.

1. INTRODUCTION/BACKGROUND

The catalytic membrane reactor (MR) concept has been actively investigated over the past decade for improving the efficiency of dehydrogenation, hydrogenation, oxidation, and other major industrial catalytic reaction processes. Although this technology could potentially offer a quantum leap in the field of reaction engineering, no commercial progress has been made in this area yet. One of the major barriers is the lack of a membrane product possessing the required material stability suitable for these applications. For most dehydrogenation applications, a hydrogen selective membrane with a hydrothermal and chemical stability is a must. Through our in-house R&D, an innovative membrane with such a property has been developed [2] recently. Thus, we believe that the time is ripe for us to revisit the MR concept and harvest the immense effort invested by the US government and private sector in the past decade.

In this SBIR Phase I project, we focus on methane steam reforming (SMR) as an application candidate for demonstrating the MR technology. Hydrogen production via steam reforming of methane is widely practiced in the refinery and chemical industries. In addition SMR is being seriously investigated as a technology for hydrogen fuel production in advanced fuel cell systems. The standard SMR process is extremely expensive because of the requirements of (i) high reaction temperatures (800 to 900°C), (ii) steam in excess of the stoichiometric requirement to improve yield in the equilibrium limited reaction, and (iii) a post water-gas shift reactor. Using an MR SMR can be carried out at lower temperatures, 450 to 600°C [7], excess steam is much reduced or not required, and the shift converter can be eliminated. For these reasons, the introduction of MR technology will dramatically lower the H₂ production cost and facilitate wider use of fuel cell technology.

In addition the proposed hydrogen selective membrane as an MR can improve the efficiency and overcome the environmental challenges of power generation. In the case of coal-based power plant hydrogen production, purification, and utilization [10] MR has been proposed to meet these objectives. Advanced high temperature hydrogen permselective membrane-based reactor technologies show one of the greatest promises for technology leaps in this area.

In summary, a hydrothermally and chemically stable hydrogen selective membrane could play a pivotal role in moving MR technology to commercial reality. We have successfully fabricated a hydrogen selective SiC-based membrane with the required stability. In this Phase I program, we have prepared a series of SiC membranes suitable for the proposed application. Further, we demonstrate the stability of this membrane as a catalytic membrane reactor (MR) for hydrogen production via methane steam reforming reaction (SMR). No reaction study has been performed due to the shortage of time.

2. ANTICIPATED BENEFITS

The use of the hydrothermally stable H₂ selective membrane for reactive separation as proposed here can overcome the key technical barriers preventing the implementation of the MR technology in SMR and dehydrogenation applications. Non-technical benefits anticipated from this proposed program are presented below in terms of the commercial, economical, and social/environmental impact:

- Commercial

The application selected in this SBIR program, hydrogen production through SMR, is ideally suited to showcase this new process technology, particularly to commercial interests in small-scale hydrogen production for fuel cell and environmental applications. The introduction of a new process technology, particularly reactive separations, requires a combination of favorable factors to facilitate commercialization. These factors include suitable application candidate, ease of implementation, and highly favorable economic impact. The proposed SMR coupled with MR meets these criteria because (i) the feed stream is at high pressure; (ii) the product stream pressure required is considered low, particularly for fuel cell applications, and can be delivered via the permeate without compression; (iii) the relative simplicity of the reactions; and (iv) the low heat transfer demand because the reforming (endothermic) and water gas shift (exothermic) reactions are combined. Once proven on a small scale, three areas of general commercial applicability are immediately apparent, namely, (i) large scale methane reforming in the CPI and coal gasification, (ii) dehydrogenation reactions in which steam is present such as ethyl benzene to styrene [13] or alkali chemicals are present, such as propane to propylene [15], and (iii) dehydrogenation reactions at an extremely high temperature such as H_2S decomposition at $\sim 1,000^\circ\text{C}$ [14].

