Gas Permeation of Y_2O_3-SiC Composite Membrane

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ABSTRACT

Y_2O_3-SiC composite membrane was dip-coated using Y_2O_3 sol solution; this membrane was compared with a non--coated one. Each membrane was characterized by XRD, FE-SEM and BET techniques. Hydrogen and CO permeation were tested with self-manufactured Sievert's type equipment. Y_2O_3 coating was enhanced for the selectivity of the membrane (H_2 versus CO). The hydrogen permeation was measured at 1 bar with increasing temperatures. In case of the coated membrane, hydrogen permeation was found to be 1.24×10^{-7} mol/m^{2}sPa with perm-selectivity of 4.26 at 323 K.

Key words : Y_2O_3-SiC composite membrane, Dip-coated, Hydrogen and CO permeation

1. Introduction

SiC is an attractive material due to its durability and its mechanical and thermo-chemical stability.[1] Transparent poly-crystalline Y_2O_3 is also a useful material for a variety of applications due to its specific optical, thermal, and chemical properties. Y_2O_3 has been used in various ceramic separation membranes as an added dopant material. In consideration of the physical and chemical properties of porous inorganic materials, SiC and Y_2O_3 can be used as either supporting or doping materials.[2]

Nano-porous ceramic membranes usually consist of three layers: support, intermediate, and selective top layer.[3,4] A number of oxides have been added to SiC matrices to prepare dense membranes and control the microstructure, including the pore size in particular. Permeation and selectivity of the membrane vary depending on the porosity and the affinity of the permeating species. A preparation that uses a combined process to make multi-component composite membranes is important. Instead of a simple method, the membrane must be fabricated using several processes such as mixing or dip-coating. Mixing SiC with prepared Y_2O_3 particles and using a dip coating process can fill up the relatively big pores caused by SiC network as supporting material.

In order to fabricate homogeneous and crack-free membranes and also control the microstructures of the membranes, sol solution was used for dip-coating on the surface of the synthesized Y_2O_3-SiC composite membrane. This solution was soaked into the pores of the membrane to help control the pore size and the microstructure. Hydridopoly-carbosilane (HPCS) was used as a binder to fabricate the composite membrane.[5] The permeability and selectivity of the hydrogen and CO gas were measured and compared for the non-coated and coated membranes. The enthalpies of the processes were calculated for both membranes.

2. Experimental Procedure

$Y(NO_3)_3 \cdot 6H_2O$ (99.8%, CAS NO. 13494-98-9, Aldrich) and oxalic acid ($C_2H_2O_4$, CAS NO. 144-62-7, Aldrich) were dissolved in ethanol. This mixture was refluxed at 353 K with vigorous stirring overnight. The pH was initially adjusted to pH = 2 ± 0.1. The powder was collected after drying at 393 K for 24 h. Y_2O_3 powder was further sintered at 1173 K in air for 3 h.

Well-grinded 10 wt. % of Y_2O_3 powder was mixed with 90 wt.% SiC (325mesh, BIT Co., Ltd) and HPCS binder (StarPCS SMP-10, Lot. # 5-20589, Starfire Systems) in cyclohexane. This mixture was put through a high energy milling process. Dried at 353 K, this mixture was fabricated into a membrane using a hydraulic press at 15 MPa; final sample had a 14.5 mm diameter and was 2 mm thick. Entire membrane was heat-treated at 1173 K for 3 h under Ar atmosphere. The obtained membrane was dip-coated with Y_2O_3 sol solution 60 times at a constant dipping speed. Every 20 dips, the dip-coated membrane was heat treated at 773 K and final heat-treatment followed at 1173 K for 3 h.

The phase identification and crystal structure analysis were performed X-ray diffraction (XRD) (Bruker D8, Focus, CuKα, 40 Kv, 40 mA) measurements. The microstructure of the powders and membranes were obtained using a field emission-scanning electron microscope (FE-SEM) (JEOL-JMS 7500F). Pore size distribution and porosity were determined by BJH (Barrett-Joyner-Halenda) analysis. The Brunner-Emmett-Teller (BET) value was measured by the adsorption -desorption of N_2 gas per unit of surface area (m^2/g)

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(BELSORP-max, mini II). For the gas permeation, our equipment consisted of a pressure controller, mass flow controller (MFC), and stainless steel 1.4-inch cell module that was constructed to withstand high temperature.

3. Results and Discussion

FE-SEM images of the Y_2O_3 powder and SiC membrane itself after sintering at 1173 K are shown with 50,000 and 2,000 magnification in Fig. 1(a) and (b), respectively. The prepared Y_2O_3 powder has thin hexagonal plate morphology; the grains look like bars or thin plate like shapes. The surface of the SiC membrane can also be seen to have an irregular size and shape with clear-edges, as shown in Fig. 1(b).

