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$HI-H_2O$ 기상 혼합물에서 silica 막의 안정성

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Stability of a Silica Membrane in the $HI-H_2O$ Gaseous Mixture

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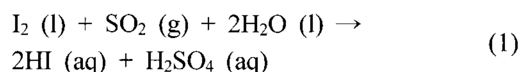
요 약: 열화학적 IS 공정에서 요오드화수소의 분해에 적용하기 위하여 화학증착법(CVD)으로 제조된 silica 막의 안정성을 $HI-H_2O$ 기상 혼합물에서 평가하였다. Si 원천으로 tetraethoxysilane을 사용하여 서로 다른 CVD 온도로 기공크기가 100 nm인 α-alumina를 처리하였다. CVD 온도는 700°C, 650°C, 600°C이었다. 600°C에서 수행한 단일 성분의 투과 실험에서 측정한 막의 H_2/N_2 선택도는 CVD 온도 700°C의 M1 막은 43.2, 650°C의 M2 막은 12.6, 600°C의 M3 막은 8.7을 나타내었다. $HI-H_2O$ 기상 혼합물에서 안정성 실험은 450°C에서 수행하였는데, CVD 온도 650°C에서 처리된 막이 다른 온도에서 처리된 막보다 더 안정성이 더 좋은 결과를 얻었다.

Abstract: The stability of the prepared silica membrane by chemical vapor deposition (CVD) method in the $HI-H_2O$ gaseous mixture was evaluated aiming at the application for hydrogen iodide decomposition in the thermochemical IS process. Porous α-alumina having pore size of 100 nm was modified by the different CVD temperature using tetraethoxysilane as the Si source. The CVD temperature was 700°C, 650°C, and 600°C. The H_2/N_2 selectivities of the modified membranes which were measured by single-component permeation experiment showed 43.2, 12.6, and 8.7 at 600°C for the M1 (CVD temperature was 700°C), M2 (CVD temperature was 650°C) and M3 membranes (CVD temperature was 600°C), respectively. Stability experiment in the $HI-H_2O$ gaseous mixture was carried out at 450°C. The prepared silica membrane at 600°C of CVD temperature was more stable than that at the other CVD temperature.

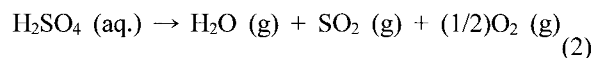
Keywords: *Inorganic membrane, Silica alumina membrane, Chemical vapor deposition, Gas separation, Hydrogen permselectivity*

1. Introduction

JAERI (Japan Atomic Energy Research Institute) has been carrying out an R&D on Iodine Sulfur (IS) process[1] that is composed of the following reactions;



$$I_2\ (l) + SO_2\ (g) + 2H_2O\ (l) \rightarrow 2HI\ (aq) + H_2SO_4\ (aq) \quad (1)$$



$$H_2SO_4\ (aq.) \rightarrow H_2O\ (g) + SO_2\ (g) + (1/2)O_2\ (g) \quad (2)$$

$$2HI\ (g) \rightarrow H_2\ (g) + I_2\ (g) \quad (3)$$

The combination of these reactions results in the "water splitting" reaction producing hydrogen, which has been considered to be an attractive energy carrier in the future. In the process development, the authors are pursuing an application of a membrane reactor to enhance the one pass conversion of thermal decompo-

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sition reaction of gaseous hydrogen iodide (HI) for the progress of Equation (3). In the previous research, the preparation of hydrogen permselective ceramic membrane (silica membrane) to be used in the membrane reactor has been studied[2-4]. In the homemade silica membranes, the hydrogen permeation was stable for 24 h of exposure to the H_2-H_2O-HI gaseous mixture. Therefore, it considered that the operation temperature of a membrane reactor for the catalytic decomposition of hydrogen iodide (HI) is carrying out at 450°C[5]. The stability of the homemade silica membrane using γ- and α-alumina tube as the support tube in the HI-H_2O gaseous mixture for a long time to use in the IS process was evaluated[6].

Modification of porous ceramics by thin silica film using chemical vapor deposition (CVD) was investigated to achieve selective gas separation targeting the large diffusivity difference of H_2 and other gases in amorphous silica[7-15], however, no assessment of the stability of that in the HI-H_2O gaseous mixture.

