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Synthesis of Faujasite zeolite membranes on stainless steel supports and their separation performance for organic/organic mixtures

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Faujasite membranes were prepared by hydrothermal synthesis on porous cylindrical stainless steel supports. The starting gel composition was $H_2O/Na_2O=45$, $Na_2O/SiO_2=0.88$, $SiO_2/Al_2O_3=25$. The outer-surface of the support with acid treatment was completely covered with randomly oriented, well-intergrown zeolite crystals at a one-time synthesis. X-ray diffraction patterns of membranes consist of peaks corresponding to the support and the zeolite. The resulting powder and membranes were also characterized by Field Emission Scanning Electron Microscopy (FE-SEM), energy dispersive X-ray spectroscopy analysis (EDX), and inductively coupled plasma analysis (ICP). These membranes showed high alcohol selectivity for several feed mixtures, such as methanol/methyl t-butyl ether, methanol/benzene, methanol/dimethyl carbonate, ethanol/ethyl t-butyl ether, ethanol/benzene and ethanol/cyclohexane systems. In addition, the membrane also exhibited a high benzene selectivity in benzene/cyclohexane separation (220 of separation factor and 0.23 kg/m^2h in flux at 423K). The separation performances of the membranes prepared on porous stainless steel support were equal or higher compared with those of the previously reported membranes prepared on porous mullite support.

Key words: *Zeolite membrane, Faujasite,* Pervaporation, Organic liquid separation, Stainless steel support

1. INTRODUCTION

Zeolite membrane is a promising candidate for a high performance membrane because of the thermal and mechanical stability and chemical resistance derived from inorganic materials, as well as the unique characteristics of zeolite crystals such as molecular sieving, ion exchange, selective adsorption and catalysis. There are many recent reports on the preparation of zeolite membranes and their separation properties for gas and liquid feed mixtures in the literatures [1-3], the pervaporation performance of the membrane seems to be the most promising one and may be feasible for industrial applications.

Recently we have reported that Faujasite zeolite membrane prepared on the porous mullite support showed a high alcohol selectivity in pervaporation of alcohol/benzene, cyclohexane, methyl tert-butyl ether (MTBE) or ethyl tert-butyl ether (ETBE) [4,5]. Moreover, the membrane also showed a high benzene selectivity in separation of benzene/cyclohexane and n-hexane [6]. However, it is difficult to use a ceramics supported membrane with a polymer sealing under the harsh condition such as a high temperature more than 200°C. The membrane fabrication on a metallic substrate has a potential to overcome these difficulties. The advantage of a metallic supported membrane compared to a ceramic supported one is the improvement of mechanical stability, the simplification of a membrane module construction as well as a sealing method by weld processing.

There are several reports of the preparation on the metal support of hydrophobic zeolite membranes such as ZSM-5 or silicalite-1, whereas that of hydrophilic zeolite membranes has been reported a few example [7,8]. Valtchev et al. [7] have been investigated the film growth kinetics and morphology for silicalite-1 and zeolite Y film formation on copper substrates. Clet et al. [8] have reported zeolite Y coating on stainless steel support using the synthesis gel with or without seed crystals. Both of them, however, have not reported the separation performance as membrane application. We have also examined the preparation of the hydrophilic zeolite membranes on the commercial metallic supports. The results revealed that the pretreatment of the supports with acid is essential to prepare the pinhole-free NaY zeolite membranes in the same synthesis condition on mullite supports [9]. In this paper, we report the stainless steel supported NaY zeolite membranes with a high separation performance.

2. EXPERIMENTAL

2.1 Membrane preparation

Faujasite membranes were grown hydrothermally on the surface of a porous cylindrical stainless steel supports (Microfilter Corp., 10 mm outer diameter, 1.7 mm thickness, 1.0 μm average pore size, 30% porosity). Initially, the supports were cut into 100 mm length and then immersed into 2N NaOH solution to remove oil and grease and then 85% phosphoric acid to neutralize at 348 K for 6 hours. The support was taken out, washed with distilled water. Then, the support was treated by 60% nitric acid to form the oxide layer on the metal surface at 348 K for 16 hours. The stainless steel support was then treated for 30 min in an ultrasonic bath that contained distilled water and dried in an oven at 353 K.