Surface and cross sectional images of Y_2O_3-SiC composite and Y_2O_3 dip-coated on this membrane are illustrated in Fig. 2. On the surface of the Y_2O_3-SiC composite membrane: shown in (a), Y_2O_3 particles or clusters fill and block up the spaces between the SiC fragments.

Due to the presence of large grains, the membrane appears to have sharp edges and to have spread over the surface of SiC by crystallite aggregation. However, in the enlarged surface image (× 30,000) of the coated sample shown in Fig. 2(b), fine grains can be observed as a homogeneous spreading pattern on the composite membrane surface. The Y_2O_3 coated layer (with a thickness of an about 2 μm) can even be easily seen in the cross sectional image of
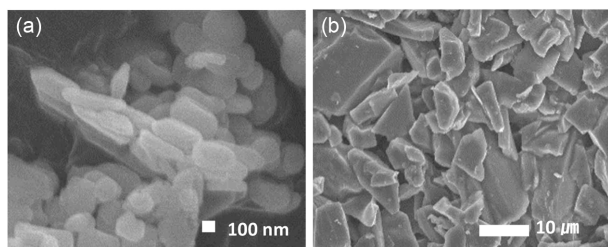

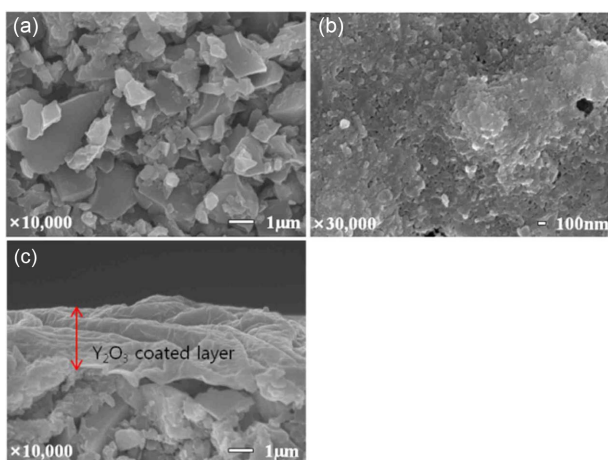**Fig. 1.** Morphology of (a) Y_2O_3 Powder and (b) SiC Membrane.

Fig. 2. Surface images of (a) non-coated sample, (b) Y_2O_3 coated sample, and (c) cross sectional image of Y_2O_3 coated composite membrane.

the coated composite membrane, as shown in Fig. 2 (c). The morphology of the coating layer is characterized by dense and remarkable particle size reduction.

The XRD patterns of the SiC membrane with Y_2O_3 powder, and of the Y_2O_3-SiC composite membrane, as well as of the dip-coated sample are shown in Fig. 3. From the results of the crystalline phase analysis, SiC peaks were assigned to the β-phase of a primitive hexagonal (P63mc) structure (a = 3.08170, b = 3.08170, C = 15.11830, JCPDS file No. 01-074-1302). The diffraction peaks were indexed to a body centered cubic structure (a = 10.59810, JCPDS file No.01-083-1326). New peaks corresponding to SiO_2 arising from the oxidation of SiC can be observed on the mixing and dip-coating membranes. After the dip-coating process, the intensity of the Y_2O_3 pattern was not stronger than before, even though the Y_2O_3 layer had formed on top of the membrane. The Y_2O_3 peaks with small intensity indicate that the Y_2O_3 existed as a nanostructure. Using Rietveld refinement, it was observed that the crystal size of the Y_2O_3 and SiC were 20.3 and 98.2 nm, respectively.

According to the results of N_2 adsorption-desorption analysis shown in Fig. 4, the non-coated membrane exhibits a type V type isotherm and the coated membrane is a typical IV type isotherm with an H_2 hysteresis loop as defined by IUPAC (International Union of Pure and Applied Chemistry).[6] This indicates that the non-coated membrane has a porous structure with a large cavity and the coated membrane has a meso-porous pore structure with uniform pore size distribution. The total pore volume (0.038 cm^3/g) and pore size (40.81 nm) of the Y_2O_3 coated Y_2O_3-SiC membrane was obtained. The corresponding BJH pore size distributions for the coated membrane, as shown in the inset diagram of Fig. 4, indicate on average pore diameter of about 100 nm.

