Properties of Synthesized Al_2O_3-CuO-ZnO/Ni Composite for Hydrogen Membranes

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ABSTRACT

An Al_2O_3-CuO-ZnO (ACZ) precursor powder was synthesized by a facial sol-gel process using a nonionic surfactant span 80 as the chelating agent to improve the surface area and morphology. When creating a hydrogen membrane, several kinds of properties are required, such as easy dissociation of hydrogen molecules, fast hydrogen diffusion, high hydrogen solubility, and resistance to hydrogen embrittlement. ACZ-Ni composite membranes (cermet) were prepared with this precursor and pure Ni powder via the hot press sintering (HPS) method. The ACZ powder was characterized by XRD, BET, and FE-SEM. Hydrogen permeation experiments were performed by Sievert's type of hydrogen permeation membrane equipment. The hydrogen permeability of ACZ/Ni 10 wt% and ACZ/Ni 20 wt% was obtained as 7.2 and 10 $molm^{-2}\ s^{-1}$ at RT, respectively. These values of the corresponding membranes were slightly increased with increasing pressures.

Key words : Al_2O_3-CuO-ZnO, Span80, Sol-gel process, Hydrogen permeability

1. Introduction

Hydrogen is emerging as a clean and renewable energy resource of the future, and a number of industrial fields have introduced applications of hydrogen.[1] The hydrogen membrane separation method is one of the most economical ways of hydrogen purification, and three kinds of membranes - metallic, ceramic, and polymer - are mainly used.

The most famous one is metallic membranes, including Pd-based and Pd alloys, because of their high hydrogen permeability and selectivity.[2] Ceramic membranes have also shown excellent potential for applications because they are great in resistance to acids and are chemically stable, although they have the drawback of low strength at high pressure. In order to solve this drawback, two types of material are combined to form a cermet (ceramic-metal) membrane. These cermetmaterials for membrane applications show excellent results in the permeability and selectivity of hydrogen.[3]

These kinds of materials have been prepared by homogeneous deposition, co-precipitation, hydrothermal synthesis, and sol-gel process. Among these methods, the advantage of the sol-gel method is to make solid state material with large specific surface area and high porosity from meso- to macro-ranges at room temperature. This solid network can be controlled from the liquid phase of molecular precursor via hydrolysis and condensation to the final solid product. Additionally, the use of template substances as organic surfactants to synthesize inorganic or hybrids networks had a remarkable effect in obtaining stable mesoporous metal-oxides and in controlling the textual of materials with high surface area. The surface area and pore volume can also be changed by controlling solution pH, solvent, water/Al ratio, the type of surfactant, and the aging time.[4] The porosity and particle size distribution can be adjusted by using several kinds of surfactants controlling temperatures and reaction conditions.

When metal nickel particles were supplemented into mixed metal oxides, they formed a kind of supported nickel-based membrane with high activity and effective hydrogen perm-selectivity. Compared with palladium, nickel could improve membrane strength to compensate for the drawbacks of ceramic materials. Thus, the purpose of this work is to prepare ceramic/metal (ACZ-80/nickel) composite membranes by a modified method with span 80 in the powder preparation stage. These membranes were prepared by hot-press sintering (HPS) with ACZ-80 and 10 or 20 weight percent of nickel powder. These composite membranes were measured for their hydrogen permeability and perm-selectivity for H_2/N_2 gas with variation of temperature and pressure.

2. Experimental Procedure

2.1. Materials and Preparation

Aluminum isopropoxide ($Al(OC_3H_7)_3$) (98+%, Aldrich) was added to the distilled water with a molar ratio of Al : H_2O = 1 : 100 with refluxing at 358 K. $Cu(NO_3)_2 \cdot 6H_2O$ and Zn

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$(NO_3)_2 \cdot 6H_2O$ (with 10 mol% of span 80 for ACZ-80 powder) were added, and it was then made into clear sol solution by peptizing with HNO_3. The powder was obtained by drying sol at 398 K for 48 h. The obtained Al_2O_3-CuO-ZnO (ACZ) and Al_2O_3-CuO-ZnO with the addition of span 80 (ACZ-80) powders were calcined from 773 to 1473 K. In order to obtain composites for hydrogen permeation, the mechanical alloying process was used for milling with a zirconia ball for 1 h to mix the ACZ or ACZ-80 precursor powder with pure Ni (99.9%, Aldrich) powders. The weight ratios of 80 : 10 and 80 : 20 was used for making 10 wt% and 20 wt% Ni composite membranes, respectively. The consolidation of powders was performed using hot-press sintering (HPS). The heating rate and the pressure were (5 K/min) and 0.2 ~ 0.4 MPa, respectively. Sintering was proceeded at 1373 K for 2 h under a vacuum. In the cooling stage, the HPS was maintained on the operating pressure in order to maintain the as-sintered density of the specimens.

