Stability of Ni-doped Silica Membranes for H_2 Separation at High Temperature

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Aiming at improvements of the stability of silica membranes against water (vapor) at room and high temperatures, nickel oxide was added to silica to obtain Ni-doped silica membranes by the sol-gel techniques. The Ni-doped silica membranes (Si/Ni=2/1) were fired at 500-550°C and the gas permeances were observed under dry and moist conditions at high temperature. A Ni-doped membrane showed a large H_2-permeance of 1.5×10^{-5} [m^3(STP)/(m^2skPa)] with selectivity of 350 (H_2/CH_4) at 200°C. After leaving the membrane in humid air (40°C, 60%RH) for 70 days, the H_2- permeance decreased by about 50% with an improved selectivity of 930 for H_2/CH_4. Little change, however, was observed in the activation energy for H_2 permeation. A Ni-doped silica membrane (Si/Ni=2/1) fired at 550°C showed high stability in dry gases at 500°C. Once exposed to H_2 at 500 °C, however, the permeances of He and H_2 decreased by about 50% and the permeance of N_2 decreased to 1/5 of initial value due to the densification followed with some reduction of nickel oxide. In order to reduce the effects of NiO-reduction on H_2-permeance, the membranes were exposed to steam for a while at 500°C before exposing to H_2. The effectiveness of this hydrothermal treatment for the membrane stability in steamed hydrogen at high temperature is discussed.

Key words: Inorganic membrane, Stability, Hydrogen, Nickel oxide, Sol-gel techniques

1.INTRODUCTION

Inorganic membranes prepared by sol-gel techniques or CVD methods have some substantial advantages such as thermal and chemical stability. Silica is one of the most attractive inorganic materials because of its possible amorphous structures of pore size less than 1nm, which is attractive for highly selective membranes. At the end of 1980's, dense silica membranes were found to show some excellent separation performance for hydrogen or helium at high temperature [1-3]. However, dense silica membranes were found not stable against water at high temperature or even at room temperature [4-7].

In order to improve the stability of membrane against water or water vapor, nickel oxide was added to silica in this work to obtain Ni-doped silica membranes by the sol-gel techniques [8]. Some gas permeances were observed to examine the effectiveness of NiO in silica for membrane stability in dry and moist conditions at high temperature.

2.EXPERIMENTAL

Ni-doped silica membranes were prepared by sol-gel techniques [8]. First of all Ni-doped colloidal silica sols were prepared, then the hot coating methods were applied to form a thin layer of Ni-doped silica membrane on a porous ceramic substrate. To discuss the membrane stability against water, the temperature- and time-dependency of gas permeance, hydrothermal stability, N_2 adsorption characteristics and XRD patterns of the membrane material were observed.

2.1 Preparation of colloidal sols

Colloidal sols were prepared by hydrolysis and condensation reactions of tetra-ethoxysilane (TEOS) in ethanol with $Ni(NO_3)_2 \cdot 6H_2O$ and water [8]. The preparation procedures are as follows, for example: A specified amount of TEOS (7.5g) was added to ethanol (50g) with a specified amount of nickel nitrate and the solution was stirred for enough time for hydrolysis and condensation reactions. After adding a specified amount (2g) of nitric acid (61%) and a large amount of water (500g), the solution was boiled for about 10 hours for a colloidal sol. The total amount of the solution during the boiling was kept constant and the organic chemicals initially contained were removed during boiling. Four kinds of colloidal sols (2, 1.5, 1, 0.5 wt% of equivalent TEOS in the final sol) were prepared.

2.2 Membrane fabrication

Porous α-alumina tubes (Porosity: 50%, average pore size: 1μm, outside diameter: 10mm, length: 100mm) were used as the support for the silica-zirconia (Si/Zr=1/1) layer of pore size at around several nm [9]. The Ni-doped silica colloidal sols were coated on the

substrate by the hot coating methods, where the substrate (module) was heated up to around 180°C before coating with the colloidal sol by contacting the module quickly with a wet cloth with the sol [8]. Then the module was fired at 500-550°C for 10-20 minutes. The coating procedures were repeated several times with each colloidal sol prepared.

2.3 Gel preparation for N₂ adsorption characteristic and XRD

Some powdered samples were prepared from the colloidal sols by drying quickly at 180°C (by dripping colloidal sols on a hot platinum plate) and fired at 500°C for 30 minutes.