The aluminosilicate gel used in the synthesis of the zeolite membrane was prepared by mixing a water glass solution (Aldrich, NaOH 14% and SiO2 27%) and alkaline aluminate solution prepared by dissolving sodium aluminate (Wako Chemical, Al/NaOH = 0.79) and sodium hydroxide (Wako Chemical) in distilled water [6]. The molar composition of the synthesis gel was H_2O/Na_2O=45, Na_2O/SiO_2=0.88, SiO_2/Al_2O_3=25. Before synthesis of the membrane, the starting gel was aging for 16 hours at room temperature. The porous support was coated with the water-slurry of seed crystals of NaY zeolite (Tosoh Co.) and then dried at 353K. The gel was poured into a reaction glass vessel fitted with a condenser and a heater and then the support was placed in the gel. After hydrothermal treatment at 373K for a specified reaction time, the membrane was taken out, washed with water and dried at 353K.

2.2 Characterization and permeation measurement

The powders collected from the bottom of the vessel and the membranes were characterized by X-ray diffraction (XRD) with a Cu-Kα radiation source using a Shimadzu XD-3. The specific element concentration of the powder was measured by inductively coupled plasma (ICP) analysis, and calculated the Si/Al ratio of zeolite components. The surface morphology of the membrane was examined by Field Emission Scanning Electron Microscopy (FE-SEM) using a JEOL JSM 6350 instrument. The surface composition of the membrane was characterized using Energy Dispersive X-ray spectroscopy (EDX) analysis (JEOL JED-2200F instrument).

Pervaporation (PV) and vapor permeation (VP) experiments were carried out using the apparatus described in previous papers [4,5]. Feed mixtures for PV or VP used methanol/methyl t-butyl ether, methanol/benzene, methanol/dimethyl carbonate, ethanol/ethyl t-butyl ether, ethanol/benzene, ethanol/cyclohexane and benzene/cyclohexane. The membrane performance was evaluated by a permeation flux (Q in $kgm^{-2}h^{-1}$) and a separation factor (α). The permeation flux was calculated by weighing the permeate collected by a trap in the liquid nitrogen. The separation factor was determined as $\alpha_{A/B}$ $=(Y_A/Y_B)/(X_A/X_B)$ where X_A, X_B, Y_A and Y_B denote the weight fraction of component A and B in the feed and the permeate, respectively, and A is the species which is preferentially permeated. The compositions of feed and permeate were determined by gas chromatography (Shimadzu GC-8).

3. RESULTS AND DISCUSSION

3.1 Membrane preparation and characterization

Porous stainless steel supports were pretreated by nitric acid for 16 hours at 348 K. Then seed crystals of NaY zeolite could be coated uniformly on the surface of the support. Therefore, it was possible to apply the same synthesis condition as reported one prepared on the mullite support [4-6]. The oxide passive layer formed by acid treatment on the metal surface would play an important role to interaction between the zeolite crystal and metallic surface. Fig. 1 shows FE-SEM photographs of the outer surface of the Faujasite zeolite membranes after 0.5-5 h of the synthesis. The surface of the membrane prepared at a crystallization time of 0.5 hour showed that the small particles were cohered around the seed crystals rather than the stainless particles. After 1