2.2. Characterization

The ACZ powder was characterized using XRD (Bruker D8 Focus, CuKα, λ = 1.5406 A, 0.2°/min, 10~80°) and field emission scanning electron microscopy (FE-SEM, JEOL JSM-7500F). A specific surface area was measured using BET (BEL SORP MINI II, BEL Co.) analysis. Membranes were characterized by our own permeability experiments with pure hydrogen gas. The equipment consists of a pressure controller, mass flow controller (MFC), permeation cell, and a stainless steel 0.635-centimeter-long tube that can withstand high temperature. The permeation-cell-equipped membrane was placed in a furnace under controlled temperatures. Before the test, it was purged under a hydrogen atmosphere for 1 h to remove contaminants on the sample surface. The temperature was increased at less than 5 K/min after the membrane was installed into the furnace to prevent cracking of the membrane due to a rapid rise in the thermal difference. Hydrogen concentration was measured using a thermal conductivity detector (TCD) for analyzing the difference between nitrogen gas as a carrier and thermal conductor.

3. Results and Discussion

Figure 1 showed the XRD patterns of (a) ACZ and (b) ACZ-80 at various temperatures. The overall peaks at 773 ~ 1173 K are observed to be broad because of their amorphous state. The stable spinel structure of CuO and $CuAl_2O_4/ZnAl_2O_4$ peaks begin to be observable at 773 K and remain until 973 K. The CuO peaks disappeared at 1173 K, while the $CuAl_2O_4/ZnAl_2O_4$ peaks increased. The metal oxide and Al_2O_3 are thought to have formed these complexes by a solid-solid interaction. α-Al_2O_3 with $CuAl_2O_4/ZnAl_2O_4$ peaks were observed on both samples at 1373 K and also at 1473 K.

The FE-SEM images of the ACZ and ACZ-80 precursor powder at 773 K, 973 K, and 1473 K are shown in Fig. 2.
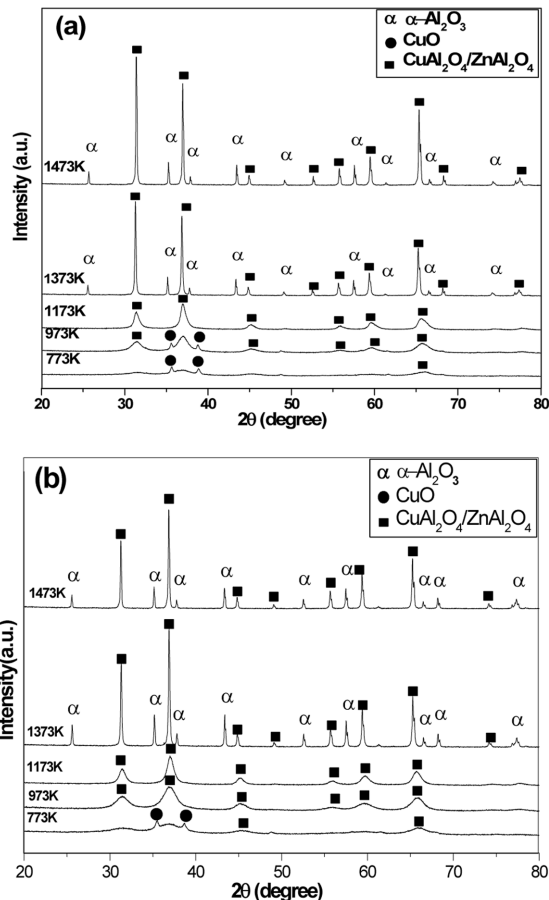

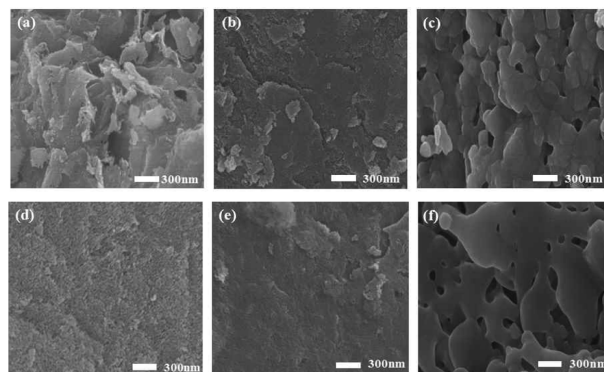**Fig. 1**. XRD result of (a) ACZ and (b) ACZ-80 precursor powder.