- Economical

Presently no economical, small to medium sized, on-site hydrogen production technology is available. The introduction of membrane-based reactive separation technology will permit economical generation of hydrogen on this scale. The successful development of the proposed membrane, resistant to both steam and chemicals, can offer significant savings for large-scale hydrogen production and dehydrogenation reactions. Hydrogen is widely used in the oil refinery, petrochemical and other industries. Estimated savings through implementation of the proposed reactive separations are well over \$1 billion/yr based upon our estimate. In summary this technology breakthrough could achieve tremendous savings in domestic chemical production and further improve US competitiveness.

- Social/Environmental

Hydrogen is considered the clean fuel choice of the future. Use of hydrogen can facilitate the recovery and sequestration of CO_2 for green house gas management [11]. Future trends in power generation, specifically fuel supply to IGCC from coal and natural gas sources, will involve reforming to hydrogen to achieve lower NO_x emissions and CO_2 control in addition to improving power generation efficiency [10]. Besides, several renewal energy concepts are proposed based upon steam reforming of biomass or waste materials. Therefore, an efficient and compact reforming technology coupled with membrane-based reactive separations will play a key role in supplying environmentally friendly energy in the US. In addition, fuel cells are more energy efficient and produce lower emissions of SO_x and NO_x than conventional combustion technology for power generation for both mobile and stationary applications. Although fuel cell technology is commercially available, a number of technical hurdles must be overcome to improve performance, certainly not the least of which is economical generation of fuel.

The above key benefits support this SBIR program, use of a hydrothermally and chemically stable hydrogen selective SiC membrane for methane steam reforming (SMR), to advance the reactive

separation process. We believe that this proposed project could play a pivotal role in turning the present laboratory novelty into process reality in the near future.

3. TECHNICAL OBJECTIVES

Our primary objective is to use a SiC-based H₂ permselective membrane (available from us) as a catalytic membrane reactor (MR) for implementing the reactive separations concept in a selected example, methane steam reforming (SMR). Key specific technical objectives are listed below:

- 1) Documenting the hydrogen permselectivity over CO, CO₂, CH₄, and other light hydrocarbons as a function of temperature in the SMR environment;
- 2) Evaluating hydrothermal and chemical stability of the proposed SiC membrane under SMR environment;
- 3) Conducting bench-scale reactive separation studies on methane steam reforming and further quantitatively determining the technical benefits offered by the proposed concept;
- 4) Conducting preliminary economic analyses to determine the economic benefit offered by the proposed technology for SMR applications.

Objectives 1) & 2) have been accomplished in this Phase I study. Objectives 3) & 4) remain to be completed due to the time shortage.

4. PHASE I ACCOMPLISHMENTS

4.1 Characterization of Hydrogen Selective SiC Membrane

Hydrogen selective nanoporous SiC membranes have been successfully developed using M&P's Al₂O₃ membranes as substrates and a unique chemical vapor deposition/infiltration (CVD/I) technique [4,5,12] developed by us. An SEM photomicrograph of the cross section of the SiC membrane is shown in Figure 1a and 1b. Since no deposition of an additional layer on top of the support is indicated, deposition of the SiC occurs inside the top layer of the support. According to our previous experience [5,12], an extremely thin film was deposited, estimated at less than 1.5μm based upon EDAX mapping. Accordingly, no thermal mismatch has been observed by us during cyclic heating and cooling. Further the CVD/I technique is currently practicing by us for full-scale membrane fabrication.