2.4 Permeation measurements and hydrothermal stability test

Single gas of high purity (He, H₂, N₂, CH₄, SF₆) was fed on the outside (upstream) of a cylindrical membrane module at 0.2MPa, keeping the down stream pressure constant at the atmospheric pressure. The temperature of the measurement cell was kept constant at a specified temperature between 35 and 300°C. The permeation rate was measured by a soap film flow meter. After measuring the permeances dependency of various gases on temperature with a fresh membrane, the membrane was kept in humid air at 40°C and 60% of relative humidity for a specified period. Then the gas permeances were observed again in the same temperature range as mentioned above.

Hydrothermal stability test was performed at 500°C in a gas mixture of N₂ and H₂O. The mixture was fed on the outside (upstream) of cylindrical membrane module under atmospheric pressure, while the permeate side (downstream) was evacuated. The partial pressure of H₂O was keeping at 70kPa. After exposing the membrane to steam at 500°C for a specified time interval, the membrane was dried completely in N₂ stream at the same temperature. Then the permeances of N₂, He and H₂ were calculated from the observed pressure difference across the membrane and the permeation rate, which was obtained by a calibrated critical nozzle placed between the permeation cell and the vacuum pump. The permeance changes during this hydrothermal test were observed in the specified time intervals by repeating the procedures mentioned above.

3. RESULTS AND DISCUSSION

Figure 1 shows some observed permeances of He, H₂, N₂, CH₄ and SF₆ in the temperature range of 35-300°C for a fresh Ni-doped silica membrane (Si/Ni=2/1) (Closed keys on solid lines). In the same figure are shown the permeances observed after leaving the membrane in humid air (40°C, 60% relative humidity)

for 70 days (Open keys on broken lines). The permeance of H₂ is quite close to that of He and slightly shows the characteristics of the activated permeation, while the permeances of other gases show little temperature dependency. The selectivity is not so large for H₂/N₂ around 100 at 300°C, but quite large for H₂/SF₆ (around 4200 at 200°C) indicating few pinholes (larger than 0.55 nm) left. After 70 days the permeances of He and H₂ have decreased by about 50%, while the permeances of N₂ and CH₄ have decreased drastically to 1/10 of the initial values, resulting in a larger selectivity of H₂/N₂ around 540 at 300°C.

In Fig.2 is shown the changes of activation energy of H₂-permeation for silica and Ni-doped silica (Si/Ni=2/1) membranes. The activation energy, ΔE, can be obtained by applying the following equation (Eq.(1)) [10] to the observed temperature dependency of permeance, P, with a little correction due to the contribution of the Knudsen flow based on O₂ permeation.

$$P = \frac{k_0}{\sqrt{MRT}} \exp(-\frac{\Delta E}{RT}) \quad (1)$$

where k_0 is a characteristic constant of porous membrane, M molecular weight of permeating gas, R the gas constant and T is the temperature. Fresh silica and Ni-doped (Si/Ni=2/1) membranes show a few kJ/mol activation energy. After leaving them in humid air for 70 days, a silica membrane showed a quite large change in activation energy from 3.1 to 14kJ/mol, while under the same conditions Ni-doped (Si/Ni=2/1) membrane showed little change. These results suggest that well dispersed NiO can prevent the densification of amorphous silica networks and Ni-doped (Si/Ni=2/1) membrane is relatively stable against water in the temperature range 35-300°C.
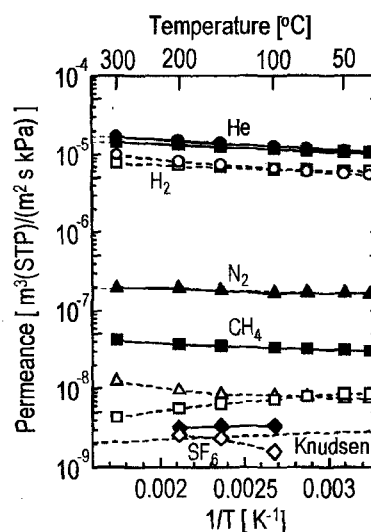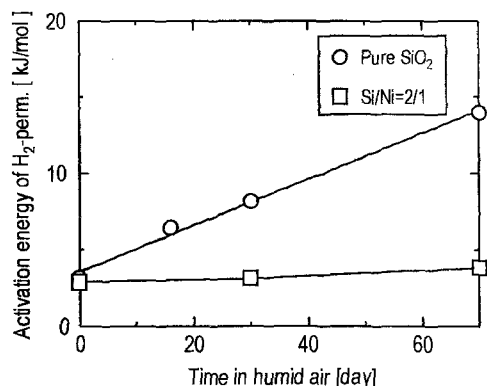