In this study, it was measured the effect of CVD treatment temperature in the gas permeation properties of homemade silica membrane using the porous α-alumina tube as a support tube and was compared its stability for a long exposure times in the HI-H_2O gaseous mixture at 450°C.

2. Experimental

2.1. Membrane Modification and Single Component Gas Permeation

Porous α-alumina tube (o.d., 5.5 mm; i.d., 3.5 mm; length, 350 mm) had an average pore size of 100 nm and porosity of about 36%, supplied by Noritake Co., was used as a support.

Before CVD treatment, the support was glazed with a SiO_2-BaO-CaO sealant (Nippon Electric Glass, GA-13) calcined at 1,200°C except for the permeating portions of 100 mm.

The CVD experimental apparatus were described elsewhere[2,4]. The support tube was fixed in a quartz reactor (o.d., 20 mm; i.d., 18 mm; length, 500 mm) and placed in an electric furnace. The CVD was carried out at 600, 650, and 700°C with the nitrogen carrier and a bubbler temperature of tetraethoxysilane (TEOS) was kept at 25°C. Throughout the CVD treatment, the inside of the tube was continuously evacuated by a rotary vacuum pump. The pressure in the evacuation side decreased continuously with the CVD progressed. In the course of the CVD treatment, the permeability of nitrogen and helium were intermittently measured by a pressure rise technique. The CVD was stopped at a certain value using He/N_2 selectivity as the indicator of the pore closure. After the CVD treatment, the temperature was decreased slowly with a cooling rate of 60°C/hr.

Single-component gas permeation experiments of hydrogen and nitrogen were performed at 300~600°C. The permeability was measured by a pressure-rise technique[2,3].

2.2. Stability Test in HI-H_2O Gaseous Mixture

The stability experimental apparatus were described elsewhere[6]. The modified membrane was fixed in quartz test tube that was placed in an electric furnace. Test gas was produced by vaporizing hydriodic acid (57 wt%). Test temperature was kept at 450°C. After a certain time, single component gas permeation experiments of hydrogen and nitrogen were performed at 300~600°C by a pressure rise technique as the indicator of the stability.

3. Results and Discussion

3.1. Membrane Modification

Table 1 shows the preparation condition of the silica membranes.

The flow rate of TEOS was calculated using the vapor pressure curve of TEOS[16].

In CVD temperature at 700°C, the silica membrane was modified in the region of the TEOS flow rate of 0.91~1.21 mL/min whereas the deposition time increased. Therefore, in those regions, the optimal flow rate of TEOS was 1.06 mL/min to prepare the silica

Table 1. Preparation Condition of the Silica Membranes

Name	CVD temp. (°C)	Temp. of TEOS (°C)	Flow rate of N_2 carrier (ml/min)	Flow rate of TEOS (ml/min)
M1	700	25	350	1.06
M2	650	25	600	1.82
M3	600	25	900	2.73

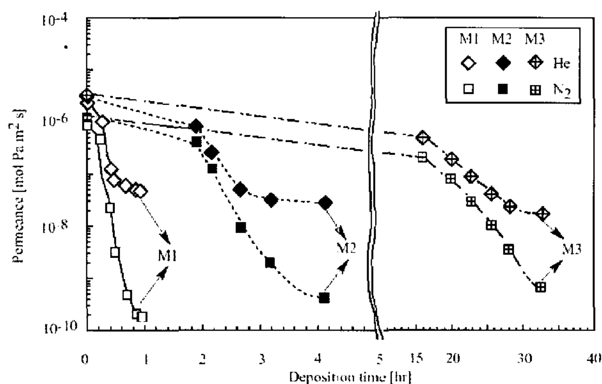

Fig. 1. Relationship between the permeances of He and N_2 and deposition time. M1 membrane was CVD treated at 700°C, M2 membrane was CVD treated at 650°C and M1 membrane was CVD treated at 600°C.

membrane at 700°C of CVD temperature. In CVD temperature at 650°C, the silica membrane was not modified in the other region of the TEOS flow rate of 1.67 ~2.12 mL/min whereas the deposition time increased. The optimal flow rate of TEOS was 1.82 mL/min to prepare the silica membrane at 650°C of CVD temperature. In CVD temperature at 600°C, the silica membrane was modified in the region of the TEOS flow rate of 2.73~6.06 mL/min with an increase of the deposition time.

Fig. 1 shows the relationship between permeances of He and N_2 and deposition time.

