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Preparation and gas separation properties of zeolite T membrane†

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Zeolite T membranes were synthesized on tubular porous mullite tubes by hydrothermal synthesis. The membranes selectively permeated carbon dioxide from CO_2/CH_4 and CO_2/N_2 mixtures with high separation performances, which were due to combined effects of molecular sieving and competitive adsorption.‡

Separation and recovery of CO_2 from flue gas and natural gas are of great interest from the viewpoint of global warming and energy industries. Membrane separation is energy-efficient and many membranes have been developed for CO_2 separation. Among the polymeric membranes developed so far, polyimides showed relatively high CO_2 separation performances, but also showed disadvantages of lower selectivity at higher temperatures and plasticization effects at high pressures of CO_2 and of coexisting CH_4 and other hydrocarbon vapors.[1] Inorganic membranes, especially zeolite membranes, have the potential to breakthrough these disadvantages. Zeolite Y[2,3] and SAPO-34[4,5] membranes have been studied on CO_2 separation. Zeolite Y membranes displayed high CO_2/N_2 separation performances due to preferential adsorption of CO_2. However, the membranes rapidly lost their selectivity with increasing temperature. Furthermore, they displayed rather low selectivity of CO_2 over CH_4. These are probably because zeolite Y has a large pore size of 0.74 nm and separation by differences in size is not expected to work for these gas pairs, that is, the working separation mechanism is only the preferential adsorption of CO_2. MFI zeolite membranes with a medium pore size of 0.55 nm also displayed very low selectivity of these gas pairs.[6–8] SAPO-34 zeolite has a smaller pore size, which was estimated to be between 0.43 and 0.50 nm from adsorption experiments, and showed molecular-size dependent gas permeance, namely, the single-gas permeances were in the order $CO_2 > N_2 > CH_4$. However, their selectivity of CO_2 over N_2 and CH_4 remained rather low, indicating that the combined effects of competitive adsorption and molecular sieving were not high enough for CO_2 separations through SAPO-34 membranes.

Zeolite T with a Si/Al ratio of 3–4 is less hydrophilic than zeolite Y with a Si/Al ratio of less than 3. Zeolite T is an intergrowth-type zeolite of erionite and offretite, of which the pore sizes are 0.36 nm × 0.51 nm and 0.67 nm × 0.68 nm, respectively.[9,10] Zeolite T crystals contain small amounts of stacking faults of erionite sheets inter-stacked in offretite. Adsorption experiments of hydrocarbon vapors indicated that the large pore openings are effectively blocked by the stacking faults.[11] Therefore, it is of great interest to investigate CO_2 separation properties of zeolite T membranes. In this communication, we report excellent CO_2 separation performances of zeolite T membranes.

Zeolite T membranes were prepared by hydrothermal synthesis onto porous mullite tubes. A milk-like aluminosilicate gel was prepared by mixing precipitated silica, alkaline aluminate, sodium hydroxide, potassium hydroxide and distilled water, followed by stirring at 303 K for 24 h. The molar gel composition was $SiO_2 : Al_2O_3 : Na_2O : K_2O : H_2O = 1 : 0.05 : 0.26 : 0.09 : 14$. The outer surface of a porous tubular mullite support (Nikkato Corp., 12 mm in outer diameter, 1.5 mm in thickness, 1.3 μm in average pore size) was simply rubbed with a water slurry of zeolite T crystal particles. The seeded support tube of 10 cm in length was placed in the 230 ml aluminosilicate gel and the hydrothermal synthesis was carried out at 373 K for 30 h. After the hydrothermal synthesis, the membranes were washed well with water and dried.

The XRD patterns of the zeolite T membrane consisted of the zeolite T crystal peaks and the substrate peaks (shown in Fig. S1†). The surface of membrane was covered with randomly oriented rod-like zeolite T crystals of less than 1 μm in diameter, but their packing was rather loose. The membrane layer of about 20 μm in thickness was composed of two layers, namely the top surface layer and the intermediate layer under the top layer (Fig. S2†). FE-SEM observation (Fig. S2 (c)†) showed the presence of the well-intergrown zeolite T crystals packed densely in the intermediate layer, which seemed to take an important role in separation rather than the top surface layer.

