Mesoporous MCM-48 membrane synthesized on a porous stainless steel support

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A mesoporous MCM-48 membrane with high thermal stability has been synthesized on a porous stainless steel support by hydrothermal treatment.

Inorganic membranes made of ceramics or metals have been of interest for separation processes owing to their superior characteristics of thermal stability, structural stability and chemical resistance. Mesoporous inorganic membranes with an average pore diameter of 2–10 nm have been studied, mainly with respect to γ-alumina, titania and zirconia membranes prepared by the sol–gel method. However, since they have a wide pore size distribution, other inorganic membranes possessing uniform pore channels have been in demand for high performance applications in nanofiltration, ultrafiltration, pervaporation and membrane reactors.

Mobil scientists discovered a new family of mesoporous molecular sieves designated as M41S in 1992.[1,2] The M41S family includes members having uniform pore structures of hexagonal (MCM-41), cubic (MCM-48) and lamellar (MCM-50) symmetry. In their method, surfactant liquid-crystal structures serve as an organic template for the polymerization of silicates. Parallel to the discovery of M41S materials, Yanagisawa *et al.*[3] and Inagaki *et al.*[4] treated a layered kanemite polysilicate in an aqueous solution of a quaternary ammonium bromide surfactant and prepared a mesoporous silicate designated as FSM-16.

Recently, Ogawa[5,6] developed a rapid synthesis route for mesoporous films under acidic conditions using a mixture of tetramethoxysilane and an aqueous solution of a trimethylammonium salt. The products were transparent films of the hexagonal phase of periodic silica–surfactant composites with a unidimensional pore structure parallel to the surface of a glass substrate. Yang *et al.*[7] fabricated continuous mesoporous silica films on mica under acid conditions. They stated that the surface structure and reactivity of the mica surface controls the orientation of the micellar precursor species.

Straight pores should be oriented perpendicularly to the membrane surface in order to utilize the materials with unidimensional pores for separations. Tolbert *et al.*[8] have synthesized mesostructured silica (MCM-41) particles with orientated hexagonal pores from a hexagonal silicate–surfactant liquid crystal in a high magnetic field. This method has promise for the production of oriented mesopores in thin membranes for use in separations and in chemical sensors. On the other hand, MCM-48 has a three-dimensionally ordered pore structure. Therefore, the MCM-48 membrane is a promising material showing great potential applications such as in filtration, pervaporation and membrane reactors. In this study, a mesoporous membrane made of MCM-48 was synthesized on a porous stainless steel support by hydrothermal treatment.

The MCM-48 membrane was prepared as follows: a stainless steel support with an average pore diameter of 1 μm was placed in tetraethylorthosilicate (TEOS). Then, a solution which consisted of the quaternary ammonium surfactant $C_{16}H_{33}(CH_3)_3NBr$, NaOH and deionized water was added to the TEOS. The molar composition of the mixture was 0.6 $C_{16}H_{33}(CH_3)_3NBr$: 1.0 TEOS : 0.5 NaOH : 60 H_2O. Although a clear solution was obtained after mixing, the solution became inhomogeneous after 30 min of stirring. After the mixture was stirred for 90 more minutes, the mixture and support were transferred to an autoclave. The stainless steel support was placed horizontally in the bottom of the autoclave. The reaction was carried out without stirring at 363 K for 96 h. The product was rinsed with deionized water and calcined at 773 K for 4 h. Powder and a membrane were simultaneously obtained after the reaction. The BET surface area of the powder was measured by nitrogen adsorption at 77 K.

With respect to the mechanical strength of the membrane, it is preferable that the MCM-48 grows in the pores of the support. When the support was covered with a silica layer *ca.* 0.5 mm thick, the layer was removed from the surface of the support by polishing with a spatula until the surface of the stainless steel support appeared. Fig. 1 shows the SEM images for the surface

