SiC-Based Hydrogen Selective Membranes for Water-Gas-Shift Reaction

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ABSTRACT

A hydrogen selective membrane as a membrane reactor (MR) can significantly improve the power generation efficiency with a reduced capital and operating cost for the waster-gas-shift reaction. Existing hydrogen selective ceramic membranes are not suitable for the proposed MR due to their poor hydrothermal stability. In this project we have focused on the development of innovative silicon carbide (SiC) based hydrogen selective membranes, which can potentially overcome this technical barrier. During Year I, we have successfully fabricated SiC macro porous membranes via extrusion of commercially available SiC powder, which were then deposited with thin, micro-porous (6 to 40D in pore size) films via sol-gel technique as intermediate layers. Finally, an SiC hydrogen selective thin film was deposited on this substrate via our CVD/I technique. The composite membrane thus prepared demonstrated excellent hydrogen selectivity at high temperature (~600EC). More importantly, this membrane also exhibited a much improved hydrothermal stability at 600EC with 50% steam (atmospheric pressure) for nearly 100 hours. In parallel, we have explored an alternative approach to develop a H_2 selective SiC membrane via pyrolysis of selected pre-ceramic polymers. Building upon the positive progress made in theYear I preliminary study, we will conduct an optimization study in Year II to develop an optimized H_2 selective SiC membrane with sufficient hydrothermal stability suitable for the WGS environment.

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1. INTRODUCTION

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3. The U.S. energy industry is undergoing a profound change as a result of legislation in a number of states mandating power generation deregulation and increasingly more stringent environmental standards. For coal-fired power plants to continue to play a significant role in the energy scene and to remain a major source (as they currently are) of electricity production for the world, new advanced coal technologies must be developed. To be competitive the new technologies must exhibit enhanced efficiencies in electricity-from-coal production. They must, furthermore, employ cost-effective environmental compliance solutions, including the removal of the key critical pollutants (NO_x and SO_x) and the capability of capturing, concentrating and disposing CO_2 in a manner that assures closure of the carbon fuel cycle.

4.

5. One aspect of the new promising technologies involves hydrogen production, purification and utilization in the coal-based power plant. Under the concept of co-production in a coal-based power plant (IGCC) [10] this means the development of better hydrogen separation technologies, which can significantly improve production economics and are robust to minimize maintenance requirements and failures. Advanced high temperature hydrogen permselective membrane-based technologies show the greatest promise for non-incremental technology leaps in this area.

6.

7. A hydrogen selective membrane has been suggested to be used to recover hydrogen from the gasification product at 550 to 1200EC and 15-70 atm. Also, this membrane has been suggested as a catalytic membrane reactor (MR) to enhance hydrogen conversion in a water gas shift reaction (WGS) and then recover hydrogen as a product at 200 to 400EC [2]. In this project, we have focused on the development of an advanced (i.e., SiC-based) hydrogen selective membrane and its use as an MR for WGS reaction. We believe that the SiC membrane can be developed cost effectively by building upon the success and experience we have in the SiO_2-based hydrogen selective membrane [5]. Furthermore, the MR-WGS reaction is considered an ideal choice to demonstrate the MR technology due to its moderate operating condition and favorable catalytic reactions. Ultimately, this robust membrane can be used to recover hydrogen from the gasification product and industrial streams.

8.

9. The primary objective of this research project has been to demonstrate the feasibility of developing a SiC-based H_2 permselective membrane suitable for implementing the reactive separation concept, in the water-gas-shift reaction (WGS). Key specific technical objectives are listed as follows:

10.

development of SiC macro- and meso-porous substrates as support for the SiC hydrogen selective membrane,
development of the nanoporous SiC membranes using the thin film coating and chemical vapor deposition/infiltration (CVD/I) preparation techniques available to us,
demonstration of the hydrogen permselectivity over CO, CO_2, CH_4, and others relevant to the proposed WGS application.
evaluation of the hydrothermal/thermal/mechanical stability in the proposed WGS reaction environment, and
estimation of economic benefit offered by the reactive separation using the developed hydrogen selective SiC membranes.
demonstrating the proposed technology in a bench-top unit simulating the WGS reaction

This annual report summarizes our progress made in Year I toward the above objectives.

1. EXECUTIVE SUMMARY

The concept of catalytic membrane reactors (MR) has been actively pursued by U.S. industry and academia in the 80's and 90's. The potential benefits that result from this reactive separation concept include enhanced productivity and improved energy efficiency for several key reaction processes in the power, chemical and refinery industries. Although the concept has been verified experimentally, existing membranes have failed to be implemented commercially due primarily to their lack of material stability in the application environment. Development of a silicon carbide (SiC) based hydrogen selective membrane is proposed here in this project to overcome this technical barrier. Use of the SiC membrane as an MR can potentially reduce the capital and operating cost of the water-gas-shift reaction (WGS), one of the key reactions for hydrogen production in coal-fired power plants. The SiC membrane is expected to have excellent hydrothermal and chemical stability under the proposed application environment, eliminating material-related problems associated with existing membranes, such as those based upon dense metal, microporous SiO_2, and their hybrids.

During the first year of this project, we have completed development, fabrication, and characterization of macroporous SiC substrates. In addition, we have successfully deposited a thin mesoporous SiC film on this macroporous substrate as an intermediate layer. Finally, the hydrogen selective SiC layer was prepared on this mesoporous substrate via a chemical vapor deposition/infiltration technique (CVD/I). The multilayer composite hydrogen selective SiC membrane thus developed is robust in its structural integrity and efficient in its gas permeation, making it ideal for the proposed high temperature high pressure application.

Specifically we have completed development, fabrication, and characterization of macroporous SiC membranes as substrates. Macroporous SiC membranes with pore sizes ranging from 0.1 to >0.2F were prepared from commercially available SiC powder with selected binders via extrusion and then sintered at >2,000EC. The narrow pore size distribution, nearly Knudsen selectivity, and the uniform top surface are indicative of a high quality, defect free substrate. Subsequent deposition of a porous thin film on this substrate with a narrower pore size as an intermediate layer has been successful.

Meso-/micro-porous SiC thin film with an average pore size of 6 to 40D have been developed as an intermediate layer. This porous thin film was prepared by coating the above substrate with polycarbosilane as a precursor and subsequent calcination at ~1,400EC. An alternative approach has also been explored with a SiC precursor sol instead of polycarbosilane. Both approaches deliver nearly defect free meso-/micro-porous thin film as evidenced by the surface photomicrograph, permeation characterization and pore size distribution analysis.