An unsupported SiC thin film was prepared under a similar condition for surface characterization purposes. Figure 2 confirms the formation of SiC according to the XRD analysis of the produced unsupported film. Crystalline SiC peaks are evident in the samples calcined at 1,200 and 1,400°C. Although the sample calcined at 1,000°C did not exhibit SiC peaks, it is believed that amorphous SiC is present at this temperature as indicated by the peak at the low angle. Literature studies using the same precursor for the CVD/I confirm the formation of SiC at ~1,000°C [6,8] based upon XPS analysis. In short the formation of SiC via the CVD/I technique is evident. The helium¹ permeance ranges from 0.65 to 5.2 m³/m²/hr/bar with a He/N₂ selectivity of 3 to 85 at 600 °C. Table 3 below summarizes the performance of typical samples produced by us:

¹ He was used as a simulate gas to hydrogen. Our past experience has verified the validity of this simulant gas for the microporous H₂ selective ceramic membrane.

Table 1. Permeance vs Temperature for H₂-Selective SiC Membranes Prepared with CVD/I Technique. Each sample represents a deposition condition

Sample	300 °C	400° C	600° C	1000° C
17B				
He Permeance *	1.11	1.39	3.32	
N ₂ Permeance		0.03	0.04	
Separation Factor		51.48	85.13	
19B				
He Permeance		0.21	0.65	
N ₂ Permeance		0.05	0.04	
Separation Factor		4.20	16.67	
20B				
He Permeance		0.19	0.42	1.47
N ₂ Permeance		0.07	0.06	0.02
Separation Factor		2.81	6.55	67.74
21B				
He Permeance		6.69	5.20	
N ₂ Permeance		2.14	1.94	
Separation Factor		3.13	2.68	
22B				
He Permeance		0.36	0.50	
N ₂ Permeance		0.11	0.07	
Separation Factor		3.14	7.26	

* in m³/m²/hr/bar

The wide range of results shown in Table 1 reflects our evaluation of several key deposition parameters as part of the membrane preparation study. Helium permeance increases significantly with temperature, indicative of activated diffusion; whereas the nitrogen permeance decreases with temperature, indicative of Knudsen flow for this penetrant. This phenomenon is consistent with our previous experience with hydrogen selective SiO₂ membranes [12]. Good reproducibility² of the CVD/I technique was demonstrated in our previous study with the SiO₂ membrane using a similar deposition technique.

²H₂ permeance of 7.58±0.6 m³/m²/hr/bar (at 600EC) with 95% confidence for the SiO₂ membrane we prepared previously using a similar deposition protocol.

High permselectivities of He to CO₂ and CH₄ have also been demonstrated. The permselectivities of He/CO₂ and He/CH₄ are 83.4 and 39.4, respectively, for membrane TPS-021 at 750°C. The He/N₂ permselectivity is 76.1 for this membrane at this temperature. The rejection of CO₂ and CH₄ are similar to N₂ so that He/N₂ represents a good surrogate gas mixture for evaluating this membrane. In summary, SiC formation via the CVD/I technique was confirmed and the permselectivity was found to be adequate for the proposed SMR reaction.

4.2. Methodology for Preparing SiC Membranes

Our in-house study has identified a practical approach for preparing a porous SiC membrane based upon the technical basis derived from the unsupported film discussed in Sec. 4.1. Using our existing Al₂O₃ porous ceramic membrane (see Figure 1) as a substrate (effective layer thickness is 3 to 5 μ m, and pore size is $\sim$ 100 Å after pre-calcination at 1000°C), we have been able to form a porous SiC thin film via the three-step protocol below:

Step 1 Deposition of Si/C Precursor Membrane.

A precursor membrane containing Si/C can be deposited within the existing porous ceramic membrane substrate via a chemical vapor deposition/infiltration (CVD/I) technique. The precursor selected here is triisopropyl silane (TPS). The CVD/I temperature is 700°C. The precursor membrane is believed to be embedded within the top surface of the substrate. Its effective thickness is $\sim$ 1 μ m. An extensive morphological characterization has been performed for a similar system, SiO₂ membrane (via a similar CVD/I technique), which is presented in Figure 1 to support our layer thickness estimation.

Step 2 Conversion of Si/C to SiC Membrane.