With an increase of the deposition time, permeance of He through M1 membrane rapidly decreased during 34 min and then almost did not change. Permeance of N_2 rapidly decreased during 1 h. The selectivity of He/N_2 in M1 membrane rapidly increased during 1 h. As for M2 membrane, permeance of He slowly decreased during the initial 1.4 h of deposition, and rapidly from 1.4 h to 2.3 h, and then did not change after 2.3 h. Permeance of N_2 slowly decreased during

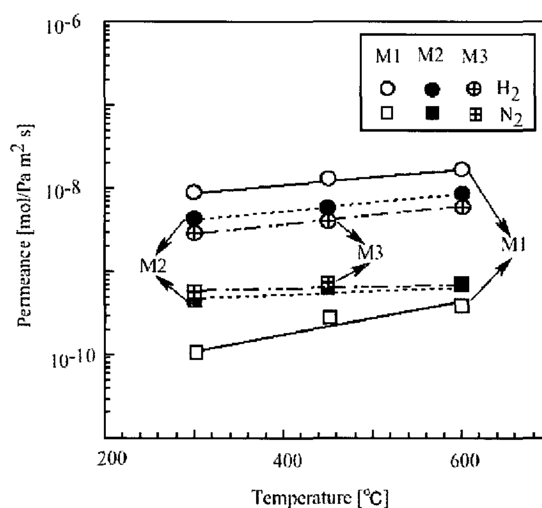

Fig. 2. Relationship between the permeances of H_2 and N_2 and temperature. M1 membrane was CVD treated at 700°C, M2 membrane was CVD treated at 650°C and M1 membrane was CVD treated at 600°C.

the initial 1.4 h of deposition, and rapidly from 1.4 h to 4 h. The selectivity of He/N_2 in M2 membrane rapidly increased from 1.4 h to 4 h. As for M3 membrane, permeance of He slowly decreased during the initial 15 h of deposition, and rapidly from 15 h to 27 h, and then did not change after 27 h. Permeance of N_2 slowly decreased during the initial 15 h of deposition, and rapidly from 15 h to 32 h. The selectivity of He/N_2 in M3 membrane rapidly increased from 15 h to 32 h.

The results showed that the membrane modification at 700°C of CVD temperature could be carried out in a shorter time by realizing higher selectivity of helium to nitrogen compared to that of the other CVD temperature.

3.2. Single Component Gas Permeation

Fig. 2 shows single component permeance of H_2 and

N_2 through the prepared silica membranes.

Permeances of H_2 through the M1, M2, and M3 membranes increased with an increase of the temperature. With an increase of the temperature, permeances of N_2 through the M1 and M2 membranes did not change. Permeances of N_2 through the M3 membrane increased at 450°C compared to that at 300°C, and increased a little at 600°C.

In the M1, M2, and M3 membranes, H_2 permeation was dominated by the activated diffusion. The activation energies of H_2 in the 300~600°C range were 9.2, 9.0, and 7.6 kJ/mol in the M1, M2, and M3 membranes, respectively. The higher activation energies in the M1 and M2 membranes compared with that in the M3 membrane indicate the presence of a dense SiO_2 layer in the former membranes.

The N_2 permeance was much smaller than the H_2 permeability in any membranes, because the kinetic diameter of N_2 is larger (3.64 Å) than that of H_2 (2.89 Å), and N_2 cannot penetrate through the nonporous layer of the membrane. N_2 gas would permeate only through much larger pores than the molecular dimension. The higher N_2 permeance in the M2 and M3 membranes compared to that in the M1 membrane suggests that the number of pores whose sizes was larger than the molecular dimension was higher than that of the M1 membrane.

Selectivities of H_2 to N_2 at 600°C were 43.2, 12.6, and 8.7 for the M1, M2, and M3 membranes, respectively.

3.3. Stability of the Prepared Silica Membranes in HI-H_2O Gaseous Mixture

Fig. 3 shows the relationship between permeances of H_2 and N_2 and exposure time in the HI-H_2O gaseous mixture, for example, at 450°C.

As for the M1 membrane, the H_2 permeance did not almost change during 120 h, and then increased. Permeance of N_2 rapidly increased with an increase of the exposure time. The selectivity of H_2/N_2 rapidly decreased with an increase of the exposure time, and reached about 3.53 after 241 h of the exposure time.