Finally the hydrogen selective SiC membrane was deposited on top of the intermediate layer via a CVD/I technique. Triisopropylsilane (TPS) was used as a precursor in our study. The helium permeance ranges from 0.65 to 13.9 m^3/m^2-hr-bar with a He/N_2 selectivity of 4 to 85 for the membranes (total of 12 samples) after conversion to SiC at 1,000EC. The wide range of results reflects our evaluation of several key deposition parameters as part of the feasibility study. Helium was used here as a simulant to hydrogen. In addition, high selectivity of He to CO_2 and CH_4 has also been demonstrated. The rejection of CO_2 and CH_4 are similar to N_2 so that He/N_2 represents a good surrogate gas mixture for evaluating the SiC membrane for WGS in Year II. An alternative to the CVD/I technique is to deposit pre-ceramic polymers, such as hydridopolycarbosilane, on the intermediate layer, which is then pyrolyzed at 600 to >1,000EC. Hydrogen selective thin films were developed via this alternative approach in a brief exploratory study in Year I. One of these two approaches will be selected in Year II for further development once the hydrothermal stability of the resultant membrane is completely evaluated.

The SiC membrane prepared at a high temperature (>1,000EC) is expected to be thermally stable at the proposed application temperature (300 to 750EC). In addition the SiC membranes prepared in this study have demonstrated their hydrothermal stability in a nearly 100 hour test at 750EC and at 50% of steam (atmospheric pressure). During Year II, long term hydrothermal stability tests will be conducted simulating the WGS environment.

In summary our preliminary study in Year I has demonstrated (i) the technical feasibility of preparing SiC-based H_2 selective membrane via the proposed approaches and (ii) their improved hydrothermal stability. Additional experimental study will be conducted in Year II to prepare optimized membranes for evaluation under a simulated WGS environment.

EXPERIMENTAL, RESULTS AND DISCUSSION

3.1 Preparation of SiC Porous Membranes as Substrates for SiC-H_2 Selective Membranes

Rationale:

Existing ceramic membranes used in the development of M&P's SiO_2 based hydrogen selective membranes (primarily (-Al_2O_3 membranes with pore sizes between 40 and 100D) may not be suitable as supports for the SiC hydrogen selective membrane for two reasons:

Thermal mismatch. The thermal coefficient of expansion of Al_2O_3 and SiC are 8.2 and $4.4x10^{-6}$ in/in/EC, respectively, at 25 to 1,000EC. Hence, it is possible that the thermal mismatch between the Al_2O_3 substrate and the SiC-H_2 selective thin film over the deposition and operating temperature range (i.e., 400 to possibly >1,200EC) could yield cracking of the membrane.

Thermal and hydrothermal stability. Sintering and pore size growth of the existing 40 to 100D (-Al_2O_3 membranes at high temperature, particularly in the presence of steam, may be problematic. In general, the 40D membrane is suitable for temperatures less than 600EC and the 100D for temperatures <1,000EC. These use temperatures are reduced considerably in the presence of low to moderate pressure steam. However, the temperature required to prepare the SiC-H_2 membranes (750 to perhaps 1,400EC) and to operate in the proposed applications (400 to 600EC at moderate steam pressures of 3 to 20 bar) present potential problems for (-Al_2O_3 based substrates.

For these reasons a SiC based membrane as a substrate for subsequent deposition of a SiC-H_2 thin film may be necessary. To facilitate the project progress, we have taken a two-prone approach: (i) development of a SiC porous membrane as substrate for depositing the SiC H_2 selective membrane layer, and (ii) feasibility test on the use of (-Al_2O_3 for depositing SiC thin film specifically for calcination at a low temperature, i.e., near 1,000EC. Our progress on the former approach is summarized in this section. The results from the later approach is addressed in Sections 3.2 and 3.3.

Experimental:

In this project, macroporous ceramic carbon substrate in a disk configuration was prepared by conventional extrusion technology using commercial SiC powder as the starting material. Then the disk was fired at >2,000EC to form SiC macroporous substrate. XRD, pore size distribution analysis and gas permeation were performed to characterize the resultant substrates.

Once the macroporous substrate becomes available, a second layer with a narrower pore size is deposited before a H_2 selective membrane layer is applied. In this section, the sol-gel technique is employed for the second layer deposition. A number of literature studies have addressed the preparation of SiC powders using sol-gel techniques. Cerovic *et al*. [1], for example, have prepared silicon carbide powders by heating at 1550 ^oC a mixture of a silica sol prepared by an ion exchange method, saccharose or activated carbon as the carbon source and boric acid as a catalyst. Mono-dispersed spherical particles of SiC was prepared by the sol-gel technique by Seog and Kim [3] using phenyltrimethoxysilane (PTMS), and/or tetraethylorthosilicate (TEOS) as the silica source. Different carbon sources such as ethycellulose, polyacrylonitrile (PAN), and starch were reacted with a silicon source at 1550^oC by Raman *et al*. [7] to produce SiC. None of these studies, however, specifically focused on preparing SiC membranes using the sol-gel technique. SiC meso- or micro-porous thin film via the sol-gel technique is expected to be feasible based upon the literature information on the SiC sol formation and our in-house experience on the sol gel technique

Results/Discussion:

A. Macroporous SiC membranes with pore sizes ranging from 0.1 to >0.2F have been developed successfully with consistent quality. The membranes were prepared from commercially available SiC powder with selected binders and then sintered at >2,000EC. Characterization data is presented for a typical membrane (Sample ID: P1). Figure 1 shows the pore size distribution of the resultant membrane and the particle size distribution of the starting powder. Figure 2 shows the helium and nitrogen permeance and selectivity (ratio of the He and N_2 permeance). Figure 3 shows an SEM photomicrographs of the top surface. The narrow pore size distribution, nearly Knudsen selectivity at low pressure, and the uniform top surface are indicative of a high quality, defect free substrate which is ideal for subsequent deposition of a mesoporous thin film. In summary, microporous SiC substrates have been fabricated for subsequent deposition of SiC thin films. No additional R&D in this area is planned in Year II. The effect of binders on the porosity and pore size distribution of the macroporous SiC membranes has also been systematically studied, which is summarized in a paper published in I&EC Research [11] recently (see Appendices).

B. Mesoporous membranes with an average pore size of ~40D have been developed via deposition of a SiC thin film on the macroporous SiC substrates described above. Using a polycarbosilane (PCS) as a precursor with subsequent calcination at ~1,400EC, we have successfully deposited a SiC mesoporous film on the macroporous substrate. Figure 4 shows the pore size distribution (BET measurement) which ranges from ~10 to 80D. Figure 5 shows an XRD pattern that confirms full conversion to SiC from this polymer precursor. The SEM photomicrograph of this microporous SiC membrane is presented in Figure 6. After calcination, the top surface is a smooth and defect-free mesoporous SiC film. He and N_2 gas permeances at room temperature are shown in Table 1. Slightly better than Knudsen separation at room temperature was obtained (2.90 to 3.25 vs 2.65), supporting the presence of extremely small pore sizes, e.g., ~10 to 20D. We believe that the mesoporous SiC membrane developed from the selected polymer is sufficient as a substrate for developing a SiC-H_2 selective membrane via CVD/I discussed in Sec. 3.3. During the Year I study, we successfully demonstrated the feasibility of preparing mesoporous SiC substrates as evidenced by the surface photomicrograph, permeation characterization and pore size distribution analysis. The fabrication procedure developed in this task will be one of the two methods to be selected in Year II to prepare SiC based mesoporous membranes to be used as supports for further development of the SiC-based H_2 selective membrane via CVD/I. The other method is through the sol-gel technique as described below.

