Hydrothermal stability of mesoporous Ni-doped $\gamma$-Al$_2$O$_3$

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Ni-doped $\gamma$-Al$_2$O$_3$ with different molar compositions has been synthesized on $\alpha$-Al$_2$O$_3$ porous supports by the sol–gel method using nitrate-alkoxide precursors. The increasing of lattice constants by Ni doping showed the formation of uniform solid solution. When the Ni content increased up to 10 mol%, NiO phase was formed. The relationship between molar compositions and hydrothermal stability under atmosphere of steam/N$_2$ = 3 at 773 K for 0–50 h was compared. The pore size distribution of 5 mol% Ni-doped $\gamma$-Al$_2$O$_3$ on $\alpha$-Al$_2$O$_3$ porous support was stable even after hydrothermal exposure at 773 K for 50 h.

1. Introduction

Hydrogen (H$_2$) has been attracting considerable attention as a clean alternative energy source for hydrocarbon fuels. In natural gas reforming, methane (CH$_4$), the main constituent of natural gas, is converted to H$_2$ and carbon monoxide (CO) through steam reforming as follows.

$$\text{CH}_4 + \text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{CO} \quad \Delta E = 206 \text{ kJ/mol} \quad (1)$$

This reaction is endothermic and is induced at approximately 1073 K. In this process, the synthesis gas then proceeds to a water-gas shift reactor where steam and CO can be converted into H$_2$ and carbon dioxide (CO$_2$). Finally, H$_2$ is separated from the gas mixture using one of several adsorption technologies, such as pressure swing adsorption (PSA). Owing to a high operation temperature and several complex purification steps, the cost to produce H$_2$ with these current technologies is too high for it to be used as an alternative source for conventional hydrocarbon fuels. Therefore, decreasing the operation temperature and combining these processes into a single step have been technical problems.

A membrane reactor has been investigated as a device for H$_2$ mass production. It is well known that the application of high-temperature membrane reactors to this steam reforming step has the potential of achieving the same conversion efficiencies as those attained using conventional reactors at a significantly low temperature of approximately 773 K.$^{[1,2,3]}$ If a membrane with a high durability under steam atmosphere at elevated temperatures is developed, these technical problems can be solved concurrently. A palladium-based membrane with high H$_2$ permselectivity is a candidate membrane reactor. However, there are some problems associated with the total cost of a resource.

Hydrothermal stability of H$_2$-permselective membrane is very important to apply steam reforming process as a membrane reactor. An inorganic membrane with a high strength at elevated temperatures and a high chemical stability is used under a high pressure and corrosion atmosphere at elevated temperatures. The pore size of mesoporous $\gamma$-alumina ($\gamma$-Al$_2$O$_3$) which is used as an intermediate layer in inorganic membranes increases under steam atmosphere at elevated temperature.$^{[3,4]}$ The increase of pore size in $\gamma$-Al$_2$O$_3$ causes membrane defect and degradation of hydrogen permselectivity. Gallaher and Liu investigated the hydrothermal (up to 90% steam) stability of commercial $\gamma$-Al$_2$O$_3$ membranes by H$_2$ gas permeation.$^{[5]}$ They found that the H$_2$ gas permeance drastically increased with hydrothermal treatment at 773 K. The results indicate that the $\gamma$-Al$_2$O$_3$ membrane is not a good candidate for use as an mesoporous intermediate layer for fabrication of microporous gas separation membranes. Nomura et al. reported that hydrothermal exposure from inside of amorphous silica membrane on $\gamma$-Al$_2$O$_3$-coated $\alpha$-alumina ($\alpha$-Al$_2$O$_3$) (SiO$_2$/$\gamma$-Al$_2$O$_3$/$\alpha$-Al$_2$O$_3$) capillary tube promoted the degradation of H$_2$ permeance to nitrogen (N$_2$) (H$_2$/N$_2$ permselectivity) in comparison with hydrothermal exposure from outside of SiO$_2$/$\gamma$-Al$_2$O$_3$/$\alpha$-Al$_2$O$_3$ capillary tube. They concluded that hydrothermal stability of $\gamma$-Al$_2$O$_3$ intermediate layer was important in durability of H$_2$ separation membrane.$^{[6]}$