Fig. 2. FE-SEM micrographs of the ACZ powder for (a), (b), (c) and the powder with span 80 for (d), (e), (f) heat-treated at 773 K, 973 K, and 1473 K, respectively.

The images of both membranes look the same for all the temperatures even though the size of particles with span 80 looks smaller than without, as shown at 773 K. These morphologies of particles seem to be smooth and aggregated each other to make a large cluster at high temperature. The tendency of particle size is increased by aggregation arising from heat-treatment in both samples.
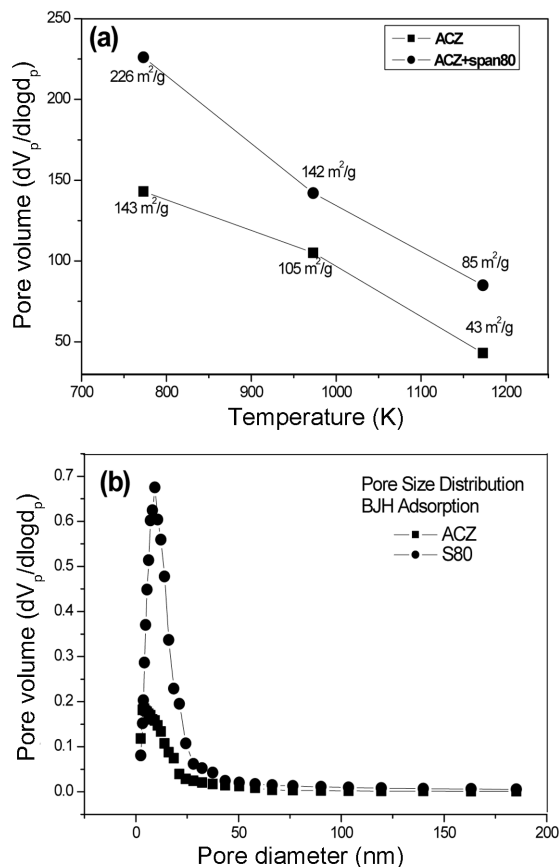
The BET surface areas of the ACZ and ACZ-80 precursor

Fig. 3. (a) BET surface area and (b) pore distribution of ACZ and ACZ-80 precursor powder heat-treated at 973 K.

Fig. 4. Hydrogen permeation fluxes of the ACZ-80 with (a) 10 and (b) 20 wt%Ni membranes.

powder were described in Fig. 3(a). ACZ was measured as 143, 105, and 43 m^2/g at 773, 973, and 1173 K, respectively. The surface area was decreased by increasing particle size. The decrease in the surface area is associated with increasing heat-treatment because of the influence of grain growth and phase formation. Therefore, the main sintering process influences material redistribution and can decrease the surface energy of particles by reducing their own surface areas.[5]

ACZ-80 was observed to be 226, 142, and 85 m^2/g at 773, 973, and 1173 K, respectively. There is an increase in surface area when span 80 is used. The presence of surfactant caused an increase of the surface area and pore volume. Fig. 3(b) shows pore distributions for ACZ and ACZ-80 heat-treated at 973 K. These have a pore diameter of 1-10 nm (ACZ) and 10-20 nm (ACZ-80). The ACZ powder has a rather broad distribution while the ACZ-80 has pores of more uniformed size. By looking at the increase in surface area of ACZ powder by adding span 80, superior hydrogen permeability is expected when producing membranes using this powder.

