The Separation of Gaseous Mixture with Composite Microporous Glass Membranes at High Temperature

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Separation of gaseous mixture was carried out up to 773 K using composite microporous glass membranes coated on the surface of a porous ceramic tubings. The composition of the metal alkoxide solution used in the coating process was $\text{Si}(\text{OC}_2\text{H}_5)_4$: 27.9, $\text{C}_2\text{H}_5\text{OH}$: 42.0, H_2O : 26.2, HCl : 0.3 and H_3BO_3 : 3.6, in weight %.

With ceramic tubings supplied from TOTO Co., Ltd., much thinner microporous glass membranes can be made because 5 times of coating was enough to get without cracks, comparing at least 7 times for TDK Co., Ltd.. The membrane can permeate only H_2O from thermochemical reaction gas mixture of H_2 and H_2O at the flux rate of $37 \text{ kg}/(\text{m}^2 \cdot \text{day})$ at trans-membrane pressure 0.196 MPa and at 773 K.

Key words : Membrane, Composite membrane, Gas separation, Ceramic tubing, Metal alkoxide coating, Inorganic membrane.

Introduction

The conversion of water into hydrogen by thermochemical water decomposition process is couple of percent¹⁾. If it is possible to separate hydrogen from the reaction gas without phase change, the thermal efficiency of the process may increase and the cost of hydrogen may decrease.

In this study, microporous composite glass membranes which might withstand the very corrosive gas containing HBr at high temperature up to 500°C , was prepared for the purpose to study the possibility of separation of hydrogen from the reaction gas of thermochemical water decomposition process.

Few reports were devoted to gas separation with the inorganic membranes, such as hydrogen separable membranes development in C_1 Chemistry project sponsored by MITI^{2, 3)}, separation of hydrogen from hydrogen and hydrogen sulfide mixture with microporous glass membranes^{4, 5)} and

Table 1 Dimensions of Porous Ceramic Tubings

Supplier	TDK Co., Ltd.	TOTO Co., Ltd.
Pore Size [nm]	500	500
Outer Diameter [mm]	5.0	5.5
Inner Diameter [mm]	2.0	3.9
Porosity [%]	c. a. 45	c. a. 45

inorganic membrane reactors such as dehydrogenation of cyclohexane⁶⁾.

The so-called Knudsen gas diffusion occurred in microporous membranes is applied to separate gaseous mixtures composed of different molecular weight components. In the case mentioned above, the lightest molecule H_2 permeates selectively through the inorganic membrane.

Silica-alumina gel membranes can effectively separate condensable gases such as water vapor from gaseous mixtures of condensable gas and non-condensable, possibly by the mechanism of

Fig. 1. Schematic diagram of the experimental apparatus.

capillary condensation⁷⁻⁹⁾. Lee and Hwang¹⁰⁾ studied the condensable vapor through microporous media experimentally as well as theoretically. In this paper, at high temperature, are studied the separation of gaseous mixture of hydrogen and water vapor, and nitrogen and water vapor with composite microporous glass membranes on ceramic tubing prepared by the method described in the previous paper.

Experimental

Membrane

A thin layer of microporous glass was deposited on the surface of two types of porous ceramic tubings of which dimensions are listed in Table 1, using the method described in the previous paper¹¹⁾. The composition of the metal alkoxide solution used in the coating process is Si(OC₂H₅)₄: 27.9, C₂H₅OH: 42.0, H₂O: 26.2, HCl: 0.3 and H₃BO₃: 3.6 in weight %.

Apparatus And Procedures

A schematic diagram of the apparatus used for the measurement of gas permeabilities and for gas separation experiments is shown in Fig. 1.

Before introducing the gas into the system, the system was either evacuated for one night or displaced by nitrogen. The feed gas (H₂, N₂, CO₂, and water vapor; a mixture of H₂ and water vapor, H₂: H₂O = 1:1, N₂ and water vapor, N₂: H₂O = 1:1) was introduced at the high-pressure side. The pressure of feed gas was kept in the range of 49~196 kPa by a pressure-control valve. The temperature of feed gas was kept in the range of 673~773 K by a thermoregulator.

The composition of feed gas and permeate after H₂O trapped was determined with a thermal conductivity gas chromatograph (Hitachi GC-164T) using a Gaskuropack 54 column (Gaskuro Kogyo). When the permeation rates measured after H₂O trapped remained constant, they were measured using the water displacement method, while the pH of the water was kept < 3 by adding HCl.

Results and Discussions

Pure gas permeability

Figure 2 shows the relationship between the pure gas permeation fluxes of H₂, N₂, CO₂ and H₂O through microporous glass membranes with 10 and 15 coatings on TDK ceramic tubing at 673 K

Fig. 2. The relationship between the pure gas permeation fluxes of H_2 , N_2 , CO_2 and H_2O through the microporous glass membranes with 10 and 15 coatings on TDK ceramic tubings and trans-membrane pressure at 673 K and 773 K.

Fig. 3. The relationship between the pure gas permeation fluxes of H_2 , N_2 and H_2O through the microporous glass membranes with 5 and 10 coatings on TOTO ceramic tubings and trans-membrane pressure at 673 K and 773 K.