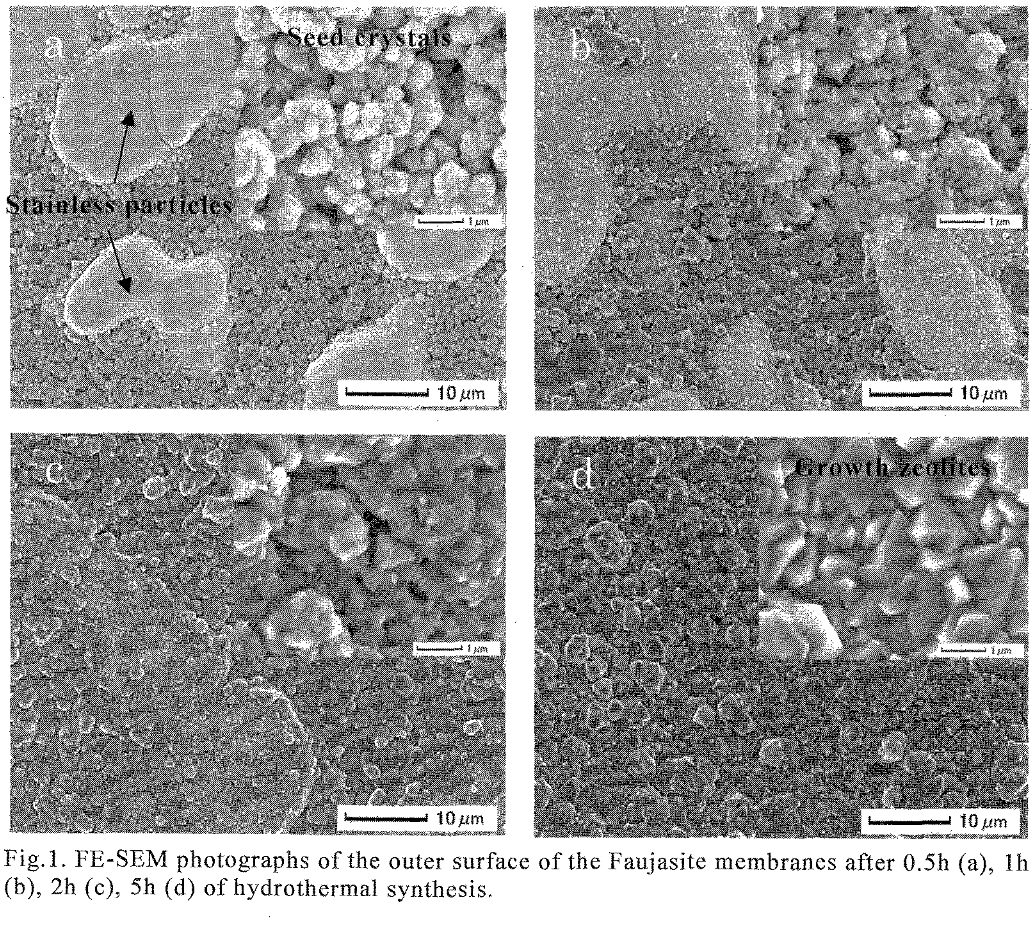

Fig.1. FE-SEM photographs of the outer surface of the Faujasite membranes after 0.5h (a), 1h (b), 2h (c), 5h (d) of hydrothermal synthesis.

hour, besides their cohesive particles on the seed, the minute particles were deposited on the surface of the sintered stainless steel particles. The crystals grew further at 2 hours, the crystal growth has been proceeding and the amorphous gel layer covered almost completely over the zeolite layer. However, the zeolite layer contained voids in the surface. After 5 hours, the outer surface of the porous support was completely covered with randomly oriented, intergrown zeolite crystals. The observation on the cross-sectional view of the membrane prepared at 5 hours resulted in the dense zeolite layer with the thickness about 10 μm on the outer surface of the support and the inner seed crystals remained after synthesis as shown in Fig. 2. It was found that the dense zeolite layer was only formed on stainless steel support compared with the results of the membrane formation onto mullite support [5], suggesting that the single top layer of pure zeolite prepared on stainless steel support attributes to the separation.

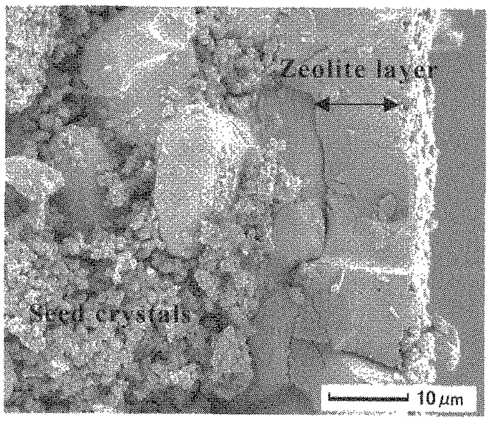

Fig.2. FE-SEM photograph of cross-section of the Faujasite membrane prepared at 5 hours of hydrothermal synthesis.