B. Mesoporous membranes with an average pore size of 6 to 12D have been developed via coating of SiC precursor gel on the macroporous SiC substrates described above. Synthesis of silicon carbide powders and thin films via sol-gel involves combining a silica sol with a carbon source, followed by the further carbothermal processing of the resulting mixture at high temperatures. A number of different silica sols are used in our experiments as the silica source. In this report only the thin film prepared from Sol #2 (8 to 11 nm in size with 30% concentration) is presented. We have also deposited the thin film on silicon carbide disk substrates which have an average pore size distribution 0.3-0.5 μm X-ray diffraction result for the sol-gel silicon carbide powder samples is shown in Figure 7. All the peaks in this figure correspond to β-silicon carbide, which indicates that no other crystalline phases are present. Using the N_2 adsorption-desorption technique we have also measured the pore volume and pore-size distribution of all the SiC powder samples are shown in Figure 8. Atomic force microscopy (AFM) was used to study the surface morphology of the sol-gel coated samples. Figure 9 shows the AFM image of the SiC membrane prepared via sol-gel technique. There are no cracks and/or pinholes observed in the membrane layer and the surface appears to be relatively smooth. The results of the permeation test are shown in Figure 10. The ideal separation factor estimated from the He and N_2 permeances is close to the ideal selectivity based upon Knudsen diffusion (He/N_2), as compared with the original substrate, which provided no separation at all (separation factor =1).

Table 1. Helium and Nitrogen Permeances of Mesoporous SiC Membranes Prepared via Calcination of Polycarbosilane

Gas	Pressure Gradient (psi)	Permeance (k)+ (cm^3/cm^2.psi.min)	Separation Factor* (He/N_2)
Helium (He)	40	0.0476	2.90
	30	0.0482	2.80
	20	0.0486	3.00
	10	0.0497	3.25
Nitrogen (N_2)	40	0.0164	-
	30	0.0172	-
	20	0.0162	-
	10	0.0153	-

* Ideal separator factor is 2.65
\+ 25EC.

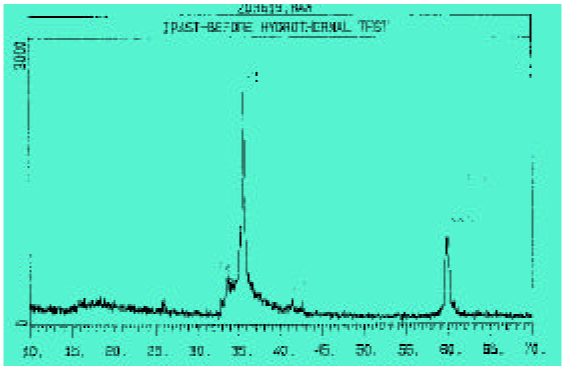


Figure 7. XRD pattern (β-SiC) of unsupported SiC thin film prepared with sol-gel technique.

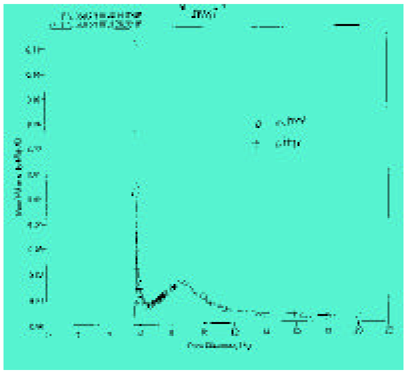


Figure 8. Pore size distribution (based upon N_2 adsorption) SiC thin film prepared via sol-gel technique. Majority of pores range from 6 to 12C

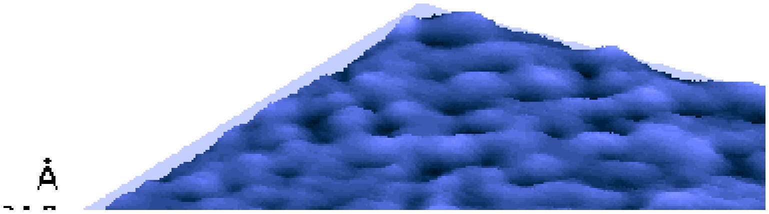


Figure 9. Surface Topograph of Microporous SiC Membrane Prepared via Sol-gel Technique (see Section 3.1c for description).

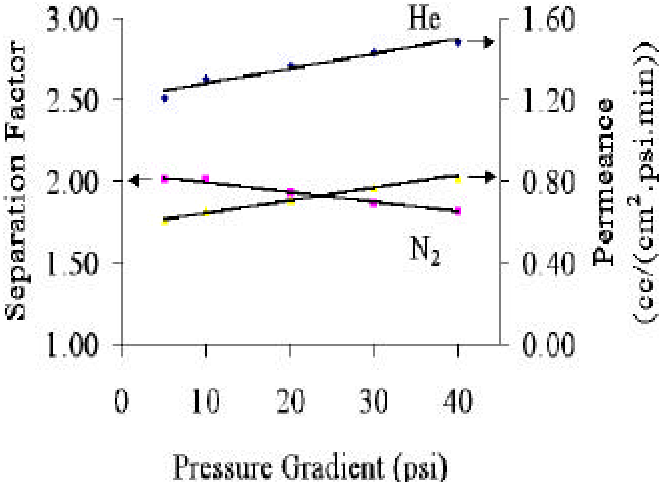


Figure 10. Gas permeance (single component) and separation factor vs. transmembrane pressure drop of microporous SiC membrane supported on SiC macroporous substrate. Calculated separation factor is close to the ideal separation factor based upon Knudsen diffusion, indicating a high quality nearly defect-free membrane.

3.2 Preparation of H_2 Selective SiC Membranes via Pyrolysis of Pre-ceramic Polymers

Rationale:

Pre-ceramic polymers are currently attracting growing attention as a means of producing ceramics, particularly non-oxide ceramics. The reason for this renewed interest is that the pre-ceramic polymers can be processed and formed at relatively low temperatures compared to the production of conventional structural ceramics. For the preparation of SiC of H2 selective membranes via the pyrolysis of pre-ceramic polymers, our rationale is based upon the following:

> Polycarbosilanes (PCS) and polysilanes are two pre-ceramic polymers known to produce silicon carbide upon controlled pyrolysis at high temperatures in the absence of oxygen. Thus it is worthwhile to explore the synthesis of SiC H_2 selective membrane using pre-ceramic polymers as an alternative to the CVD/I technology described in Section 3.3.
>
> The organometallic to inorganic (mineral) conversion occurs mostly in the temperature range between 500 to 800 ^{o}C. Nucleation and crystallization processes occur in the temperature range between 800 to 1000 ^{o}C along with the formation of nanosize crystalline SiC. Since the appearance of the crystalline phase is accompanied by the disappearance of the amorphous material, the presence of such a crystalline phase may not be beneficial for the preparation of microporous SiC membranes for the H_2 separation. On the other hand, crystalline SiC is known to have a higher corrosion and oxidation resistance and mechanical strength than amorphous SiC. Consequently, one expects that an optimal pyrolysis temperature may exist which produces membranes with an acceptable separation factor and sufficient mechanical and thermal resistance for the proposed separation.