The precursor membrane is then converted to a SiC membrane via calcination at $\sim$ 1000°C. XRD characterization of the unsupported film shows the presence of amorphous SiC as discussed in Sec. 4.1. Obviously some residual carbon and silicon remain as expected. Along with conversion, we also found the densification of the membrane structure as indicated by the He and N₂ permeance reduction with temperature increase shown in Table 3. For example He permeance was reduced from 2.46 m³/m²/hr/bar at 700°C to 1.73 m³/m²/hr/bar at 1000°C, and then 0.621 m³/m²/hr/bar during cooling down at 700°C of TPS-138C. Their >Knudsen selectivity of He/N₂ indicates that the thin membrane deposited remains intact after the conversion.

Step 3 Porous Structure Development via Removal of Residual Carbon.

In this step, excess carbon is removed through the carbon steam activation at 700°C. Activation opens additional microporous volume as evidenced by the significant increase in helium permeance while minor change in nitrogen as shown in Table 3. For example, He permeance increases from 0.61 to 5.64 and its He selectivity increases from 14 to 91 at 700°C after steam activation for TPS-138C. The presence of the SiC membrane is obvious because the resultant membrane appears black color even after oxidation or steam exposure.

In summary, our experience thus far has shown that a synthesis approach has been established to develop a microporous SiC membrane with hydrogen selectivity.

Table 3 He and N2 permances of three SiC porous membranes:
Before Step 1, Step 2, and Step 3 and After Step 3

Starting Substrate Characterization			
Parts ID	Temp	He	N2
129C	700	95.3	33.3
138C	700	75.5	30.3
131C	700	110	44.2

After CVD/I at 700C (Step 1)			
He	N2	Selectivity	Min After Dep.
30.000	2.040	14.71	1
13.500	0.224	60.27	60
3.270	0.043	76.94	30 - 90
35.600	1.680	21.19	25 - 45

Calcined at 1000C (Step 2)			
He	N2	selectivity	Temperature
0.380	0.061	6.23	986
0.362	0.076	4.74	852 - 726
2.400			692
1.730			1000
0.621	0.045	13.96	698
1.920	0.114	16.84	996

Before Steam Activation (Before Step 3)				
Parts ID	He	N2	Selectivity	Temperature
129C	0.451	0.088	5.13	726
138C	0.621	0.045	13.96	698
131C	0.645	0.124	5.20	700

Final Product Permeances				
After Steam Activation (After Step 3)				
He	N2	Selectivity	Temp	
3.070	0.090	34.11	700	
5.640	0.062	90.68	700	
5.766	0.260	22.18	700	

In summary, during this Phase I study, we have performed a methodical study to identify the three-step mechanism involved in the preparation of a supported SiC membrane. This understanding will facilitate our Phase II study to optimize the product development.

4.3 Hydrothermal Stability of Hydrogen Selective SiC Membrane

Our in-house evaluation of the thermal and hydrothermal stability of the porous SiC membrane is briefly presented below:

- Thermal Stability.** According to our past experience with the SiO₂ hydrogen selective membrane, thermal stability of thin films produced via CVD/I is in general excellent [3]. The SiC membrane was prepared at a much higher temperature (>1,000°C) and is thus expected to be thermally stable at the proposed application temperature (300 to 500°C). Therefore only very brief, about 20 hours, experimental work was conducted to demonstrate its stability. Since the SiC membrane has demonstrated the hydrothermal stability (see below), its thermal stability is considered given. No additional work in Phase I is planned in this specific area.
- Hydrothermal Stability.** The SiC membranes prepared in this study have demonstrated their hydrothermal stability. Figure 4 indicates that the SiC membranes are stable during a nearly 30 hour test at 300 to 400°C and 1 to 3 bar steam. This harsh testing condition, i.e., high steam pressure, was selected to simulate the steam partial pressure present (nearly stoichiometric steam/CO ratio) in the water-gas-shift (WGS) reaction using a membrane reactor. As a comparison, the SiO₂ membrane prepared via CVD/I lost ca. 60% of its permeance in the first few hours of a similar test at 600°C but a much lower steam pressure (i.e., 0.2 bar) as shown in one of our previous studies [12]. According to thermodynamics, the surface area of metal oxides is dependent on steam pressure at a given temperature. Thus, it is expected that the degradation would be much worse under a high steam partial pressure condition. The hydrothermal stability at 3 bar

of steam demonstrated by the proposed SiC membrane offers unusual material stability strength for the proposed application.