Single-gas permeation experiments for the membranes (19 cm² in effective membrane area) were carried out for several gases at 303–473 K by means of a vacuum method. As shown in Fig. 1, with increasing kinetic diameter from 0.33 nm for CO_2 to 0.43 nm for C_3H_8, the gas permeance R decreased by more than three orders in magnitude. It is noted that R values were about ten times less for CH_4 than for N_2. This is quite different from the case of other zeolite membranes. These strongly indicate that the zeolite T membranes prepared in this study had little or a very little defects (or nonzeolitic pores) and their gas permeation behavior was controlled by zeolitic pores of erionite inter-stacked in offretite, of which the pore size is 0.36 nm × 0.51 nm. Thus, methane molecules with kinetic diameter of 0.38 nm could permeate through the zeolite T membranes to only a small extent, and propane molecules with kinetic diameter 0.43

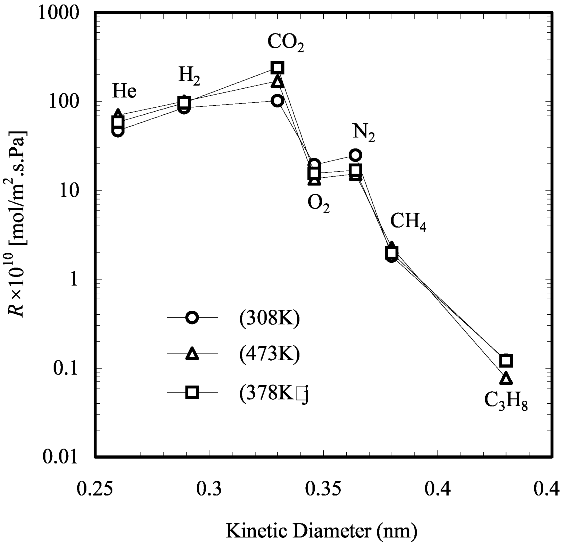

Fig. 1 Plots of permeance R *versus* kinetic diameter of gas molecule for zeolite T membrane at 303, 378 and 473 K.

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† Electronic supplementary information (ESI) available: XRD patterns and FE-SEM photographs. See http://www.rsc.org/suppdata/cc/b3/b305947b/

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nm hardly at all. CO_2 molecules with the smaller kinetic diameter showed the highest permeance among the gases investigated. The adsorptions of CO_2, CH_4 and N_2 on zeolite T crystal powder were 3.4, 0.83 and 0.25 mmol g^{-1}, respectively, at 50 kPa and 298 K. The affinity of CO_2 molecules to zeolite T, which is due to the interaction of the electric field in zeolite T and quadrupole moment of CO_2, resulted in a high adsorption coverage of CO_2 in zeolitic pores and a high permeability. This is similar to the case of zeolite Y membranes.[2]

Mixed-gas permeation experiments for CO_2/CH_4 and CO_2/N_2 were carried out by means of the vacuum method followed by the gas-chromatographic analysis of the permeate. In order to confirm the steady state permeation, the mixed gas was continued to be fed in the upstream side, and the downstream side was kept at a pressure less than 5 torr by interrupted evacuation. During the interruption of evacuation, the permeation flux and the permeate composition were measured. For the CO_2/CH_4 system, at a low temperature of 308 K, with elapsed time the permeance of both components decreased initially and then levelled off, whereas the separation factors hardly changed. The steady-state permeation was attained after about 20 h, with gas permeance values about 30% lower than the initial values. After the membrane was desorbed under a vacuum at 473 K for 1 h, the initial gas permeance values were recovered. At a higher temperature of 378 K, such reduction in gas permeance with elapsed time was not observed. The reduction in gas permeance at lower temperatures may be due to adsorption of water vapor. Similar results were also obtained for the CO_2/N_2 system. The data obtained about 2 h after the feed gas introduction are presented in this study, because the data are rather close to the steady-state values.

Fig. 2 shows the feed composition dependence of R for each component and the separation factor α at 308 K. Permeance of N_2, R_{N2}, significantly decreased in the mixed-component system compared with the single-component one, whereas permeance of CH_4, R_{CH4}, hardly decreased. On the other hand, permeance of CO_2, R_{CO2}, decreased in the range of mole fraction of CO_2 in feed, x_{CO2}, below 0.2. In this range of x_{CO2}, the R_{CO2} was smaller for CO_2/CH_4 than for CO_2/N_2. The α was lower in the range of lower x_{CO2} and was much higher for CO_2/CH_4 than for CO_2/N_2. The permeation and separation behavior can be explained based on the combined effects of competitive adsorption, molecular sieving and single file diffusion in the zeolitic pores. The differences in adsorption strength and in the diffusivity between CO_2 and N_2 or CH_4 caused the different degree of contribution of each effect, resulting in the different separation behavior for each gas pair.

