Preparation and Hydrogen Permeability of SiC-Y_2O_3 Composite Membranes

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ABSTRACT

SiC-Y_2O_3 porous composites were fabricated using Y_2O_3 powders synthesized by sol-gel process to control physical and thermo-chemical properties. Y_2O_3 powders were mixed with SiC powders by co-pressing with HPCS (hydridopolycarbosilane) binder at moderate temperature. The properties of membranes were characterized by XRD, FE-SEM, and BET surface analysis. Hydrogen permeability was performed at various temperatures.

Key words : SiC, Y_2O_3, HPCS, Hydrogen Permeance tests

1. Introduction

Hydrogen selective SiC membranes have been used for application in membrane reactors. SiC as a structural material has advantages such as thermal-mechanical stability and chemical inertness. SiC also has disadvantage in terms of its porosity and mechanical property of hardness. Since SiC has the covalent character of Si-C bonds, SiC ceramics can be sintered at high temperature and are limited in terms of applications. However, very little has been reported on the fabrication of porous SiC ceramics.

Transparent poly-crystalline yttria is also an interesting ceramic material for a variety of applications owing to its specific optical, thermal, and chemical properties. Composite membranes for separation and purification depend on the microstructures of the membranes, as well as on the porosity and the affinity between permeating species and the pore walls. Also, high specific surface area and thermal stability are the major requirements for making a porous ceramic membrane.

To improve the mechanical strength and to control the microstructure of membranes, we prepared SiC-based Y_2O_3 composite membranes while maintaining the thermal-mechanical stability. 1, 9, and 23 wt% of Y_2O_3 was chosen because a large amount of Y_2O_3 addition can lead to the degradation of the high temperature stability of SiC-based composites. Using the uniaxial pressing method, the composite membranes in this experiment were fabricated with 20 wt% hydridopolycarbosilane (HPCS) as a binder; this was followed by heat-treatment at moderately low temperature (1173 K). The differences of H_2 and CO obtained from the gas flux were compared and the activation energy was calculated.

2. Experimental Procedure

2.1. Preparation and Characterization of the composite membranes

Waste SiC sludge from a company in the solar cell industry (BHI Co., LTD) was obtained after centrifugation and magnetic separation process. The obtained SiC powder was washed with diluted HCl, NaOH and H_2O, followed by drying at 373 K. This process has a double advantage of reusing waste material via an environmentally-friendly process. The SiC powders were analyzed using the Rietveld Analysis method. The amounts of α-phase of SiC-6H, β-phase of SiC-3C, and Si were 59.40%, 35.1%, and 4.5%, respectively. The purified average 325 mesh SiC powders with different amounts (1, 9, and 23 wt%) of about 300 nm sized Y_2O_3 powder modified by oxalic acid were mixed using a milling process (Fitsch, TH-080) with 10 wt% of HPCS as a binder. These mixed powders were pressed mechanically at 35 MPa into disc pellets of about 14.5 mm diameter and 2 mm thickness. Composite membranes were obtained after heat-treatment at 1173 K under Ar condition.

The structure of the membranes was determined by XRD (X-ray powder diffraction, Bruker D8 Focus with TOPAS). The working voltage of the instrument was 40kV and the current was 40 mA with Cu Kα (λ = 1.5418 Å) radiation. The intensity data were collected at room temperature in a 2θ range from 10° to 80° with a scan rate of 0.2/s. The surface morphology of the membranes was examined using a JEOL-JMS 7500F FE-SEM operated at 0.5 – 30kV. The BET surface area was determined by the adsorption of N_2, measured with a BELSORP-mini II surface area analyzer. The hydrogen permeation equipment was consisted of a pressure controller, mass flow controller (MFC), permeation cell, and stainless steel 0.35-inch-long tube that could withstand high temperature. Hydrogen concentration was measured using a thermal conductivity detector (TCD) that analyzed the difference between hydrogen and CO gasby.
considering the thermal conductivity. Separation of a gas mixture can take place based on differences in molecular mass, size, or shape, or on differences in the affinity of the gas molecules to the membrane materials. Selectivity is generally increased along with decreases of the pore size and of the overall porosity of the membrane.