- Thermal Cycling. The above hydrothermal stability test was performed in a 2 - 9 hour/cycle; thus, the test results shown in Figure 5 in fact underwent thermal cycling of 8 times from room to 300 – 400°C. Thus, we conclude that the SiC membrane is robust and can endure the thermal cycling without degradation.

In summary the thermal and hydrothermal stability and the thermal cycling tests conclude that the porous SiC hydrogen selective membranes prepared by us demonstrate an adequate hydrothermal stability under the condition simulating the hydrogen separation for hydrogen production

Literature Cited

1. Armor, J.N., J. Memb. Sci., **147**, 217 (1998).
2. Doctor, R.D., etc., Gasification Combined Cycle: Carbon Dioxide Recovery, Transport, and Disposal, Argon National Lab, ANL/ESD-24.
3. Hou, K., M. Fowles, and R. Hughes, Catal Today, **56**, 13, (2000).
4. Lin, C. L., Flowers, D. L. and Liu, P. K.T., J. Memb. Sci., **92**, 29(1994).
5. Liu, P.K.T., and Wu, J.C.S., US Patent 5,415,891, May 16, 1995.
6. Megiris, C., and J. H. Glezer, Ind. Eng. Chem. Res., **31**, 1293(1992)
7. Minet, R. G., S.P. Vasileiadis, and Tsotsis, T. T., in, G. A. Huff, and D. A. Scarpiello, eds., Proc. of Symp. on Natural Gas Upgrading, **37**, 245, 1992
8. Sea, B.K., etc., , J. Memb Sci, **146**, 73 (1998).
9. Suwanmethanond, S., E. Goo, G. Johnston, P. Liu, M. Sahimi, and T.T. Tsotsis, Ind. Eng. Chem. Res., **39**,
10. Stiegel, G., "A New IGCC Program Strategy to Meet Future Energy Market Requirements", Advanced Coal-Based Power and Environmental Systems '98 Conference, FETC.
11. US DOE, Working Paper on Carbon Sequestration Science and Technology, February 1999.
12. Wu, J.C.S., Sabol, H., Smith, G.W., Flowers, D.F., Liu, P.K.T., J. Memb. Sci., **96**, 275 (1994).
13. Wu.J.C.S., T.E.,Gerdes, J. L. Pszczolkowski, R. R. Bhave, P. K. T. Liu, Sep. Sci. Tech., **25**,11489(1990)
14. Ohashi H., etc., J. Memb. Sci., **146**, 39(1998).
15. Gallaher, G. R., Liu,P. K.T., etc., CatCon '94 , June 26 -28, 1994, Philadelphia, PA.
16. Edlund, D., Friesen, Johnson, B., Pledger, W., Gas Sep. Pur., **8**, 3 (1994).

Figure 1a. SEM Photomicrograph of M&P's alumina microporous substrate (ca. 100Δ) with SiC thin film deposition via CVD/I.

Figure 1b. Higher magnification showing that an extremely thin SiC film was deposited because no visible difference can be seen between the SiC at the top surface and the underlying alumina substrate

Figure 3. Pore Size Distribution (above) and XRD (below) of SiC (unsupported) Film Before and After

Testing Condition

Time (hr)	Steam (bar)	Temp °C
0	1	300
1.5	1	300
1.51	1	400
4	1	400
5.5	1	400
8	1	400
10	2	400
10.25	2	400
15.25	2	400
24.25	3	400