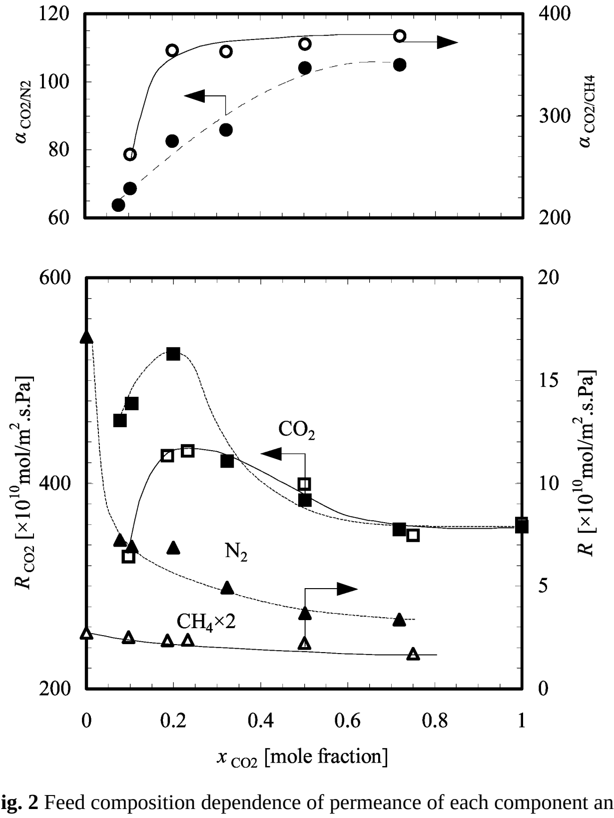

Fig. 2 Feed composition dependence of permeance of each component and separation factor for CO_2/N_2 (closed symbols) and CO_2/CH_4 (open symbols) 308 K with a feed pressure of 100 kPa.

Table 1 Comparison of CO_2 separation performances of zeolite T membrane and other zeolite membranes

Membrane	T [K]	System	$R_{CO2} \times 10^8$ [mol (m^2.s.Pa)$^{-1}$]	α	Ref.
		CO_2/N_2			
T	308	20/80	5.5	81	This
T	308	50/50	3.8	104	This
T	473	20/80	1.5	20	This
Y-Na	303	50/50	4	100	2
Y-Na	403	50/50	15	20	2
Y-Na	308	50/50	130	30	3
Y-K	308	50/50	88	48	3
SAPO-34	300	50/50	3.0	16	5
		CO_2/CH_4			
T	308	50/50	4.6	400	This
T	473	50/50	1.5	52	This
ZSM-5	393	50/50	0.4	10	7
ZSM-5	393	10/90	0.4	17	7
ZSM-5	453	50/50	0.8	4	7
ZSM-5	300	50/50	64	5.5	6
Y-Na	300	50/50	10	20	2
SAPO-34	300	50/50	2	36	5
SAPO-34	473	50/50	0.9	5.2	5

Table 1 shows comparison of CO_2 separation performances of zeolite membranes for CO_2/N_2 and CO_2/CH_4 systems. Although strict comparison of separation performance among these membranes is not appropriate because of the difference in experimental methods, the following were reasonably deduced. For CO_2/N_2 separation, the zeolite T membranes are comparable to the FAU-type (Y-Na) membrane with the higher selectivity,[2] and much better than the SAPO-34 membranes.[7] For CO_2/CH_4 separation, the zeolite T membranes showed excellent performance compared with other zeolite membranes. The α value of 400 at 308 K is much higher than that of other membranes. Furthermore, it is noted that the zeolite T membranes retained the high selectivity of α = 52 and 20 for CO_2/CH_4 and CO_2/N_2, respectively, even at 473 K. This is the first case in which the zeolite membrane has high selectivity for CO_2 separation due mainly to the molecular sieving effect.

Notes and references

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1 W. J. Koros and R. Mahajan, *J. Membr. Sci.*, 2000, **175**, 181.
2 K. Kusakabe, T. Kuroda, A. Murata and S. Morooka, *Ind. Eng. Chem. Res.*, 1997, **36**, 649.
3 K. Kusakabe, T. Kuroda, K. Uchino, Y. Hasegawa and S. Morooka, *AIChE J.*, 1999, **45**, 1220.
4 J. C. Poshusta, V. A. Tuan, J. L. Falconer and R. D. Noble, *Ind. Eng. Chem. Res.*, 1998, **37**, 3924.
5 J. C. Poshusta, V. A. Tuan, E. A. Pape, R. D. Noble and J. L. Falconer, *AIChE J.*, 2000, **46**, 779.
6 J. C. Poshusta, R. D. Noble and J. L. Falconer, *J. Membr. Sci.*, 1999, **160**, 115.
7 M. C. Lovallo, A. Gouzinis and M. Tsapatsis, *AIChE J.*, 1998, **44**, 1903.
8 M. C. Lovallo and M. Tsapatsis, *AIChE J.*, 1996, **42**, 3020.
9 C. L. Cavalcante Jr., M. Eic, D. M. Ruthven and M. L. Occeli, *Zeolites*, 1995, **15**, 293.
10 K. H. Lillerud and J. H. Raeder, *Zeolites*, 1986, **6**, 474.
11 S. Yang and N. P. Evmiridis, *Microporous Mater.*, 1996, **6**, 19.