The X-ray diffraction patterns of the membranes hydrothermally grown on the porous stainless steel support consist of peaks corresponding to NaY zeolite and the support. The intensities of the diffraction peaks corresponding to zeolites increased with an increase in the crystallization time. The powders collected from the bottom of the vessel at the crystallization time of 5 hours also showed the XRD patterns of NaY zeolite. The Si/Al ratio of the powder determined by ICP was 2.68 and that of the membrane determined by EDX analysis was 2.54. These ratios were the range of 1.5-3.0 of Y-type zeolites.

3.2 Permeation properties of Faujasite membranes

Single component fluxes of several organics through the stainless steel supported NaY zeolite membrane prepared at 373K for 5 hours are shown in Fig. 3. The single component fluxes for all organics decreased remarkably with increasing kinetic diameter [10,11]. The large molecules close to the pore size of Faujasite zeolite (0.74nm) become difficult to permeate through the membrane, suggesting that zeolite layer would have very few defect by the one-time synthesis. Fluxes of all organics increased with temperature because of the increase of diffusivity of the permeating molecules. The alcohol fluxes are significantly high, especially 4.1 kg/m^{2}h at 423K was obtained for the methanol permeation.

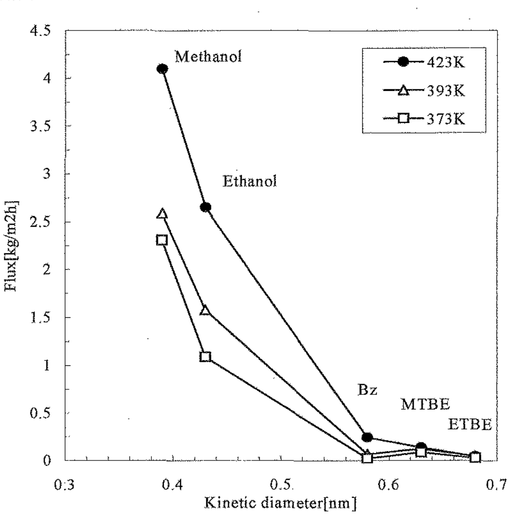

Fig.3. Temperature dependence of the single component fluxes of several organics through the stainless steel supported NaY zeolite membrane as a function of kinetic diameter of the permeating molecules.

Table 1 shows the flux and the separation factor of pervaporation or vapor permeation for several feed mixtures containing methanol or ethanol through Faujasite membranes on the

Table 1 Comparison of pervaporation (PV) and vapor permeation (VP) performances through Faujasite membrane prepared on stainless steel support and mullite support.

Feed solution A/B (wt.% of A)	Method	Temperature [℃]	Flux [kg/m^{2}h]	Separation factor [-]
Water/Ethanol (10)	PV	75	5.08 (1.38)	55 (130)
Methanol/benzene (10)	PV	50	1.13 (1.02)	2800 (7000)
Ethanol/benzene (10)	PV	50	0.17 (0.22)	550 (930)
Ethanol/cyclohexane (50)	PV	50	0.37 (0.27)	1100 (1000)
Methanol/DMC (50)	PV	50	1.06 (1.53)	970 (480)
Methanol/MTBE (10)	PV	50	1.38 (1.70)	9900 (5300)
	VP	100	2.18 (2.13)	10000 (6400)
	VP	150	3.11 (2.59)	1300 (600)
Ethanol/ETBE (10)	PV	60	0.74 (0.43)	9000 (4500)
Benzene/cyclohexane (50)	VP	100	0.015 (0.023)	48 (28)
	VP	120	0.045 (0.075)	170 (180)
	VP	150	0.23 (0.30)	220 (190)