Recently, authors succeeded to improve hydrothermal stability in $\gamma$-Al$_2$O$_3$ by metal doping.$^{[4,5,6]}$ To develop H$_2$ separation membrane with high hydrothermal stability, we compared permeance change between amorphous silica membranes on $\gamma$-Al$_2$O$_3$-coated $\alpha$-Al$_2$O$_3$ and metal-doped $\gamma$-Al$_2$O$_3$-coated $\alpha$-Al$_2$O$_3$ synthesized by counter diffusion chemical vapor deposition.$^{[7]}$ Hydrogen permeance decreased with hydrothermal exposure time due to the densification of amorphous silica. On the other hand, N$_2$ permeance was not stable during hydrothermal exposure due to the lack of hydrothermal stability of $\gamma$-Al$_2$O$_3$. Nitrogen mainly permeates through membrane defects in H$_2$-permselective membrane. Accordingly, N$_2$ permeance mainly depends on pore size change in intermediate layer during hydrothermal exposure. Therefore, it is important to suppress both densification of amorphous silica and sintering of $\gamma$-Al$_2$O$_3$ under hydrothermal atmosphere.

Nickel (Ni) is a unique element for gas separation membrane. For example, Ikuhara et al. synthesized Ni nanoparticle-
dispersed amorphous silica membrane on anodic-oxidized alumina porous support by sol–gel method and reported remarkable increase of H₂ permeability. Okubo et al. demonstrated that a modification of a boehmite sol by Ni was effective in pore size control of γ-Al₂O₃. Kanazashi et al. synthesized Ni-doped silica membranes on silica-zirconia-coated α-Al₂O₃ porous tube by sol–gel technique. They reported that the densification of amorphous silica after hydrothermal treatment under N₂ atmosphere was suppressed in Ni-doped amorphous silica and N₂ permeance decreased after initial hydrothermal exposure.

In this study, we investigated the Ni addition effect for γ-Al₂O₃ to develop mesoporous intermediate layer with higher hydrothermal stability.

2. Experimental procedure

Sols were prepared by reacting 0.05 M of aluminum-tri-sec-butoxide (Al(O-sec-Bu)₃) = ASTB, 97% Aldrich, USA) and 0.1 M isopropyl alcohol (Kanto Chemical Co., Inc., Japan) with double-distilled water at 363 K. After the addition of ATSB, the mixture was maintained at 363 K for at least 1 h to evaporate off the isopropyl alcohol and the butanol that formed. The mixture was subsequently cooled down to room temperature and peptized with 1 M HNO₃ at pH of about 3. During the synthesis, the sol was stirred vigorously. The peptized mixture was refluxed at 363 K for 15 h, yielding a very stable 0.05 M boehmite sol with a clear whitish-blue appearance. Doping of this sol was performed by mixing it with an aqueous solution of Ni(NO₃)₂·6H₂O (Wako Pure Chemical Industries, Ltd., Japan). The compositions [metal nitrate (mol%): boehmite (mol%): boehmite (mol%)] of various precursor solutions for sol synthesis are shown in detail in Table 1. For example, the amount of Ni(NO₃)₂·6H₂O corresponding to the added 10 mol% Ni was calculated as

\[(\text{mol Ni/mol Ni} + \text{mol ATSB}) \times 100\% \]  

(2)

The increase in sol viscosity upon addition of the nitrate solution was probably a result of a decrease in the pH due to the acidity of the nitrate solution. Doped boehmite sols were therefore prepared without the addition of HNO₃.

An α-Al₂O₃ porous capillary tube (150 nm in mean pore diameter, 2.9 mm in outer diameter, 2.1 mm in inner diameter, 85 mm in length, NOK Corporation, Japan) was used as the substrate.

The dip-coating solution for γ-Al₂O₃ was obtained by diluting boehmite sol (γ-AlO(OH)) with a 3.5 wt% solution of polyvinyl alcohol (PVA #500, Kanto Chemical Co., Inc., Japan) at room temperature. The end of the α-Al₂O₃ substrate was plugged. The outer surface of the substrate was dipped in the solution for 10 s, whereas the inner surface of the capillary was evacuated to obtain a pinhole free membrane using a vacuum pump. After dipping, the membrane was dried for 1 h in air. It was then calcined at 1073 K for 2 h at a heating/cooling rate of 1 K/min. This dipping–drying–firing sequence was repeated once.