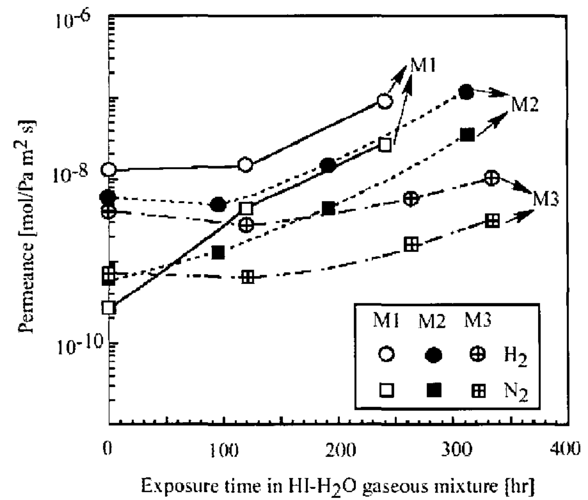

Fig. 3. Relationship between the permeances of H_2 and N_2 at 450°C and the exposure time in the HI-H_2O gaseous mixture. M1 membrane was CVD treated at 700°C, M2 membrane was CVD treated at 650°C and M1 membrane was CVD treated at 600°C.

As for the M2 membrane, the H_2 permeance did not almost change during 100 h, and then increased. Permeance of N_2 rapidly increased with an increase of the exposure time. The selectivity of H_2/N_2 rapidly decreased with an increase of the exposure time, and reached about 3.5 after 309 h of the exposure time.

As for the M3 membrane, with an increase of the exposure time, permeances of H_2 and N_2 and selectivity of H_2/N_2 remained nearly constant during exposure time of 120 h in the HI-H_2O gaseous mixture, indicating that the SiO_2 structure was not altered. Permeances of H_2 and N_2 slowly increased and the selectivity of H_2/N_2 slowly decreased after 120 h.

It would be supposed that the prepared silica membrane at 600°C of CVD temperature was more stable than those at the other CVD temperature.

The stability of M3 membrane in the HI-H_2O gaseous mixture showed the different results compared to that of the membranes in the earlier published our paper [6]. The prepared silica membrane in the earlier published our paper was prepared by the TEOS flow rate of 4.54 mL/min at 600°C of CVD temperature, and showed constant stability during exposure time of 340 h in the HI-H_2O gaseous mixture with the constant

permeances of H_2 and N_2 and selectivity of H_2/N_2. It would be supposed from this result that the TEOS flow rate would be effect in the stability of the silica membrane in the HI-H_2O gaseous mixture.

In the results of our paper[6], the membrane shown the rapidly increasing H_2 and N_2 permeance and the rapidly decreasing selectivity of H_2/N_2 during the longer exposure to the HI-H_2O gaseous mixture had the low selectivity of H_2/HI. It is assumed from this result that the selectivity of H_2/HI in M1 and M2 membrane might be show the low value.

In the M1 and M2 membranes, permeances of H_2 and N_2 increased and the selectivity of H_2/N_2 decreased during the longer exposure to the HI-H_2O gaseous mixture. It seems that the pore size in the membrane changed during longer exposure time in the HI-H_2O gaseous mixture and a complex temperature variation for a single-component permeation experiment, and then the number of pores whose size was larger than the molecular dimension of N_2 increased. Those pore size and pore structure changes could be explained that the SiO_2 was weakly deposited on α-alumina, and the structure of SiO_2 changed during the longer exposure time in the HI-H_2O gaseous mixture and a complex temperature variation for a single component permeation experiment, and then the pore size increased with reiterating stability test experiment and the single component permeation experiment, and finally the increased pore size led to decrease of the H_2/N_2 selectivity.

4. Conclusions

(1) The silica membranes using α-alumina tube as the support tube were prepared by CVD method. The CVD treatment temperature was 700°C, 650°C, and 600°C. The membrane modification at 700°C of CVD temperature can be carried out in a shorter time by realizing higher selectivity of helium to nitrogen compared to that of the other CVD temperature.

(2) The H_2/N_2 selectivities of the modified membranes which were measured by single-component permeation experiment showed 43.2, 12.6, and 8.7 at 600°C for the M1, M2 and M3 membranes, respectively.

(3) From the stability experiments in the HI-H_2O gaseous mixture, it was obtained that the prepared silica membrane at 600°C of CVD temperature was more stable than those at the other CVD temperature.

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