( ) : mullite support

stainless steel support and the mullite support [6]. Faujasite membrane shows water selectivity for water/ethanol mixture because of hydrophilic nature of zeolite. High separation factors through NaY zeolite membranes on stainless steel support as well as mullite support were obtained for the various organic liquid mixtures such as methanol/benzene, DMC, MTBE, ethanol/benzene, cyclohexane and ETBE. The flux is also high enough to put the membrane into practical use. It can be concluded that the sufficient dense zeolite layer was formed on the surface of stainless steel support. Moreover, the membrane prepared on the stainless steel support also exhibited significantly high benzene selectivity in benzene/cyclohexane mixture. Current separation methods based on distillation are very expensive due to close boiling points [12]. The NaY zeolite membrane, especially prepared on stainless steel support, is a promising candidate combined a high separation performance with some advantage of the simplification for a membrane module construction and a sealing method by weld processing.

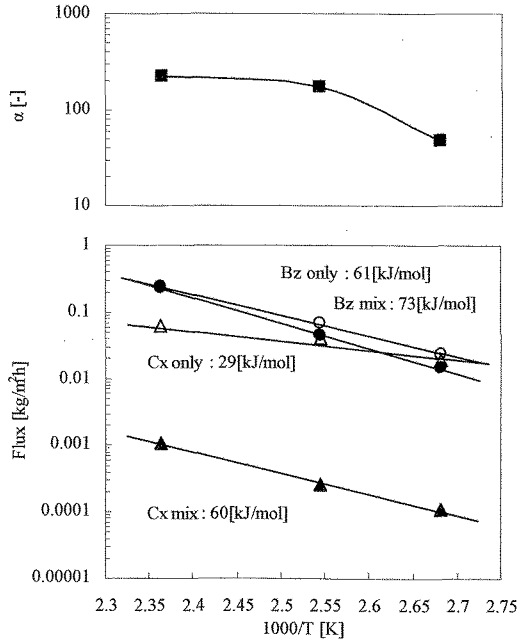

Fig.4. Temperature dependence of flux and separation factor through the stainless steel supported NaY zeolite membrane for benzene (Bz)/cyclohexane (Cx) (50/50 wt.%) mixture.

Fig. 4 shows the temperature dependence of the flux and the separation factor through the NaY zeolite membrane on stainless steel support for vapor permeation of benzene/cyclohexane mixture. Pure benzene flux and benzene flux of the mixture were almost the same, whereas cyclohexane flux decreased remarkably compared with the pure flux. The separation factor significantly increased with the increase of temperature and reached to 220 at 423K. Activation energies of benzene were almost constant in pure and mixture, while that of cyclohexane increased from 29 kJ/mol at pure component to 60 kJ/mol at mixture. The permeation of cyclohexane was hindered by the presence of benzene. Due to the previous adsorption data of these molecules to NaY zeolite [6], it can be also considered that benzene molecules are preferentially adsorbed in zeolite pores and hinder the permeation of cyclohexane. This behavior was in agreement with a previous report on mullite supported membrane [6]. The separation performance of NaY zeolite membranes is far satisfactory compared with the other membranes reported for pervaporation and vapor permeation of organic mixtures [13].

4. CONCLUSIONS

Faujasite membrane was prepared hydrothermally at one-time-synthesis on the surface of a porous cylindrical stainless steel support treated with nitric acid. The outer-surface of the porous support was completely covered with randomly oriented, intergrown NaY zeolite crystals after synthesis of 5 hours. The thickness of the membrane was about 10 μm. Compared with the membrane prepared on mullite support, the NaY zeolite membrane prepared on stainless steel support showed equal or high alcohol or benzene selectivity in separation of alcohols/ethers and aliphatic hydrocarbons mixtures or benzene/cyclohexane mixtures, which can be attributed to the sufficient dense zeolite layer formation on the stainless steel support. A stainless steel supported membranes have some advantage of the simplification of a membrane module construction by weld processing as well as they can use under the harsh condition.

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