Fig.1 Observed gas permeances for Ni-doped silica membrane (Si/Ni=2/1) (Closed keys: fresh, Open keys: after 70 days in humid air)

Fig.2 Observed activation energy of H_2- permeation

In order to examine the thermal stability of Ni-doped membranes (Si/Ni=2/1), the time-dependency of gas permeances were observed in dry gases at 500°C. Some of the results for Ni-doped silica membrane (Si/Ni=2/1) are shown in Fig.3. In the region I in this figure, the membrane was not exposed to H_2. The He-permeance seems to approach a constant value after a little decrease in a few days, while the N_2-permeance seems to decrease a little even after one week, preferably giving a larger selectivity. In the region II, where the membrane was exposed to H_2 for the first time after fabrication, was observed a relatively large decrease in permeance clearly due to the reduction of NiO by H_2 in the silica networks. Though the color of a Ni-doped silica membrane (Si/Ni=2/1) after the fabrication was slightly gray, it was found to turn into dark gray after being exposed to H_2 for a while at 500°C. This suggests that well dispersed NiO in the silica networks may move through the network and gather to form lager Ni particles after reduction by H_2 at high temperature. The activation energy of He-permeation slightly increased from 8.4kJ/mol in region I to 10kJ/mol in region II. This indicates that the densification of Ni-doped amorphous silica networks are triggered mainly by the reduction of NiO by H_2 at high temperature.
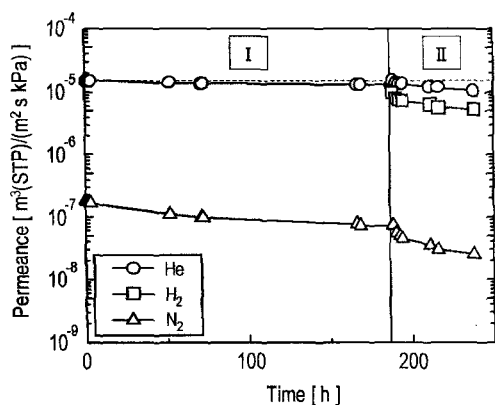

Fig.3 Observed permeance changes (I : in He and II : in H_2) for Ni-doped silica membrane (Si/Ni=2/1)

Figure 4 shows some observed XRD patterns of Ni-doped silica powders. SiO_2-NiO composite gel (Si/Ni=2/1) shows NiO broad peaks, which are quite different from those for a simple mixture of SiO_2 and NiO (Si/Ni=2/1). This indicates that some of NiO of SiO_2-NiO composite gel was dispersed well. After fired SiO_2-NiO composite gel (slight gray) in H_2 at 500°C for 30min., NiO crystal particles turn into metal Ni particles (black) by reduction and a large difference in pore size distribution was observed by N_2 adsorption method as shown in Fig.5. These results also suggest that reduction of NiO dispersed in micro pores, grain boundaries and amorphous silica networks causes the densification and aggregation of metal Ni.
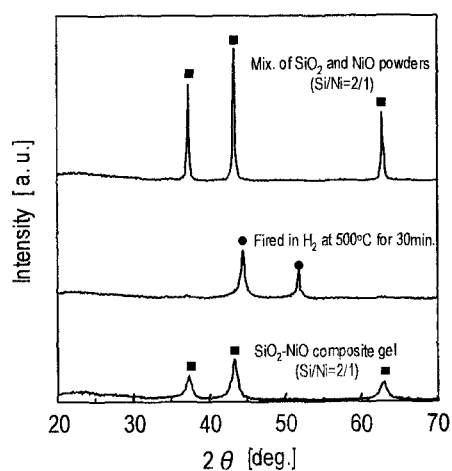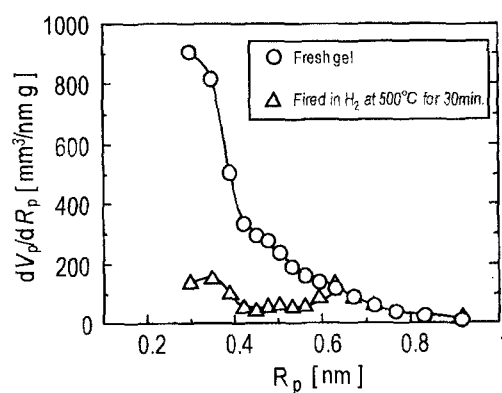