Thus, an empirical approach has been taken in this project to identify an optimum condition to develop a SiC membrane qualified for our application.

Experimental:

> Unsupported SiC ceramic thin film was prepared from allyl-hydridopolycarbosilane (AHPCS) and hydridopolycarbosilane (HPCS) (kindly provided to us by Starfire Systems). After pyrolysis and calcination, the powder was then characterized with XRD and pore size distribution (BET method). The results were then used to select an optimum pyrolysis and calcination condition for preparing a supported SiC membrane from the pre-ceramic polymers.
> H_2-selective SiC microporous membranes were prepared by coating AHPCS on the SiC substrate prepared in Sec. 3.1 (pore size in the range of ~300D) following pyrolysis at a selected temperature of 600EC. Multiple coating/pyrolysis is applied to reach a desirable separation efficiency. Calcination at a temperature >600EC will be pursued later if necessary.

Results/Discussion

A. H_2 selective ceramic membranes were prepared from pyrolysis of AHPCS and HPCS. In this report, we focus on the result from the former polymer. X-ray diffraction patterns of the ceramic powders resulting from the pyrolysis of AHPCS2 at different temperatures (i.e., 1,000 to 1,600EC is shown in Figure 11. For the sample produced at 1600^{o}C the spectrum completely agrees with the Powder Diffraction File for SiC. At lower pyrolysis temperatures the XRD spectra are very noisy, potentially signifying the presence of amorphous SiC which crystallizes at higher temperatures. As the temperature increase the amorphous SiC converts into crystalline SiC. The size of the SiC crystallites calculated from the diffraction peak widths by the Scherrer's equation is presented in Figure 12, showing that the crystal grows significantly from ~20 to >100D through calcination from 1,000 to 1,600EC. The powder study confirms that (i) the formation of SiC after pyrolysis of the selected pre-ceramic polymer, and (ii) SiC crystal increases along with the temperature increase. These results suggest that the pyrolysis in the neighborhood of 600 to 1,000EC may be a good starting point for us to identify the optimum pyrolysis temperature for the formation of a hydrogen-selective SiC membrane. In Year II, we will pursue surface analysis, such as XPS to confirm the chemical state of SiC for samples produced at <1,000EC.

B. H_2-selective microporous membranes were prepared with multiple coating/pyrolysis of AHPCS in order to reach a desirable separation efficiency, i.e., >20 for H_2/N_2 at 200EC. The permeation characteristics (at room temperature) vs the number of coatings are shown in Figure 13. As the number of coatings increases the permeances for both He and N_2 decrease; however, the separation factor remains unchanged and close to the Knudsen regime. Until the fifth coating the separation factor increases to over 3.5, signifying that the membrane has molecular sieving properties. The pre-ceramic polymer selected in this study generates a porous structure of ~5D under the proposed pyrolysis temperature (i.e., 600EC) as shown in Figure 14a. Additional layers of coating primarily minimizes the defects as shown in Figures 14 and 15. The permeation characteristics of the same membrane at higher temperatures are shown in Figures 16 and 17. Note that as the temperature increases the nitrogen permeance decreases (as one would expect from Knudsen diffusion through cracks and pinholes). The He permeation, however, shows an activated type diffusion with permeance increase along with the temperature increase, typical of the behavior observed in other amorphous membranes, SiO_2 microporous membranes. In summary we have successfully developed the SiC hydrogen selective membrane using the pre-ceramic polymer as a precursor. Whether the selection of 600EC is sufficient to deliver a membrane material with a satisfactory hydrothermal stability remains to be evaluated, which is discussed in Sec. 3.4.

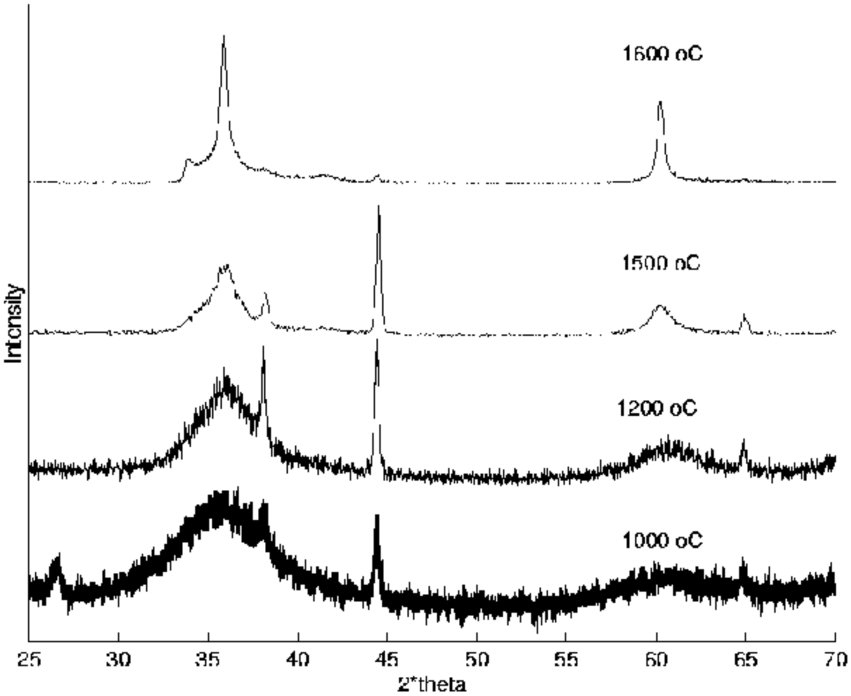
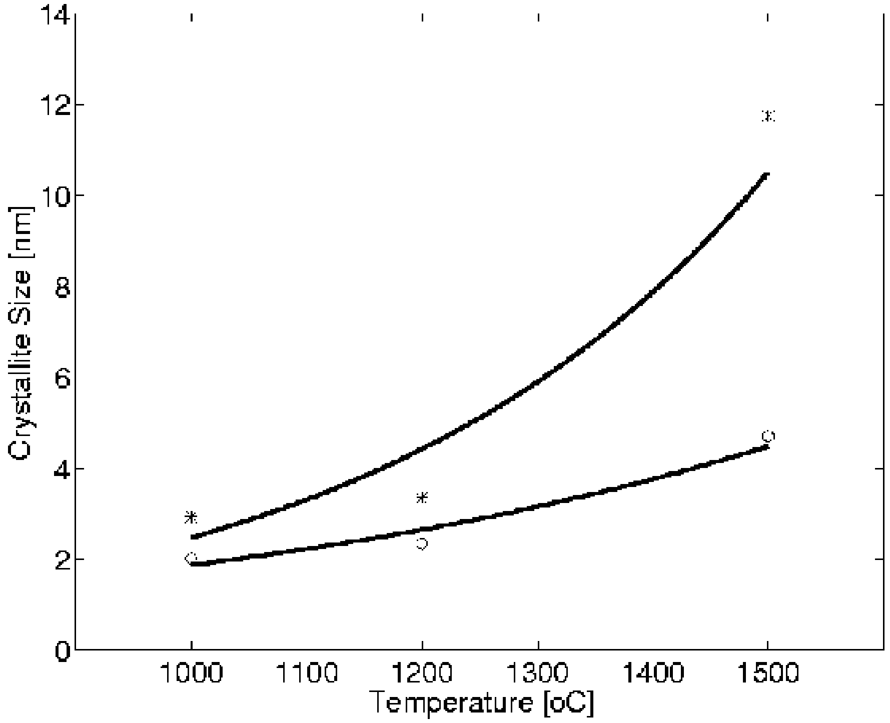


Figure 11. XRD pattern of SiC powder prepared from pre-ceramic polymer (AHPCS) calcined at 1,000 to 1,600°C.