3. Results and Discussion

The XRD patterns of the composite membranes heat-treated at 1173 K are shown in Fig. 1. The main phase of SiC can commonly be observed in three membranes. A trace amount of the single $Y_2O_3$ (cubic, SG = fm-3 m, $a = 1.0604$ nm) phase started to show up in the 1 wt% sample (JCPDS file No. 01-083-0326). $Y_2O_3$ peaks are progressively enhanced with increasing amounts of $Y_2O_3$.

Figures 2(a) and (b) show the nitrogen sorption isotherms and the pore size distributions for these composite membranes measured using the BJH (Barrett-Joyner-Halenda) method. With the addition of 1 wt% of $Y_2O_3$, a macro porous shape of the typical III type of the $N_2$ hysteresis loop, as defined by IUPAC (International Union of Pure and Applied Chemistry), was obtained with an average pore diameter of 71.5 nm. This material consists of interconnected pores with irregular shapes and large distributions of pore size, as shown in Fig. 2(b). With the addition of a further amount of $Y_2O_3$, the porosity developed more in the meso portion. In the case of 23 wt%, the pore diameter was the smallest, with a value of 2.44 nm. There was also a higher portion of meso-porous SiC with an S-shaped structure of the typical IV type of the $N_2$ hysteresis loop. This type of hysteresis loop is commonly associated with slit pores or voids between close-packed spherical particles. Comparing samples, the composite membrane with the higher $Y_2O_3$ powder addition has the most uniform pore size distribution and the highest total pore volume, along with the smallest

![Fig. 1. XRD patterns of porous SiC composite membrane containing 1, 9, and 23 wt% of $Y_2O_3$.](image)

![Fig. 2. (a) Nitrogen adsorption-desorption isotherms and (b) Pore size distribution of the corresponding membranes.](image)

![Fig. 3. Surface morphology of porous SiC composite membrane containing (a) 1, (b) 9, and (c) 23 wt% of $Y_2O_3$.](image)
pore, as shown in (b).

Figure 3 shows the surface morphologies of the composite membranes. It should be noted that the large SiC agglomerates are mainly observed with small Y$_2$O$_3$ particles. These particles were uniformly distributed onto the SiC surface with the increase of the Y$_2$O$_3$ contents.

The values of the H$_2$ and CO flux are displayed in Fig. 4(a). The general permeation tendency of all these membranes was found to decrease with increasing temperatures. Straight lines were obtained and this tendency was seen to follow a $(1/T)^{0.5}$ dependence on temperature, indicative of results typical of Knudsen-type transport. There was a decrease not only the quantity of hydrogen but also that of CO gas with increasing Y$_2$O$_3$ content. The values for the corresponding 1, 9, and 23 wt% samples were measured and found to be $1.2 \times 10^{-6}$, $8.9 \times 10^{-7}$, and $7.9 \times 10^{-7}$ mol/m$^2$ s Pa at 298 K, respectively. The differences in these values are due to the pore size and shape of these membranes, which are all slightly different, as shown in Fig. 2.

Figure 4(b) provides an Arrhenius’s plot for the hydrogen flux data. The heat of the process ($\Delta H^\circ$) for the 1, 9, and 23 wt% membranes were $-1.58$, $-1.41$, and $-1.33$ J/mol, respectively. The differences between the resulting values are gradual because the pore shape and distribution of pore size changed slightly from macro to meso-porous with different distributions. Separation can take place based on differences in molecular mass, size, or shape, or on differences in the affinity of the gas molecules to the membrane material. Selectivity is generally found to increase along with decreases of the pore size and of the overall porosity of the membrane.

4. Conclusions

Dense SiC-based composite was prepared by adding Y$_2$O$_3$ to recycled SiC waste sludge. The resulting microstructures were slightly different among the three membranes and all maintained thermo-chemical stability even after gas flux. Hydrogen permeability was the best in the case of the 23 wt%.

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REFERENCES