멤브레인(Membrane Journal)
Vol.7, No.1, April, 1997, 11-14

총 설

일본의 무기막 개발 현황

Shoji Kimura

Dept. of Chemical Engineering, Osaka University
1-3 Machikaneyama, Toyonaka 560, Japan
(1997년 1월 15일 접수)

Recent Development of Various Inorganic Membranes in Japan

Shoji Kimura

Dept. of Chemical Engineering, Osaka University
1-3 Machikaneyama, Toyonaka 560, Japan
(*Received January 15, 1997*)

Abstract: Two membrane-related research projects are now being developed in Japan and their main target is to develop new inorganic membranes. The first project is the R & D of membranes for carbon dioxide recovery at high temperature, conducted by the Japan Fine Ceramics Center (JFCC) and Japan Fine Ceramics Association (JFCA) under the supervision by the New Energy and Industrial Technology Development Organization (NEDO). The second one is the R & D of membranes for petroleum refinery and chemical processes, conducted by the Japan High Polymer Center (JHPC) under the supervision by the Petroleum Energy Center (PEC). Cooperating with these projects researchers in many universities and research institutes have been publishing many interesting data of inorganic membranes manufactured by various methods. Many such results are summarized and reported.

1. Introduction

Recently researches of various inorganic membranes become vary active in the world. The causes of this trend are due to weakness of durability and selectivity of various polymeric membranes, which limit application of membrane technology for wider fields. This trend is also same in Japan. Two development projects of inorganic membranes are now underway, which will be introduced first.

The New Energy and Industrial Technology Development Organization (NEDO) is conducting various R & D projects, which are related to the global environmental problems. One of them is R & D on High Temperature Carbon Dioxide Separation, Fixation and Utilization, included in "Development of Technology for CO_2 fixation and Utilization". Its objective is to develop an industrial technology system which can separate CO_2 from high temperature flue gas and change it to useful substances. For this purpose membranes, which can separate CO_2 at 300 to 900℃, should be developed. The scheme of this project is shown in Fig. 1. The project was entrusted by NEDO in 1992 to Japan Fine Ceramics Center (JECC), which is in charge of R & D, while Japan Fine Ceramics Association (JFCA) is in charge of