Fig. 4. The relationship between permeabilities of H_2 , N_2 , CO_2 and H_2O and reciprocal of the square root of the product of the molecular weight and absolute temperature on TDK ceramic tubings.

and 773 K. Fluxes with 10 coatings are about 3 times larger than with 15 coatings.

Figure 3 shows the relationship between the pure gas permeation fluxes of H_2 , N_2 and H_2O through microporous glass membranes with 5 and 10 coatings on TOTO ceramic tubing at the same temperatures. Fluxes with 5 coating are about 4 times larger than with 10 coatings. The H_2 fluxes at 0.196 MPa and at 773 K through the microporous glass membranes with 10 coatings on TDK and TOTO ceramic tubings are both 1.22×10^{-2} mol/($m^2 \cdot s$). As mention in the previous paper, at least 7 times coatings was necessary to get microporous glass membranes without cracks on TDK ceramic tubing, but on TOTO ceramic tubing, 5 times coating is enough to get perfect membrane, which shows the H_2 flux at 0.196 MPa and at 773 K is 5.0×10^{-2} mol/($m^2 \cdot s$) by 4 times more than that with 10 coatings on TDK. Therefore, ceramic tubing supplied from TOTO Co., Ltd. is better than

Fig. 5. The relationship between permeabilities of H_2 , N_2 , and H_2O and reciprocal of the square root of the product of the molecular weight and absolute temperature on TOTO ceramic tubings.

TDK Co., Ltd..

Figure 4 and 5 show the relationship between permeabilities of H_2 , N_2 and H_2O (CO_2 only in Fig. 4) and reciprocal of square root of the product of the molecular weight and absolute temperature. The relationship shows good linearity which means Knudsen flow may be predominant in this permeation mechanism.

Permeability of gaseous mixture

Figure 6 and 7 show the relationship between permeation flux of 50–50% gaseous mixture of H_2O – H_2 and H_2O – N_2 and transmembrane pressure. The analysis of the permeate showed that H_2 and N_2 were not found and that all the constituent of the permeate was H_2O . The solid lines shown in Fig. 6 and 7 are drawn from the data shown in Fig. 2 and 3 respectively. It is very interesting that the permeation flux of H_2O through the membrane from 50–50% gaseous mixture of H_2O – H_2 and

Fig. 6. The relationship between permeation flux of 50-50% gaseous mixture of $\text{H}_2\text{O}-\text{H}_2$ and trans-membrane pressure on TDK ceramic tubings.

$\text{H}_2\text{O}-\text{N}_2$ is same as that measured with pure H_2O gas at the same trans-membrane pressure of the mixture. These two facts mean that H_2O vapor may absorb on the surface of the micropore in the membrane and flow through it under the pressure of the gaseous mixture or pure water vapor as suggested by Asaeda et al.⁷⁻⁹⁾. Flux of H_2O decreases with the increase of temperature and coating time.

Conclusion

1. Ceramic tubing supplied from TOTO Co., Ltd. was better than TDK Co., Ltd. and was coated at least 5 times to get microporous glass membranes without cracks.

2. Knudsen flow is considered to be predominant in this gas permeation mechanism for pure gases, H_2 , N_2 , H_2O and CO_2 .

3. When 50~50% gaseous mixture of $\text{H}_2\text{O}-\text{H}_2$ and $\text{H}_2\text{O}-\text{N}_2$ were pressured through the microporous glass membrane up to 773 K, only water

Fig. 7. The relationship between permeation flux of 50-50% gaseous mixture of $\text{H}_2\text{O}-\text{H}_2$ and trans-membrane pressure on TOTO ceramic tubings.

vapor permeated through the membrane and it was found separation factor was virtually infinite.

4. The microporous glass membrane with 5 coating on TOTO ceramic tubing will do the job to separate H_2O from thermochemical reaction gas mixture of H_2 and H_2O at the flux rate of 37 kg/($\text{m}^2 \cdot \text{day}$) at trans-membrane pressure 0.196 MPa and at 773 K.

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主題 = 高機能, 高性能新素材のフロンティア

——スーパー微粒子/スーパーフィルム/スーパー繊維の開発動向——

最近, スーパー微粒子, スーパーフィルム, スーパー繊維がめざましい発展をとげ, 産業界, 学会で注目されている。スーパーとは, 従来の機能, 性能をはるかに越えた高機能, 高性能化をめざす意味であり, 新しいスーパー工業材料ともよぶべき技術のフロンティア領域について展望する。

微粒子, フィルム, 繊維はそれぞれ別の分野のようにも見えるが実はそうではない。超微粒子クラスターから超薄膜が得られ, ノズルの違いからフィルムや繊維に分かれることから十分理解されよう。

本講座では, 最近, とくに開発の著しいスーパー微粒子, スーパーフィルム, スーパー繊維に総合的なスポットをあて, 特別企画として参加者との質疑応答によるパネル討論を加え, 開発動向と将来を展望したい。21世紀に通用するスーパー機能材料を創造, 開発しようとする研究者・技術者の方々にとって, 必ず役立つものと確信している。

奮って関係各位のご参加を期待しています。

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