A Defect-free Mordenite Membrane synthesized by Vapour-phase Transport Method

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A defect-free MOR membrane is synthesized on a porous alumina plate by a vapour phase transport method: shape selectivity is apparent in the pervaporation of a benzene–*p*-xylene mixture (the separation factor exceeded 160).

It is well known that the molecular sieving properties of zeolites have been utilized in chemical and physical processes such as gas separation and heterogeneous catalysis. Zeolites are attractive materials due to their high thermal resistance, chemical inertness and mechanical strength, in addition to their unique pore structures. These properties make it possible to separate mixtures at a molecular level under severe conditions where organic polymer membranes cannot be utilized. Zeolitic membranes are generally obtained by hydrothermal synthesis, and many reports of MFI membranes (silicalite[1–4] and ZSM-5[5–7]) have been published. Aluminosilicate dry gels can also be converted to zeolites under the vapours of organic templating agents and water.[8–11] This is referred to as the vapour-phase transport (VPT) method. We have previously applied the VPT method to the preparation of a FER membrane[12] and a membrane containing a mixture of MFI and FER.[13] In the present communication, we report the first synthesis of a large pore zeolite, MOR, as a membrane in a compact form by the VPT method.

The zeolitic membrane on a porous alumina support was prepared as follows. An aluminosilicate gel with a composition of $10Na_2O:25SiO_2:Al_2O_3$ was prepared using NaOH, $Al_2(SO_4)_3$ and colloidal silica (ST-S; Nissan Chemical Industries, Ltd.). The alumina support, which had an average pore diameter of 0.1 μm (Nihon Gaishi Co.), was dipped in the parent gel for 1 day. It was then taken out of the gel and dried for 2 h at 363 K. The alumina support covered with the aluminosilicate gel was set in an autoclave with organic compounds [triethylamine and ethylenediamine (2 : 1)] and water set at the bottom as vapour sources. The gel was crystallized under autogeneous pressure at 453 K for 4 days. The products were characterized by XRD, SEM and pervaporation.

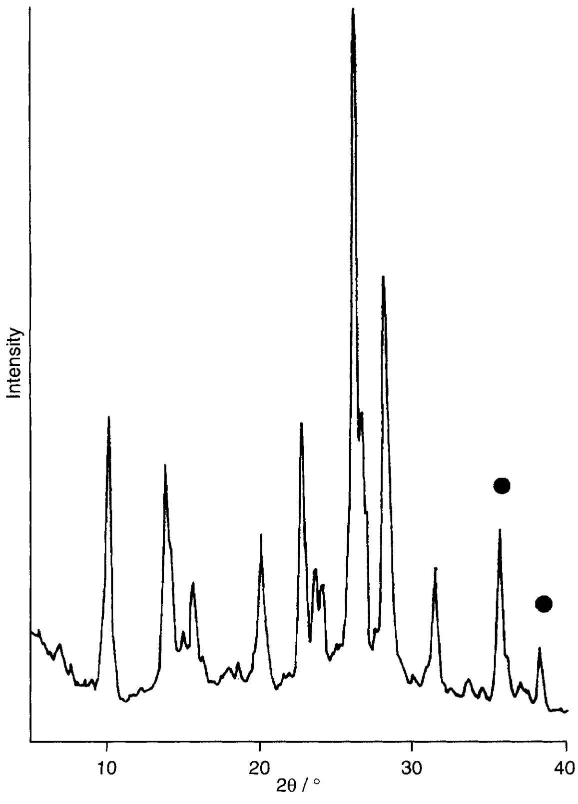

Fig. 1 XRD pattern of the MOR membrane: ● = Al_2O_3 support

No powdery forms were observed on the alumina support. However, a gel prepared with a composition of $5Na_2O:25SiO_2:Al_2O_3$ (a lower concentration of Na) was transformed to a powdery form during crystallization. These results strongly suggest that the alkalinity of the gel is essential for making a compact MOR membrane. The X-ray diffraction pattern of the product on the alumina support contained reflection peaks for both α-alumina and MOR, as shown in Fig. 1. The XRD pattern suggested that MOR formed in a polycrystalline fashion on the surface of the alumina support.

The compactness of the MOR membrane was examined by a permeation test of 1,3,5-triisopropylbenzene (TIPB) at room temperature. The kinetic diameter of TIPB is 0.85 nm, which is larger than the MOR pore dimension of 0.65 × 0.7 nm. The MOR membrane, attached to a stainless tube with a cross-sectional area of 2.2 cm^2, was placed in the TIPB solution with the permeation side kept under vacuum. The condensed permeate was collected in a cold trap cooled by liquid nitrogen, and the amount of the permeate was determined by gas chromatography. No permeation of TIPB was observed (the minimum flux of TIPB determined using the gas chromatography was 4×10^{-9} mol/m^2 s). This result suggested that the MOR membrane was defect-free: there existed no pinholes and cracks at the boundaries of MOR crystals.

SEM images of the top and the cross-sectional views of the MOR membrane are shown in Fig. 2. MOR particles have accumulated on the alumina surface [Fig. 2(*a*)], and boundaries and vacancies among particles can be observed. However, the cross-sectional view [Fig. 2(*b*)] indicates that the gel has penetrated into the alumina pores and a composite layer of alumina and MOR has formed. The composite layer, approximately 10 μm thick, was intact and had a mechanical strength high enough to withstand permeation tests with a pressure drop of 0.3 MPa.