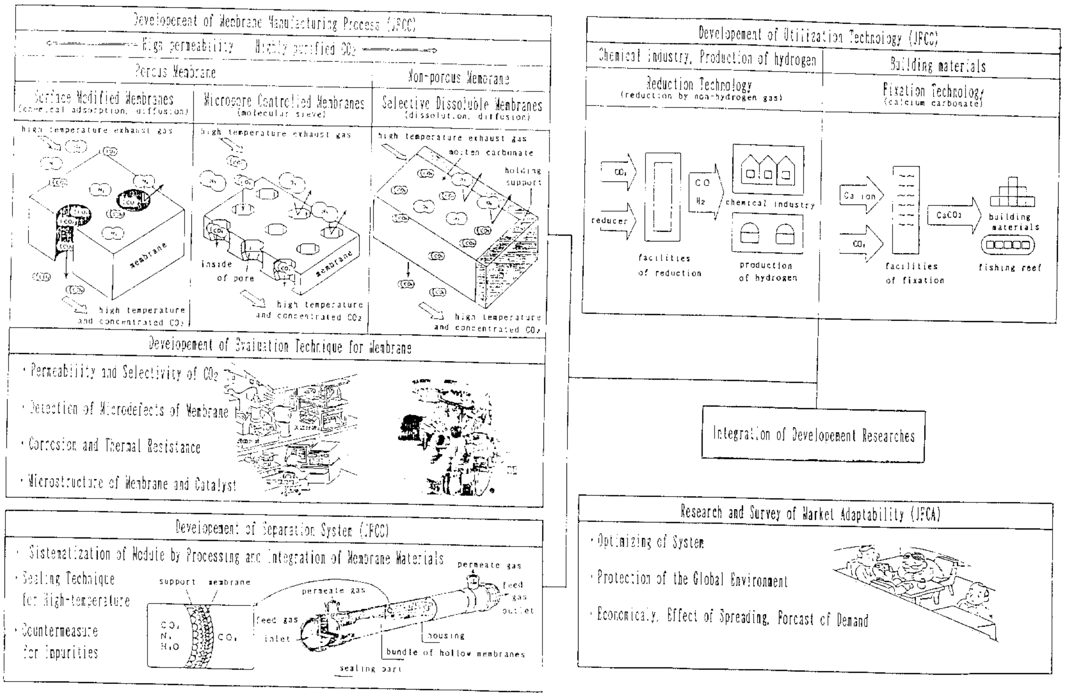

Fig. 1. The total scheme of the Japanese national project on CO_2 senaration and utilization.

the survey research. Now various researchers in universities, research institutes and companies are cooperating with JFCC.

The Petroleum Energy Center, Japan, has been cooperating mainly with OPEC countries to develop new technologies related with petroleum refinery and utilization industries. Initially R & D subjects were on catalysts and biotechnology. From 1993 R & D of membranes was entrusted to the Japan High Polymer Center (JHPC). In this project the real target is not so clear as the previous one, although many possibilities exist for such applications. So various researchers are now developing new membranes which may be effective for separating aliphatic from aromatics, paraffin from olefins, or for other systems, seeking various possibilities. Membrane materials are not limited to polymeric materials and from the point of view of real applications inorganic membranes can be more suitable.

Since results of these projects will officially be reported at the end of each fiscal year, I will explain about results of new inorganic membranes published in open journals in the following. Some of them may related to the projects.

2. Membranes made by CVD method

The group of University of Tokyo has been working on manufacturing "molecular sieving" membranes by reducing the pore size of porous Vycor glass using CVD method[1]. The fundamental scheme is to diffuse TEOS (tetraethylorthosilicate) from one side of a glass and the diffuse ozone from the other side to react them inside pores to form SiO_2 and to reduce pore sizes. By controlling reaction temperature, reactant concentration and reaction time it was possible to manufacture a membrane, whose separation factor for H_2/N_2 reached to 950.

Prof. Kusakabe and his group of Kyushu University has been working on various inorganic membranes using porous alumina, whose pore size is

150nm, as substrate. Usually pores of this substrate should be reduced by some methods before coating the final layer. Recently, however, they succeeded to form hydrogen-permselective SiO_2 membranes directly in macropores of alumina substrate by thermal decomposition of TEOS[2, 3]. The important point is to plug pore by flowing TEOS through them by evacuating the inside of a substrate tube.

3. Zeolite membranes

Prof. Sano and the group of the National Institute of Materials and Chemical Research at Tsukuba succeeded to prepare pure silicalite membranes on porous supports of sintered steel or alumina discs by using traditional hydrothermal synthesis method [4]. This membrane has alcoholpermselectivity against water and a separation factor was 60 at 5% aqueous ethanol solution at 30℃ in pervaporation. From adsorption experiments of ethanol and water on silicalite, it was found that the high permselectivity is due to the selective sorption of ethanol to silicalite membrane. This membrane also shows selective permeation of acetic acid against water[5].

Prof. Okamoto and his group of Yamaguchi University have recently been working on various zeolite membranes besides many polyimide membranes they used to manufacture. They made A-type zeolite membranes on porous alumina substrate tube, whose pore size is 1 micrometer, by using the hydrothermal method[6]. This membrane is water-permselective and has a very large separation factor for the ethanol-water system, which is comparable to that of GFT membrane, while permeation flux is larger than that of GFT membrane. They are now working on Y-type zeolite membranes.

Dr. Matsukata and the group of Osaka University have been also working on various zeolite membranes. Their manufacturing method is not based on the usual hydrothermal method, but one based on the vapor phase transport method[7], which was initiated by Dong et al.[8, 9]. Recently they succeeded to manufacture defect-free mordenite membranes on alumina support tubes, whose pore size is 0.1 micrometer[10].