Fig.4 Observed XRD patterns of Ni-doped silica powders (Si/Ni=2/1) (■: Nickel oxide, ●: Metal Ni)

Fig.5 Observed pore size distribution of Ni-doped silica powders (Si/Ni=2/1) by N_2 adsorption

In order to prevent the densification of Ni-doped amorphous silica networks due to the reduction and the following aggregation of metal Ni, the hydrothermal treatments (partial pressure of H_2O: 70kPa) were

performed at 500°C before being exposed to H_2.

Figure 6 shows some observed permeance changes of He, H_2 and N_2 in steam (500°C, 70kPa) for Ni-doped silica membrane (Si/Ni=2/1) fired at 550°C. The closed keys on solid lines show permeance changes after the hydrothermal treatments for 1.75 hr and the open keys on the broken lines are those without the hydrothermal treatments. The initial characteristics of these two kinds of membranes are quite similar and show a relatively large H_2-permeance of 2.3×10^{-5} $[m^3(STP)/(m^2skPa)]$ with selectivity of 160 (H_2/N_2) and 190 (He/N_2) at 500°C. However, large differences were observed after hydrothermal stability test for these membranes. For the membrane with the hydrothermal treatments for 1.75h before exposed to H_2, the permeance of He slightly decreased. And the H_2-permeance decreased by about 60%, while the N_2-permeance decreased drastically to 1/15 of the initial value, resulting in a larger selectivity of 482 (H_2/N_2) and 1360 (He/N_2) at 500°C after the hydrothermal stability test for 63 hr. On the other hand, the permeances of He and H_2 decreased drastically to 1/5 and 1/10 of initial values, respectively, for the membrane without the hydrothermal treatments. The activation energy of H_2-permeation of the membrane with the hydrothermal treatments is 17kJ/mol after 63 hours in steam (500°C, 70kPa), while that of the membrane without initial hydrothermal treatments is 21.6kJ/mol after about 40 hours. Considering that larger activation energy of gas permeation suggests more dense structures of the membrane, the hydrothermal treatments before being exposed to H_2 seems to prevent the densification of the membrane in steam at high temperature.
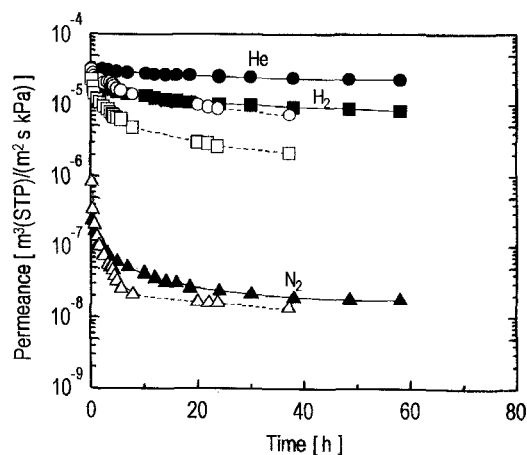

Fig.6 Some gas permeance changes for Ni-doped silica membrane (Si/Ni=2/1) in steam (500°C, 70kPa)
(Closed keys: with the hydrothermal treatment for 1.75h,
Open keys: without the hydrothermal treatment)

CONCLUSIONS

Porous Ni-doped silica membranes for selective permeation of H_2 and He were prepared by the sol-gel techniques. In a temperature range of 35-300°C, Ni-doped silica membrane (Si/Ni=2/1) showed a large permeance with a large selectively of H_2 and He, and showed relatively stable against water. And Ni-doped silica membrane (Si/Ni=2/1) fired 550°C showed high stability in dry gases at 500°C. At high temperature, however, the stability of Ni-doped silica membrane (Si/Ni=2/1) was affected by reduction of dispersed NiO. To perform the hydrothermal treatment before being exposed to H_2, it was effective to prevent the densification of Ni-doped amorphous silica networks by reduction and sintering.

ACKNOWLEDGEMENT

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