• after 2nd pyrolysis * after 3rd pyrolysis

Figure 12. Calculated crystal size of the SiC powder prepared from pre-ceramic polymer (AHPCS) calcined at 1,000 to 1,500°C

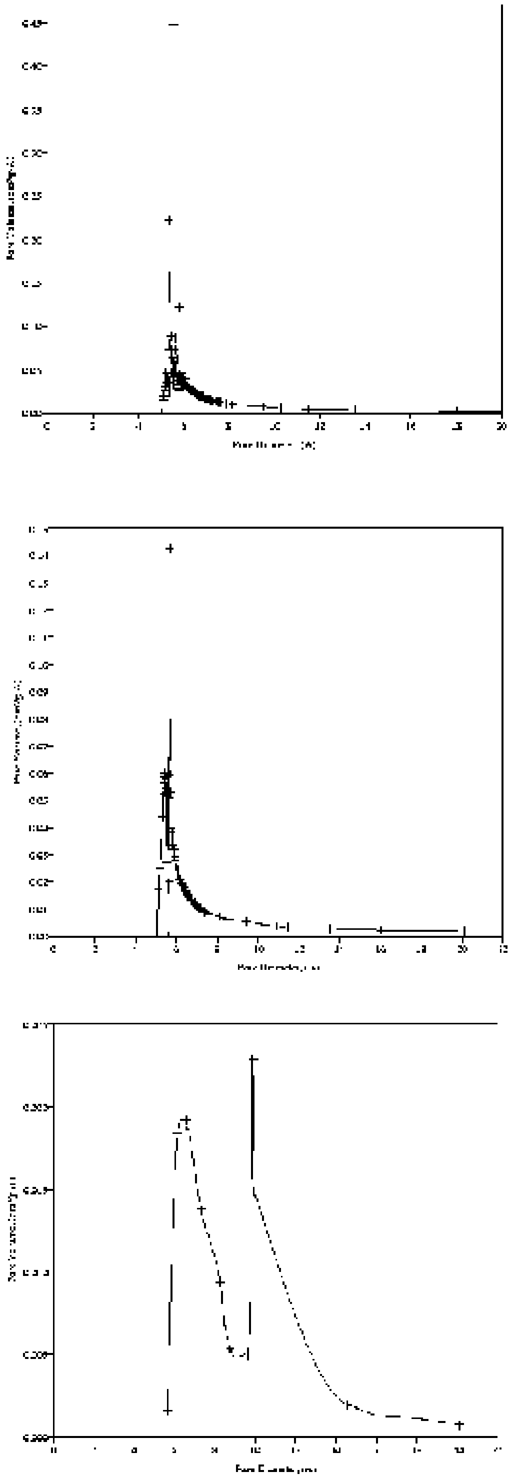
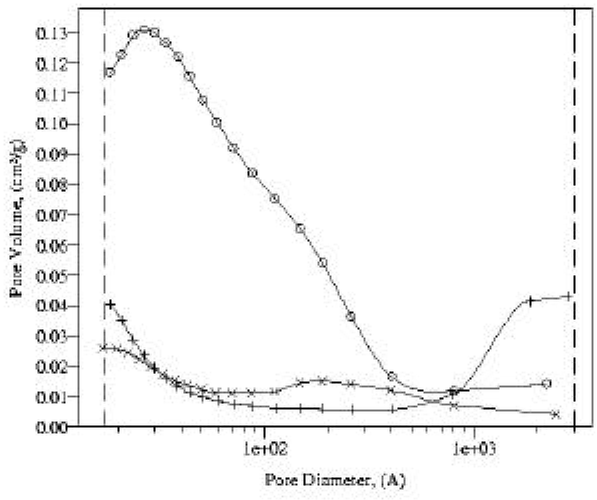


Figure 14. Pore size distribution (microporous range) of SiC powder prepared via pyrolysis (1s, 2nd and 3rd) of pre-ceramic powder



+ First Pyrolysis
o Second Pyrolysis
X Third Pyrolysis

Figure 15. Pore size distribution (meso- and macro-porous range) of SiC powder prepared from pyrolysis of pre-ceramic polymer (AHPCS).

3.3 Preparation of H_2 Selective SiC Membranes via Chemical Vapor Deposition/Infiltration (CVD/I)

Rationale:
The CVD/I approach has been proposed as a route to H_2 selective SiC membranes for several reasons:

Highly permselective H_2-selective silicon oxide (SiO_2) membranes [12] and the necessary CVD/I hardware [20] were developed previously by Media and Process Technology Inc. (M&P). Although this SiO_2 membrane shows limited hydrothermal stability, the CVD/I technique coupled with the selection of a proper precursor and deposition conditions can be used to develop a H_2-selective SiC membrane.

One literature study [8] presents the deposition of a thin SiC film via CVD/I using triisopropylsilane (TPS) as a precursor. Although the membrane selectivity for H_2 & He over N_2 was no better than Knudsen separation, the deposition and formation of a true SiC film on a microporous substrate via a CVD/I approach was confirmed based upon XPS analysis. Another literature study confirms the presence of SiC under a similar preparation condition [6].

. Our proposed SiC CVD/I technique allows us to maximize hydrogen permeance and selectivity by removing excess unreacted, deposited carbon. This offers a direct and controllable technique to develop a high performance SiC membrane.

Based upon the above rationale, we conducted a study to assess the feasibility of preparing a H_2 selective SiC membrane via the CVD/I technique as part of the Year I objectives.

Experimental:

An unsupported SiC film (i.e., powder) was prepared via CVD/I using TPS as a precursor. This unsupported film was used to expedite the characterization of the resultant SiC. Briefly, the protocol involved (i) deposition at 750EC in helium to form a thin film and (ii) calcination at 1,000 to 1,400EC to convert the deposit into SiC.

Following a similar protocol, we applied the proposed CVD/I technique on as the Al_2O_3 substrate[1] (i.e., 100D) at 750EC until the helium/nitrogen selectivity was maximized. This CVD/I treated substrate and was subsequently calcined at 1,000EC for two hours for conversion to SiC.