4. Carbon membranes

Dr. Haraya and his group made carbon membranes by carbonizing Kapton polyimide membrane, which show molecular sieving nature by adopting proper carbonizing temperature[11]. For practical applications the capillary form is considered to be better, and they developed carbon capillary membranes by casting asymmetric polyimide membranes on the surface of PTFE tube and then by pyrolyzing them under same conditions used to make flat membranes[12].

A similar membranes were made by the Prof. Kusakabe's group by casting Kapton membranes on porous alumina substrate tube and then pyrolyzing them[13].

5. Membranes made by the sol-gel method

Many researchers have been working on inorganic membranes by the sol-gel method, which is fundamentally simple and is considered to make defect-free ones easily. Since it is difficult to summarize all of these results, two interesting works will be introduced here.

Prof. Kusakabe and his group tried to manufacture CO_2 permselective membrane by coating porous alumina substrate with $BaTiO_3$, which is considered to be a very good adsorbent of CO_2[14]. This idea is same as one listed in Fig. 1 as "Surface Modified Membrane". The separation factor for CO_2/N_2 was 1.12 Ÿ 1.2. Although this is still small, it is remarkable that this is larger than 1.

Prof. Asaeda and his Hiroshima University group have been successfully manufactured silica membranes by the sol-gel method. Initially they made them by using silica sol, made of TEOS, H_2O and HNO_3 and by dip coating on alumina substrate tubes, whose pore size is 0.1 micrometer. This membrane showed a very large separation factor for the H_2/N_2 system[15]. Then they adopted a spray coating method at 160 to 180℃ instead of the dip coating. They reported a very large separation factor for the C_3H_6/C_3H_8 system, which is larger than that estimated from the adsorption experiment[16, 17].

6. Conclusion

Many new inorganic membranes are introduced in this report. Some of them may have the "molecular sieving nature", while the other show the interesting effect of adsorption. It is important to know true transport mechanisms as well as to develop new membranes.

References

1. T. Suzuki, MS thesis, University of Tokyo, March(1995).
2. S. Yan, H. Maeda, K. Kusakabe and S. Morooka, I & EC Research, **33**, 2096(1994).
3. S. Morooka, S. Yan, K. Kusakabe and Y. Akiyama, J. Memb. Sci., **101**, 89(1995).
4. T. Sano, H. Yanagishita, Y. Kiyozumi, F. Mizukami and K. Haraya, J. Memb. Sci., **95**, 221(1994).
5. T. Sano, S. Ejiri, M. Hasegawa, Y. Kawakami, N. Enomoto, Y. Tamai and H. Yanagishita, Chemistry Letters, 153(1995).
6. H. Kita, K. Horii, Y. Ohtoshi, K. Tanaka and K. Okamoto, J. Material Sci. Letters, **14**, 206 (1995).
7. M. Matsukata, N. Nishiyama and K. Ueyama, Microporous Materials, **1**, 219(1993).
8. W. Xu, J. Dong, J. Li and F. Wu, J. Chem. Soc., Chem. Commun., 755(1990).
9. J. Dong, T. Dou, X. Zhao and L. Gao, J. Chem. Soc., Chem. Commun., 1056(1992).
10. N. Nishiyama, K. Ueyama and M. Matsukata, J. Chem. Soc., Chem. Commun., to be published.
11. H. Suda and K. Haraya, J. Chem. Soc., Chem. Commun., 1179(1995).
12. K. Haraya, H. Suda, H. Yanagishita and S. Matsuda, J. Chem. Soc., Chem. Commun., to be published.
13. J. Hayashi, M. Yamamoto, K. Kusakabe and S. Morooka, submitted to I & EC Research.
14. K. Kusakabe, K. Ichiki and S. Morooka, J. Memb. Sci., 95, 171(1994).
15. S. Kitao, H. Kameda and M. Asaeda, MAKU (Membrane), 15(4), 222(in English)(1990).
16. M. Asaeda, A. Yamamichi, M. Sato and M. Kamakura, Membrane Symposium No. 6, 9-12(in Japanese with English abstract)(1994).
17. M. Asaeda, A. Yamamichi, M. Satoh and M. Kamakura, Paper presented at the 3rd. ICIM, Worcester(1994).