The hydrogen permeability performances of the ACZ-80/10 and 20 wt% of different Ni amounts are demonstrated in Figs. 4(a) and (b). The evaluations of permeation were per-
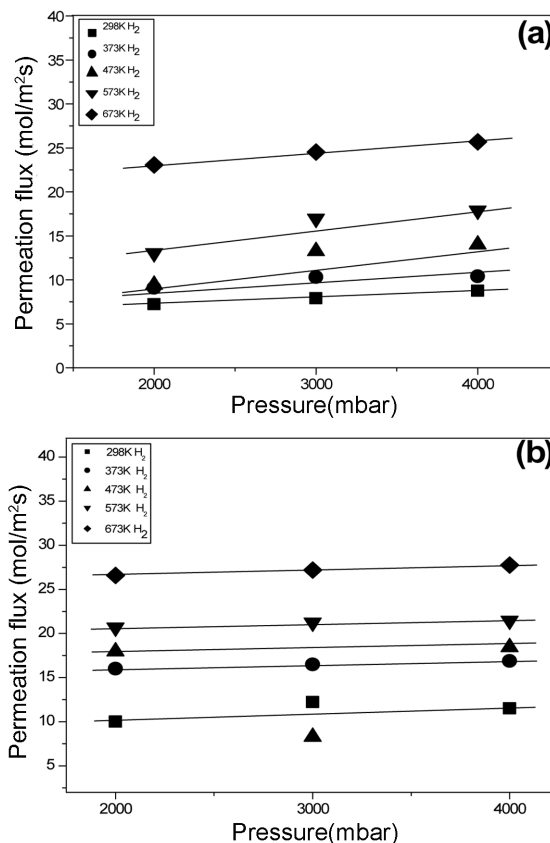
formed at various temperatures from 298 K to 673 K. The hydrogen permeability of ACZ-80/10 wt% Ni and ACZ-80/20 wt% Ni were obtained as 7.2 mol m^{-2} s^{-1} and 10 molm^{-2} s^{-1} at room temperature under 2 bar, respectively. The tendency of hydrogen fluxes were increased with increasing pressures but were not correlated with temperatures. These membranes were expected to follow Knudsen diffusion mechanism, but the results differ with temperature variations. However, these values were higher than for other cermet membranes (4.20×10^{-8}molcm^{-2} s^{-1} at 1173 K)[6] and Al$_2$O$_3$-20 wt%Ni cermet (0.374 molm^{-2} s^{-1} at 473 K)[3], even though mixing material was different.

The perm-selectivity of the ACZ-80/20 wt%Ni membrane is demonstrated in Fig. 5. The evaluations of gas fluxes were performed at (a) 573 K and (b) 673 K. Both of the hydrogen and nitrogen fluxes were increased with increasing pressure. The nitrogen permeability of these were measured as 11.8 molm^{-2} s^{-1}at 573 K and 21.7 molm^{-2} s^{-1} at 673 K, showing an unremarkable perm-selectivity compared to hydrogen permeability due to the porosity (micro-porous) through whole system during experiments, while the hydrogen permeability was obtained as 20.7 molm^{-2} s^{-1}at 573 K and 26.6 molm^{-2}s^{-1} at 673 K. The results show that hydrogen perm-selectivity at 573 K was better than at 673 K. The condition of 0.2 MPa appears from Fig. 5(a) to be the best in terms of perm-selectivity.
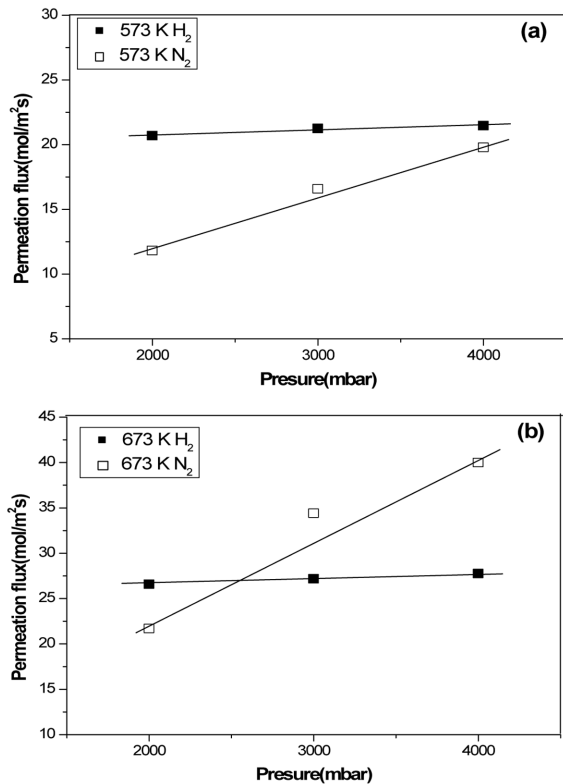
Fig.5. Gas fluxes of ACZ-80/20 wt% Ni membrane obtained (a) at 573 K and (b) 673 K.

4. Conclusions

The separation cermets were obtained by Al_2O_3-CuO-ZnO powder with or without span 80 and also different ratios of Ni powder by the HPS method. The surface areas of these powders were reduced with increasing heat-treatment temperatures. These results are agreed with the morphology results. The values of hydrogen permeability for the membrane with span 80 were better than them without. However, the porosity, density, and crystallites of the membrane should be controlled with further research, such as a dip-coating process, to improve gas permeation selectivity.

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