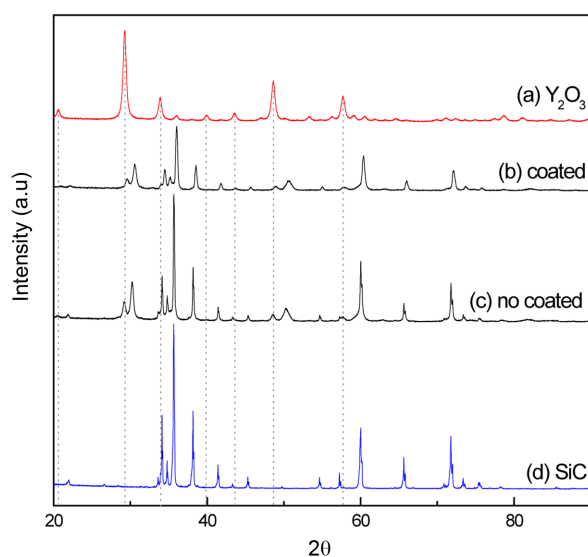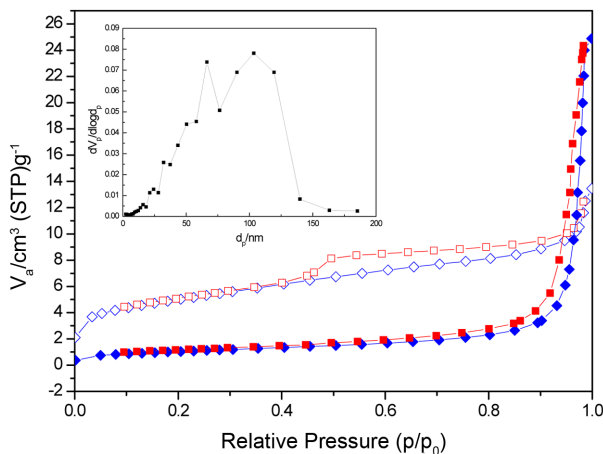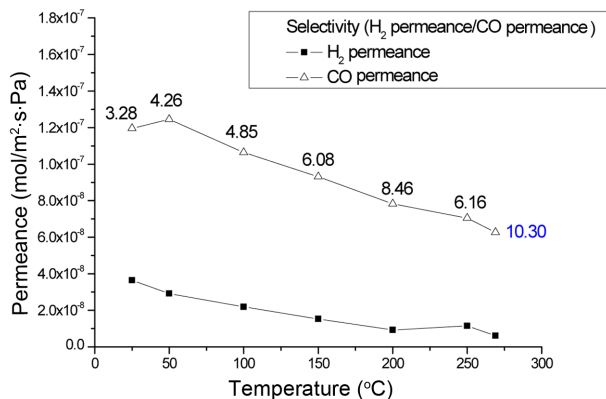Figure 5 (a) and (b) show the results of the fluxes (mol/m²sPa)

Fig. 3. XRD Patterns of (a) Y_2O_3 powder, (b) Y_2O_3 coated sample, (c) non-coated Y_2O_3-SiC sample, and (d) only SiC membrane.

Fig. 4. Adsorption-desorption isotherm of the Y_2O_3 coated (■) and non-coated (□) composite membranes (The left inset is for the BJH plot of the Y_2O_3 coated composite membrane.).

Fig. 5. H_2 and CO gas permeance and perm-selectivity of Y_2O_3 coated SiC membrane.

of both membranes of H_2 and CO gases with increasing temperatures. Analysis of hydrogen permeation and selectivity against CO were performed depending on temperature at 1 bar. The gas fluxes of both membranes show decreasing tendencies with increasing temperature, followed by a Knudsen diffusion mechanism.[6] The hydrogen flux of the coated membrane, which was found to be 1.24×10^{-7} mol/m²sPa, is highest at 323 K. The CO permeation flux at the same temperature was found to be 0.29×10^{-7} mol/m²sPa. The perm-selectivity of H_2/CO is 4.26±0.015 (standard deviation) at 323 K. The greatest difference was 10.30 at 542 K; the average is 6.20 on the dip-coated membrane. On the other hand, the Y_2O_3-SiC membrane without the dip-coating process

shows a small difference (2.36) between the H_2 and CO permeation fluxes at the same temperature. The calculated enthalpies, determined from the Arrhenius plots of all the permeation tests for the non-coated and coated membranes were 0.29 and 1.56 J/mol, respectively. Thus, it is possible to control the perm-selectivity using these combined processes to make a composite membrane.

4. Conclusions

Nano-crystalline Y_2O_3 particles on the surface of Y_2O_3-SiC composite membrane have been successfully prepared using a dip-coating process. The dip-coating process not only provided a meso-porous microstructure, but also promoted the formation of nano-sized Y_2O_3 particles on the surface as well as on the cross section of the membrane. This process could be used to control the porosity and density of the membrane and thereby to influence the membrane's gas permeation properties.

Acknowledgments

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