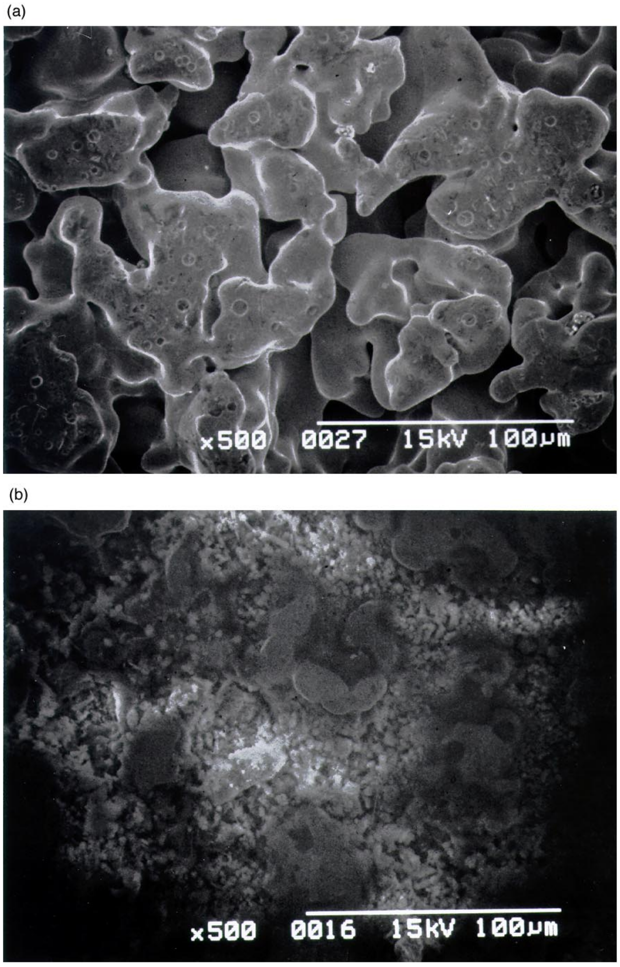

Fig. 1 Scanning electron micrographs of (a) the stainless steel support and (b) the MCM-48 membrane

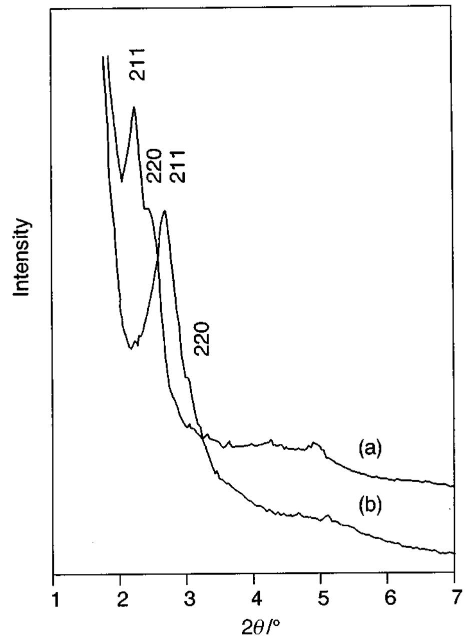

Fig. 2 X-Ray diffraction patterns of MCM-48 membranes (a) before calcination and (b) after calcination

of the original stainless steel support and the polished membrane before calcination. Particles with diameters of about 1 μm can be observed in the pores of the stainless steel.

The X-ray diffraction pattern of the polished membrane before calcination is shown in Fig. 2(a). The peaks for MCM-48 were found in the X-ray diffraction pattern even after the removal of the MCM-48 layer on the support, which indicates that MCM-48 grew in the pores of the stainless steel support. Fig. 2(b) shows the X-ray diffraction pattern of the polished membrane after calcination. The d_{211} values decreased from 3.9 nm to 3.3 nm after calcination because of the shrinkage of the structure. However, the peak intensity was not reduced even after calcination, showing that the ordered structure was maintained even after the removal of the surfactant. This result shows that the MCM-48 membrane prepared in this study has high thermal stability up to 773 K. The powder formed in the solution was MCM-48 with a BET surface area of 1025 $m^2\ g^{-1}$, showing its high quality.

We performed gas permeation tests using the MCM-48 membrane before and after calcination. The tests were carried out using a pressure drop of 100 kPa at room temperature. The permeances of nitrogen are shown in Table 1. Only pinholes and cracks between the MCM-48 particles can be gas permeable before calcination because the mesopores of MCM-48 are blocked by surfactant molecules. The MCM-48 membrane before calcination was impermeable to nitrogen gas. This result shows that MCM-48 particles were densely packed in the pores of the support and formed a compact composite membrane before calcination. The calcined membrane was permeable to nitrogen gas. The compactness of the MCM-48 membrane and the effect of the shrinkage of the structure by calcination on permeation properties will be reported in the near future.

Table 1 The permeance of N_2 through MCM-48 membranes

	Permeance/10^{-5} mol $m^{-2}\ s^{-1}\ Pa^{-1}$
Before calcination	0.0
After calcination	1.5

In conclusion, we have prepared a mesoporous inorganic membrane made of MCM-48 which has a three-dimensionally ordered pore system. A composite layer of stainless steel/ MCM-48 was obtained in a compact form.

We thank GHAS at the Department of Chemical Engineering at Osaka University for SEM and XRD measurements. This study was partly supported by the Shimadzu Science Foundation.

Notes and References

1 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710.

2 J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmidtt, C. T-W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins and J. L. Schlenker, *J. Am. Chem. Soc.*, 1992, **114**, 10834.

3 T. Yanagisawa, T. Shimizu, K. Kuroda and C. Kato, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 988.

4 S. Inagaki, Y. Fukushima and K. Kuroda, *J. Chem. Soc., Chem. Commun.*, 1993, 680.

5 M. Ogawa, *J. Am. Chem. Soc.*, 1994, **116**, 7941.

6 M. Ogawa, *Chem. Commun.*, 1996, 1149

7 H. Yang, A. Kuperman, N. Coombs, S. Mamich-Afara and G. A. Ozin, *Nature*, 1996, **379**, 703.

8 S. H. Tolbert, A. Firouzi and G. D. Stucky, *Science*, 1997, **278**, 265.

Received in Cambridge, UK, 13th July 1998; 8/05419C