**Preparation of high CO2 permeable CHA type zeolite membrane using TEAOH.**

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**Highlights**

* A high-silica CHA-type zeolite membrane was prepared by using TEAOH.
* The CO2 permeance of the membrane showed 3.5×10-6 mol m-2 s-1 Pa-1.
* The CO2 permeance was 2-fold value of that of TMAdaOH.

**1. Introduction**

At the present time, carbon dioxide is generally separated by chemical absorption. As an alternative to the chemical absorption, membrane separation technologies have attracted much attention due to their low energy consumption and compact device designs. Among the large number of membrane materials, zeolite have been extensively studied owing to their high chemical and mechanical stabilities. Particularly, CHA-type zeolite membranes show the excellent CO2 permeability and high selectivity because the CHA-type zeolite has a suitable pore size (0.38×0.38 nm) for CO2/CH4 owing to the effects of molecular sieving.

In our previous study, it was found that the CHA membrane with a high Si/Al ratio showed of a high water flux for water/ethanol pervaporation and high CO2 permeance for CO2/CH4 gas separation [1]. On the other hand, there were few reports about the preparation of CHA zeolite with a high Si/Al ratio using organic structure directing agents (OSDAs) except for N,N,N-trimethyl-1-adamantammonium hydroxide(TMAdaOH). In this study, we prepared a high silica CHA membrane using tetraethyl ammonium hydroxide (TEAOH) as OSDA. The gas permeances and separation properties for this membrane were determined by gas permeation test.

**2. Methods**

The high-silica CHA-type zeolite seed crystals were prepared by the following literature [2]. High-silica CHA-type zeolite seed crystals were applied to the outer surface of a porous α-alumina support tube (pore size: 0.5–1.0 μm; Hitachizosen Corp.) by rubbing. The membrane synthetic gel was prepared with TEAOH, ion exchanged water, sodium hydroxide, and FAU-type zeolite. The α-alumina support tube with the high-silica CHA type zeolite seed crystals was placed in a Teflon container, and immersed in the synthesis gel. After installing the Teflon container in an autoclave, the hydrothermal treatment was performed at 160 ℃ for 3 days. The membranes were characterized by XRD and FE-SEM. The single gas permeance of N2, CO2, and CH4 for the CHA membranes were measured at 40 ℃. Gas separation properties for the membranes were confirmed by the gas permeance (mol m−2 s−1 Pa−1) which was calculated as the permeate flow rate of each gas divided by the partial pressure difference and membrane area.

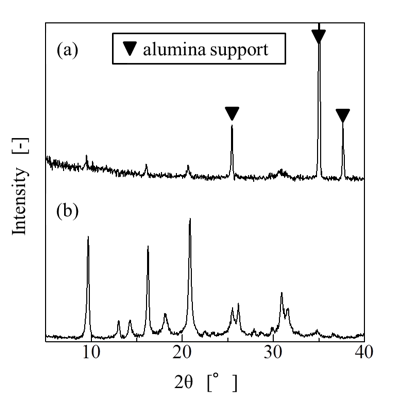
**3. Results and discussion**

Fig. 1 shows XRD patterns of the CHA membranes prepared by TEAOH. The peaks at 2θ=9.4°, 20.5°, and 30.4° correspond to (1 0 0), (2 0−1), and (3−1−1) planes of the CHA-type zeolite and large peaks appearing at 2θ=35.2°, 37.9°, and 43.2° are related to the α-alumina support. Typical peaks positions of the FAU-type zeolite (2θ=6.8°, 11.9°, and 15.6°) were not observed. This result indicates that a CHA type zeolite layer was successfully formed on the surface of the α-alumina support by using TEAOH. Fig. 2 shows cross-sectional FE-SEM images of the CHA membrane. The thickness of the polycrystalline zeolite layer was ca. 10 μm.

Fig.2 FE-SEM image of CHA membrane

Fig.1 XRD patterns of (a) CHA membrane and (b) CHA seed crystal

Table 1 shows the comparison of gas permeation properties for CHA membranes prepared using TEAOH and TMAdaOH [1]. The CHA membrane of TEAOH showed the two-fold CO2 permeance than that of TMAdaOH with the similar CO2/CH4 selectivity. Generally, the permeance is proportional to the reciprocal of the membrane thickness. The thickness of the CHA membrane of TMAdaOH reported to be about 3.0 mm. Therefore, the increase of CO2 permeance by using TEAOH is not due to the membrane thickness. This reason might be the differences of pore structure caused by OSDAs．

Table1 Gas permeances and selectivity of CHA membranes prepared using TEAOH and TMAdaOH

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Membrane | |  | TEAOH | TMAdaOH [1] |
| Permeance [ mol m-2 s-1 Pa-1] | CO2 |  | 3.5×10-6 | 1.7×10-6 |
| N2 |  | 3.4×10-7 | 1.2×10-7 |
| CH4 |  | 3.6×10-8 | 1.8×10-8 |
| Selectivity [-] | CO2/CH4 |  | 97 | 98 |

**4. Conclusions**

In this study, the high-silica CHA-type zeolite membrane was synthesized on the α-alumina support tube by TEAOH as OSDA. The membrane showed the excellent separation performance for CO2/CH4 gas.

**References [Calibri 10]**

1. S. Imasaka et al., Sep. Purif. Technol. 199 (2018) 298-303.
2. N. Kosinov et al. , J. Mater. Chem. A, 2 (2014) 13083-13092