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[1] 40D (-Al_2O_3 membrane was pre-calcined at 1000EC to insure its thermal stability at this temperature for CVD/I and calcination. The resultant pore size is estimated ~100A.

Results/Discussion:

A. An unsupported SiC film (i.e., powder) was successfully produced via the CVD/I protocol developed in-house using TPS as a precursor. Figure 18 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 1,400EC. Although the sample calcined at 1,000EC did not exhibit SiC peaks, it is believed that amorphous SiC is present at this temperature indicated by the peak at the low angle end. Literature studies using the same precursor confirm the formation of SiC at #1,000EC [6, 8] based upon XPS analysis. In addition, the XRD analysis shows excess unreacted (not incorporated into the SiC) crystalline carbon is present in the sample calcined at 1,200EC. The disappearance of this peak at 1,400EC suggests that additional SiC is formed. From this study, it was concluded that (i) SiC formation occurs at 1,000 to 1,400EC; (ii) higher calcination temperatures, Tc, yield higher degrees of SiC crystallinity; and (iii) unreacted carbon residue is present at <1,400EC with the selected precursor and protocol. In summary, the feasibility of forming a SiC film via the CVD/I technique has been clearly demonstrated here. In Year II we plan to conduct a similar, but quantitative, study with an array of similar precursors (e.g., different C/Si ratio) to develop an optimum SiC membrane.

A. SiC hydrogen selective nanoporous membranes following the above CVD/I protocol and using the selected precursor (i.e., TPS) have been successfully prepared using M&P's Al_2O_3 membranes as substrates. An SEM photomicrograph of the cross section of the SiC membrane is shown in Figure 19a and b. 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 with SiO_2 H_2 selective membranes, an extremely thin film was deposited, estimated at less than 1.5µm based upon EDAX mapping of our earlier SiO_2 membranes. Further, this black SiC film remained visibly intact after oxidation in air at 400EC for two hours, indicating that a thin SiC film was prepared on the white Al_2O_3 substrate. An SEM photomicrograph of the oxidized SiC membrane is presented in Figure 20. In summary, SiC formation via the CVD/I technique was confirmed and has been successfully deposited as a thin film on a mesoporous support with the selected precursor. In Year II, we plan to conduct XPS examination (available at our subcontractor, USC) of the supported film to determine the presence of SiC, Si, C, and others and their relative composition.

A. The helium[1] permeance ranges from 0.65 to 13.9 m^3/m^2/hr/bar with a He/N_2 selectivity of 4 to 85 for the membranes after conversion to SiC at 1,000EC. Table 2 summarizes the results from these membranes (total of 12 samples). Figure 21 presents permeance vs. temperature for one of the membranes. 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 SiO_2 hydrogen selective membranes. The wide range of results shown in Table 2 reflects our evaluation of several key deposition parameters as part of the feasibility study. Good reproducibility[2] of the CVD/I technique was demonstrated in our previous study with the SiO_2 membrane. As a general trend, conversion to SiC at 1,000EC does not drastically alter the permeance and selectivity of the membrane deposited at 750EC. This phenomenon is expected because the SiC calcined at this temperature is very amorphous (see Figure 18). This trend offers us an unique and practical fabrication method, i.e., developing a high quality SiC membrane via on-line monitoring of the membrane permeance during deposition. From the results of this feasibility study it was concluded that (i) nanoporous SiC membranes suitable for high temperature hydrogen separations could be developed and (ii) on-line monitoring of the progress of the CVD/I deposition is feasible and practical to optimize the membrane synthesis in a reproducible manner. In Year II we plan to conduct a similar study to evaluate the permeance and selectivity for samples produced at conversion temperatures, Tc, of >1,000 to 1,400EC. The degree of crystallinity generated in this temperature range (see Figure 18) may play a significant role in shifting the permeance vs. temperature relationship, which can be tailored to deliver a membrane for a given application temperature.

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[1] He was used as a simulate mixture to hydrogen. Our past experience has verified the validity of this simulate mixture for the microporous H_2 selective ceramic membrane.

[2] H_2 permeance of 7.58±0.6 m^3/m^2/hr/bar (at 600EC) with 95% confidence.

A. High selectivities of He to CO_2 and CH_4 have also been demonstrated. The selectivities of He/CO_2 and He/CH_4 are 83.4 and 39.4, respectively, for membrane TPS-021 at 750EC. The He/N_2 selectivity is 76.1 for this membrane at this temperature. The rejection of CO_2 and CH_4 are similar to N_2 so that He/N_2 represents a good surrogate gas mixture for evaluating this membrane. Table 3 lists the permeance vs. temperature up to 1,000EC for several samples prepared in Year I. Evidently, some of the samples demonstrate an excellent selectivity at a higher temperature, i.e., >600EC; while others show the selectivities even at a lower temperature i.e., #600EC. It is believed that the pore size distribution plays a significant role in determining its permeance vs. temperature behavior. To achieve an excellent selectivity at a lower temperature, e.g., 300-600EC, a larger pore size is essential. During the Year II study, we will fine tune the CVD deposition and calcination temperature to enhance the permeance and selectivity at a lower temperature.

B. The presence of excess carbon in the SiC membrane was verified via XRD as shown in Figure 18. The removal of this excess carbon has been proven to be a useful tool to enhance the permeance of the membrane. Steam was introduced with the objective of removing excess carbon via carbon-steam gasification from the thin SiC porous film. The resultant membrane after this treatment showed enhanced He permeance as depicted in Figure 22. Steam treatment at 750EC increases the He permeance about 5-fold in this case. Furthermore, this enhanced permeance was shown to be sustainable at one of the proposed application conditions, specifically in the presence of ca. ~50% of steam at 450EC. In summary, the removal of excess carbon has been demonstrated to be a useful tool for enhancing the micro porosity of the SiC membrane. During the Year II study, we plan to investigate various Si to C ratios through proper selection of the precursor to derive an optimized protocol for forming a hydrogen selective SiC membrane.

.4 Thermal and Hydrothermal Stability of SiC Membranes

Rationale:
The key advantages of the SiC membrane are their thermal, hydrothermal and chemical stability which result from two factors:

> Conversion temperature. The conversion temperature (1,000 to 1,400°C) is much higher than the application temperature (300 to 600°C). Hence, the SiC membrane is expected to be stable under these conditions.
>
> Covalent bonding. The source of the stability is the covalent bonding of the SiC. This compares with ionic bonding that prevails in metal oxide based hydrogen selective membranes. The ionically bonded materials are very susceptible to sintering in the presence of steam at high temperatures. No such problem exists for SiC [4].

Although oxidation of SiC was reported at high temperatures in highly oxidizing environments [1], our proposed application is at lower temperatures, i.e., 300 to 600°C under mildly reducing conditions. Since hydrothermal stability is one of the key features offered by the proposed SiC membrane, demonstration of this property in a membrane configuration is essential.