X-ray diffraction (XRD) patterns were identified using an X-ray diffractometer (Rigaku Corporation, RINT–2500 Japan) with Cu Kα radiation of 50 kV and 300 mA with a monochromator over a diffraction angle range of 2θ from 10 to 80° at a scan rate of 1°/min by analyzing the respective powdered samples prepared by calcining the original boehmite sols. The lattice parameter value was obtained with silicon used as an external standard.

In order to understand hydrothermal stability of Ni-doped or non-doped mesoporous γ-Al₂O₃ on α-Al₂O₃ porous supports, the hydrothermal treatment was performed under atmosphere of steam/N₂ = 3 at 773 K for 2–50 h.

The pore size distribution before and after hydrothermal treatment was evaluated to read N₂ flow rate through out pores which is not blocked by fluid of condensable water vapor (Seika Corporation, Nano-permporometer, Japan). Single gas permeance (P) was evaluated by a constant-volume manometric method. The gas permeance at each temperature was evaluated in the order of helium (He), H₂, and N₂. Permeability was defined as the permeance ratio of the two gases. For example, the He/H₂ permeability is given by the ratio \(P_{\text{He}}/P_{\text{H}_2}\).

3. Results and discussion

The XRD patterns of as-prepared γ-Al₂O₃ and Ni-doped γ-Al₂O₃ are shown in Fig. 1. The observed peaks of γ-Al₂O₃ are broad, thereby implying that the size of crystallites is small. No X-ray detectable phase was present other than γ-Al₂O₃ upon the addition of 5 mol% Ni. When the Ni content increased up to 10 mol%, however, NiO phase was slightly detected. In the addition of 30 mol% Ni, NiO phase was strongly detected. The peak shifts at 2θ = 45.8° and 66.8°, which can be assigned to γ-Al₂O₃ (400) and (440), toward lower angles, suggested the formation of a uniform solid solution.

In order to examine these shifts in detail, the crystal structure of Ni-doped γ-Al₂O₃, changes in the XRD peaks assigned to γ-Al₂O₃ (400), (440), and their lattice constants with Ni contents (mol%) were measured. The lattice constants of Ni-doped γ-Al₂O₃ as a function of mol% of Ni²⁺ ions are shown in Fig. 2. The average lattice constant of γ-Al₂O₃ (440) and (400) was similar to that of the JCPDS card No. 29–0063. A linear correlation was observed in the region of Ni content up to 30 mol%.

Figure 3 shows effect of hydrothermal treatment under atmosphere of steam/N₂ = 3 at 773 K on H₂ permeance in γ-Al₂O₃.
and Ni-doped γ-Al₂O₃. After the first measurement at 0 h, the remainder of the permeance data was obtained after hydrothermal exposure. The H₂ permeance in γ-Al₂O₃ increased from 2.31 × 10⁻⁵ mol/m²·s·Pa to 2.51 × 10⁻⁵ mol/m²·s·Pa with hydrothermal treatment for 20 h. After hydrothermal treatment for 50 h, the permeance in γ-Al₂O₃ slightly decreased to 2.44 × 10⁻⁵ mol/m²·s·Pa. On the other hand,
Hydrothermal exposure for 50 h became lower than that in as-prepared 5 NA and 10 NA. Therefore, the suitable quantity of Ni doping is very effective to suppress the sintering of γ-Al2O3 under hydrothermal atmosphere.

4. Summary

Hydrothermal stability of γ-Al2O3 and Ni-doped γ-Al2O3 on α-Al2O3 porous supports was investigated. The pore size distribution in γ-Al2O3 on α-Al2O3 shifted toward larger pore radii after hydrothermal exposure under atmosphere of steam/ N2 = 3 at 773 K for 50 h. No X-ray detectable phase was present other than that of γ-Al2O3 upon the addition of 5 mol% Ni. The XRD peak shifts which can be assigned to γ-Al2O3, towards lower angles, showed solid solution of Ni.

Therefore, the improving of hydrothermal durability in Ni-doped γ-Al2O3 on α-Al2O3 was thought to be caused by solid solution of Ni into γ-Al2O3.

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References