Table 1 compares the result of the pervaporation of a benzene–*p*-xylene mixture, with a molar ratio of 0.860, and a theoretical separation factor at the gas–liquid equilibrium. The separation factor {[(benzene–*p*-xylene)Feed]/[benzene–*p*-xylene)Permeate)]} in the steady state (> 160) was much greater than the value of 11.3 theoretically predicted by the gas–liquid equilibrium. We believe that the shape selectivity occurred at the pore mouths of MOR for benzene and *p*-xylene. The possibility of highly selective separation of aromatic hydrocarbons using the MOR membrane is now presented.

Table 1 Pervaporation of the MOR membrane for a benzene–*p*-xylene mixture. Molar ratio of benzene to *p*-xylene in the feed (mol/mol) 0.860. Feed temperature 295 K.

Total flux/mol m^{-1} s^{-1}	1.19×10^{-4}
Separation factor [(benzene–*p*-xylene)feed]/ [(benzene–*p*-xylene)permeate]	164
Separation factor theoretical value at the gas–liquid equilibrium	11.3

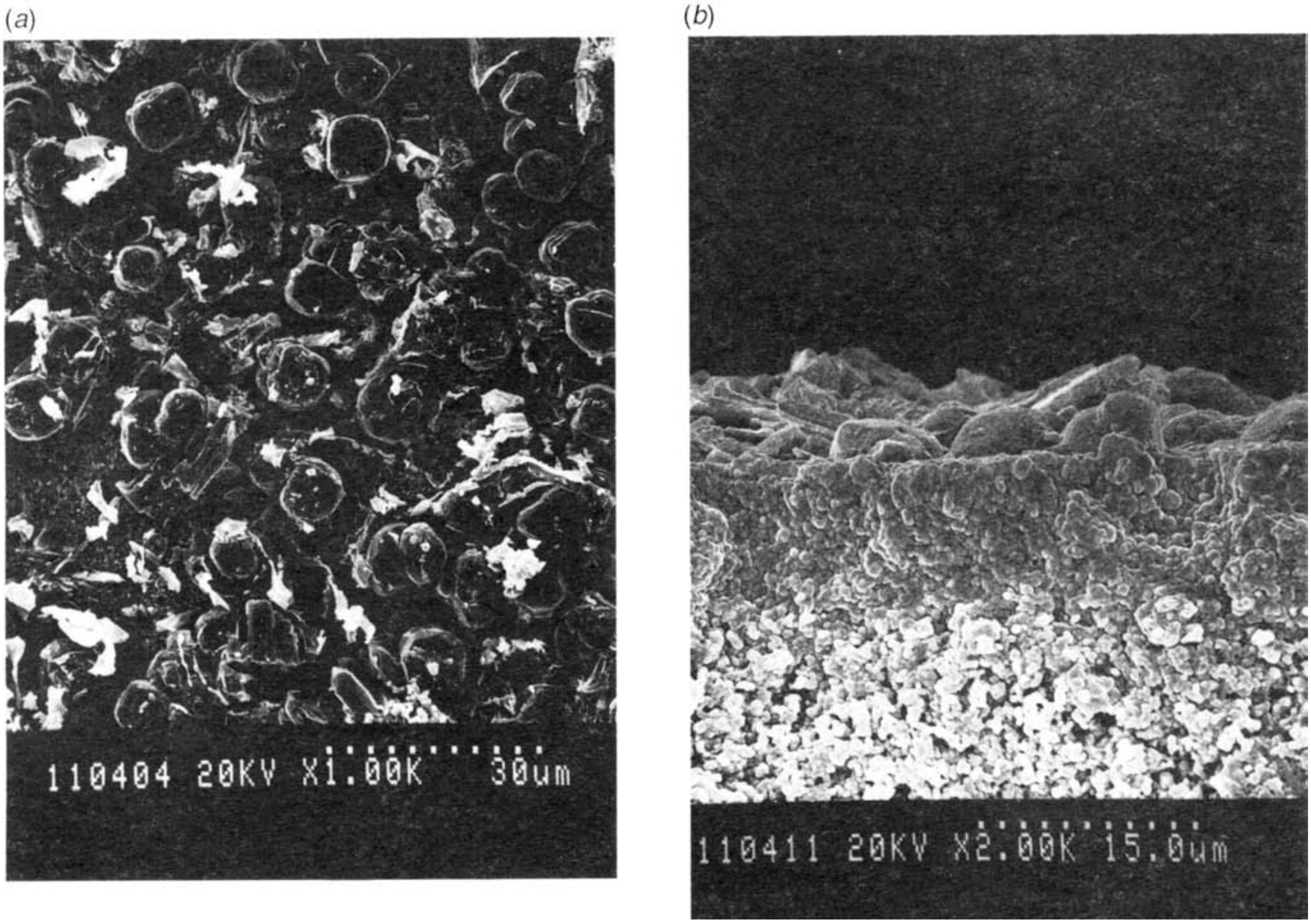

Fig. 2 SEM images of (*a*) the top view and (*b*) the cross sectional view of the MOR membrane

In conclusion, a defect-free MOR membrane, first synthesized by the VPT method, showed a promising potential to separate organic compounds such as aromatic hydrocarbons.

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