Experimental:
Two approaches were pursued to evaluate the thermal and hydrothermal stability of the SiC membrane. They are discussed as follows:

> The SiC unsupported thin film prepared from sol-gel technique was used to study the thermal and hydrothermal stability of the SiC membrane. Use of the unsupported film allows us to reliably measure the pore size change before and after the hydrothermal stability test because the measurement is not diluted by the bulk inert substrate. Since the sol-gel prepared SiC membrane with a larger pore size (e.g., 6 to 12Å) does not deliver any hydrogen separation. This sol-gel prepared membrane is and will be used as a substrate only. Thus, the hydrothermal stability test of the sol-gel prepared unsupported thin film will provide background information on the stability of the support, not the H_2 selective membrane.
>
> Under the second approach, we use the CVD/I prepared SiC H_2 selective membrane for the hydrothermal stability test. Since the bulk substrate contributes to majority of the sample weight, gas permeation, instead of surface area measurement, was used to infer the structure change under the selected hydrothermal condition.

The hydrothermal test selected in this study covers the temperature ranging from 300 to 750°C and the 50% steam at ambient pressure. The temperature range selected is consistent with the condition currently employed by the WGS reaction. The steam partial pressure is much lower than the actual pressure in the WGS reaction environment; however, it is a good starting point to screen the hydrothermal stability of the SiC membranes prepared in Year I.

Results/Discussion:

A. According to our past experience with the SiO_2 hydrogen selective membrane, thermal stability of thin films produced via CVD/I is in general excellent [12]. The SiC membrane prepared at a much higher temperature (>1,000°C) is expected to be thermally stable at the proposed application temperature (300 to 750°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 Year II is planned in this specific area.

A. The X-ray diffraction patterns of the SiC powder (made from the Sol2 via sol-gel technique) after being subjected to the hydrothermal stability test at 350 ^{o}C for 24 hrs is shown are Figure 23. The material after the hydrothermal test remains to be pure β-SiC similar to that before the test. In addition, the pore size distribution of the SiC powder before and after the hydrothermal treatment appears similar as shown in Figure 24. However, the pore volume increase substantially after the hydrothermal stability test, possibly due to the carbon-steam reaction which generates additional pore volume. Additional study is required in this area to obtain a concrete evidence about the hydrothermal stability of the SiC powder prepared from the sol-gel technique. We may pursue this topic further in Year II if the sol-gel technique is chosen for preparing the intermediate layer.

A. The SiC membranes prepared in this study have demonstrated their hydrothermal stability. Figure 25a indicates that the SiC membrane is stable during a nearly 100 hour test of the hydrothermal stability at 750EC and at 50% of steam (atmospheric pressure base). As a comparison, the SiO_2 membrane prepared via CVD/I lost ca. 60% of its permeance in the first few hours of a similar test at a much lower temperature (600EC) and steam pressure (20%) as shown in Figure 25b. In addition, the permeance enhancement obtained by the removal of excess carbon as discussed in Sec. 3.2 was also demonstrated in a short test to be stable in the presence of steam as shown in Figure 21. Clearly, the SiC membrane displays a much improved hydrothermal stability over the SiO_2-based hydrogen selective membrane. During Year II, long term hydrothermal stability tests will be conducted simulating the WGS environment once an optimum SiC membrane is finalized.

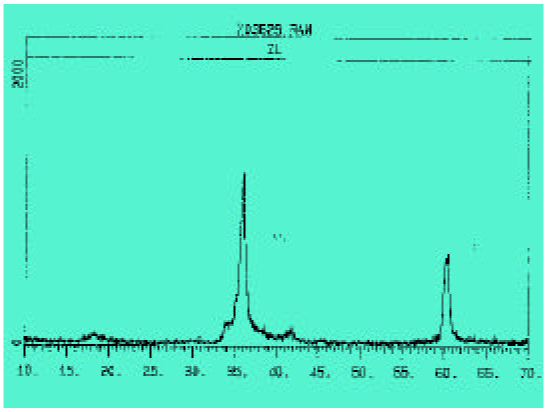

Figure 23a. XRD pattern of SiC powder (prepared from Sol6) before the hydrothermal stability test at 350EC and 50% steam (ambient pressure).

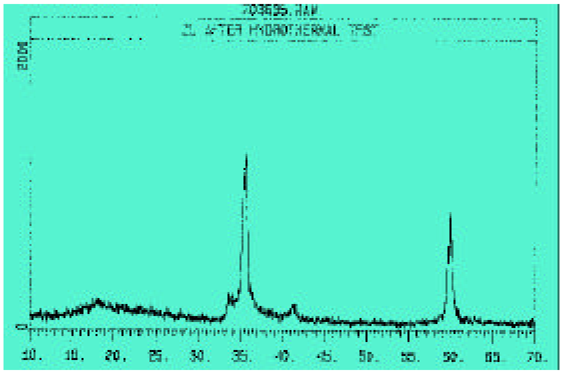

Figure 23b. XRD pattern of SiC powder (prepared from Sol6) after the hydrothermal stability test at 350EC and 50% steam (ambient pressure).

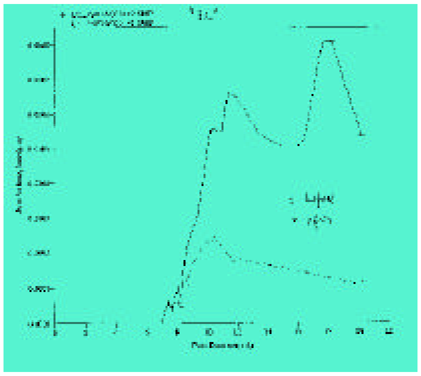

Figure 24. Pore size distribution of SiC powder (prepared from Sol6) before and after hydrothermal stability test at 350°C and 50% steam (ambient pressure).

3.5 Development of Al_2O_3-supported SiC Substrates for SiC Hydrogen Selective Membranes

Rationale:

As stated in Sec. 1, SiC microporous substrates were proposed for the development of the SiC hydrogen selective membrane. In our Year I study, Al_2O_3 membranes (~100D) were used in the development of the SiC hydrogen selective membrane discussed in Sec.3.3. Al_2O_3 membranes were chosen more or less for pragmatic reasons; we did not have a SiC support available in the beginning of the project. We conducted a parallel study on the development of the SiC substrate and the SiC CVD thin film in order to accomplish the feasibility study in Year I. Additionally, since Al_2O_3 membranes are commercially available from M&P, we could accelerate commercialization if the selected Al_2O_3 membrane turns out to be an acceptable candidate. Therefore we believed that further investigation was worthwhile although this activity was not covered under the Year I plan.

Accomplishments:

A. The potential thermal mismatch of the Al_2O_3 substrate vs. the SiC thin film has been proven acceptable in the proposed composite configuration of the SiC membrane. A SiC H_2 selective membrane deposited on the Al_2O_3 membrane (~100D pore size) was subjected to a heating and cooling cycle to determine the effect of the thermal mismatch. Figure 26 shows the helium and nitrogen permeance of the SiC membrane through a complete heating and cooling cycle over an extreme temperature range (25 to 1,000EC). The He permeance at 1,000EC remains virtually unchanged during this heating/cooling cycle. More importantly, the extremely low permeance measured at room temperature indicates no crack generation during thermal cycling. Although the thermal expansion coefficient difference between Al_2O_3 and SiC is significant, stresses in the proposed SiC membrane structure may have been minimized, since it is believed that the active SiC deposit is distributed throughout the Al_2O_3 substrate as nano-scale SiC patches not as a continuous film. In summary the thermal mismatch between Al_2O_3 and SiC appears acceptable in the proposed SiC membrane configuration in this very preliminary thermal cycling study.

B. To be a commercially viable product for WGS, the Al_2O_3 substrate must be the hydrothermally stable in the presence of 5 bar of steam and at 300 to 600EC (as opposed to the ~50% steam and 750EC tested in Year I). The Al_2O_3 substrate with 100D pore size may be inadequate under this harsh condition. According to our past experience, this pore size will enlarge to ~0.2 µ ("-Al_2O_3 phase) at equilibrium. Unfortunately this range of pore size, i.e., ~0.2 µ, is too large to prepare a high quality CVD/I thin film based upon the Year I study as well as our past experience in SiO_2 membrane. Therefore a hydrothermally stable substrate with a pore size of <100D must be employed in our Year II study. Based upon the positive results of this SiC/Al_2O_3 composite membrane, we propose to investigate the feasibility of 0.2 µ Al_2O_3 membrane as a substrate coated with microporous SiC substrate developed from Year I.

1. CONCLUSION

Major activities carried out during Year I of this project include membrane preparation, gas separation characterization, and hydrothermal stability testing. Key conclusions from this Year I study are drawn as follows:

Preparation of SiC Substrates

Silicon carbide (SiC) macroporous and meso-/micro-porous membranes were successfully prepared as potential substrates for the SiC-based H_2 selective membrane. Composite SiC based membranes with pore sizes of 40D to >0.1Fm were prepared with consistent quality. The macroporous SiC substrate was prepared by pressing commercial SiC powder into disk with aluminum, boron, and/or carbon as a binder; then the disk was calcined at >2,000EC. The resultant membranes were characterized by the pore size distribution analysis, gas permeance measurement, XRD and SEM. The meso-/micro-porous SiC membrane was prepared by deposition of (i) polycarbosilane (as a precursor), or (ii) SiC precursor sol on the SiC macroporous substrate, then calcined at ~1,400EC. The conversion of polycarbosilane and the sol to SiC at this temperature was verified with XRD analysis. In addition, this mesoporous membrane was characterized by the helium and nitrogen gas permeance and BET surface area as an indicator of pore size distribution.

Preparation of Hydrogen Selective SiC Membranes via CVD/I

Hydrogen selective nanoporous SiC-based membranes were successfully prepared using a chemical vapor deposition/infiltration (CVD/I) technique developed by M&P. CVD/I conditions were investigated under the assistance of on-line helium and nitrogen measurement. Deposition at 750EC with subsequent calcination at 1,000EC was selected for further membrane preparation and gas permeation study. A total of 12 membranes were successfully developed under this task for gas permeance and hydrothermal stability tests. In addition, unsupported SiC film, i.e., SiC powder, was generated under a similar condition for surface analysis. This powder after calcination at 1,000, 1,200 and 1,400EC was examined using XRD to confirm the formation of SiC and its crystal formation.

Preparation of Hydrogen selective SiC Membranes via Pyrolysis of Pre-Ceramic Polymers

In Year I preparation of the SiC hydrogen selective membrane via pyrolysis of pre-ceramic polymers was explored as an alternative to CVD/I. The membranes were prepared with multiple coating/pyrolysis (3 times) of allyl-hydridopolycarbosilane (AHPCS) in order to reach a desirable separation efficiency, i.e., >20 for He/N_2 at 200EC. This pre-ceramic polymer generates a porous structure of ~5D in pore size under the proposed pyrolysis temperature (i.e., 600EC). Whether the selection of 600EC is sufficient to deliver a membrane material with a satisfactory hydrothermal stability remains to be evaluated in Year II.

Mechanical Stability Tests of SiC Membranes

SiC membrane prepared via CVD on the commercial Al_2O_3 macroporous substrate (available from M&P) was subjected a heating and cooling study to determine its impact on the microporous layer structure and its physical attachment. Membranes prepared at 750EC and calcined at 1,000EC went through the heating cycling twice in this study. Gas permeation rate remains similar for the sample through the heating/cooling cycles. The mechanical stability of the SiC/Al_2O_3 composite membrane is thus confirmed at 25 to 1,000EC in inert atmosphere. Additional tests in the presence of the high pressure steam will be conducted to determine the thermal mismatch between SiC and SiC/Al_2O_3 under the proposed WGS environment. Then the selection between SiC/SiC and SiC/Al_2O_3 will be made for membrane fabrication and testing in Year II.

Thermal and Hydrothermal Stability Test

The hydrogen selective nanoporous SiC membranes prepared in Year I displayed excellent thermal and hydrothermal stability. No loss in permeance or selectivity was observed with a SiC hydrogen selective membrane in a roughly 100 hour hydrothermal test conducted at 750EC and 50% steam (at atmospheric pressure). In addition, thermal stability was conducted very briefly. Since the membrane was calcined at 1000EC, its thermal stability at 750EC is expected to be excellent. No further work in this area is deemed necessary.

Gas Separation Study

Gas separation characteristics of the hydrogen selective membrane prepared in this study was determined its single gas permeation of helium, nitrogen, CO_2 and CH_4. Depending upon the deposition and calcination conditions, the nanoporous membranes produced displayed a high helium permeance of 0.65 to 13.9 m^3/m^2/hr/bar and high selectivities for He over N_2, CO_2, and CH_4 of 4 to 85.

In summary our preliminary study in Year I has demonstrated (i) the technical feasibility of preparing SiC- based H_2 selective membrane via the proposed approaches and (ii) their improved hydrothermal stability. Additional experimental study will be conducted in Year II to prepare optimized membranes for evaluation under a simulated WGS environment.

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LIST OF ACRONYMS AND ABBREVIATIONS

AFM: Atomic Force Microscopy
AHPCS: Allyl-hydridopoly Carbosilane
CVD/I: Chemical Vapor Deposition/Infiltration
MR: Membrane Reactor
PCS: Polycarbon Silane
SEM: Scanning Electron Microscopy
TPS: Tripropyl Silane
WGS: Water-Gas-Shift
XPS: X-Ray Photospectroscopy
XRD: X-Ray Diffraction

APPENDICES

1. Publication as a result of current research under this project:

V. Suwanmethanond, E. Goo, G. Johnston, P. Liu, M. Sahimi, and T.T. Tsotsis, “Porous SiC Sintered Substrates for High Temperature Membranes for Gas Separations,” Ind. Eng. Chem. Res., 39, 3264-3271 (2000).