A novel preparative route to a silicalite membrane

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A silicalite membrane, without cracks, attached just onto the inner surface of a porous α-Al_2O_3 ceramic tube is synthesized successfully.

Synthesis of zeolite membranes *in situ* on a porous inorganic substrate has received much attention in recent years due to their potentially good separation properties.[1–4] Most reports use the following preparation procedure, *viz.* mixing the reagents, *e.g.* silica, sodium hydroxide, tetrapropylammonium bromide and water, according to the required composition and transferring the mixture into an autoclave followed by dipping of the porous support in this mixture wholly or partially to allow zeolite crystals to grow *in situ* on the support. Obviously, such an operation can not prevent colloidal particles entering and crystallizing within the pores of the support. During treatment, the surface of the support often becomes rougher, which indicates that the zeolite membrane is heterogeneous. In this work, a novel method is used to prepare a zeolite layer attached just to the surface of a porous support.

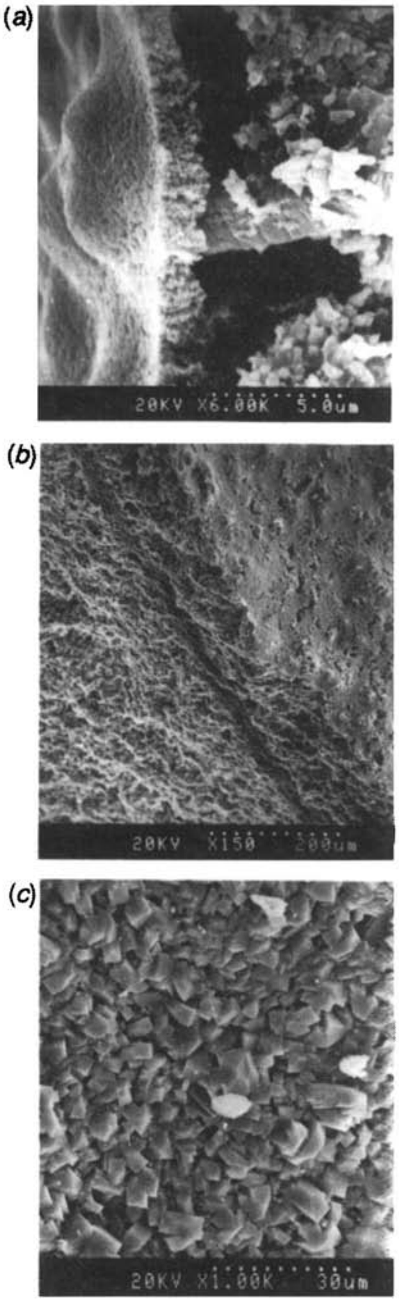

Fig. 1 SEM images of (*a*) a cross-section of the gel layer, (*b*) the side view of the zeolite membrane and (*c*) a top view of the morphology of the zeolite membrane

The sol was prepared by mixing NaOEt (prepared by dissolving 2.5 g Na in 50 ml EtOH), TPABr (prepared from NPr_3 and PrBr), TEOS (Tianjin Chemical Reagents Factory)

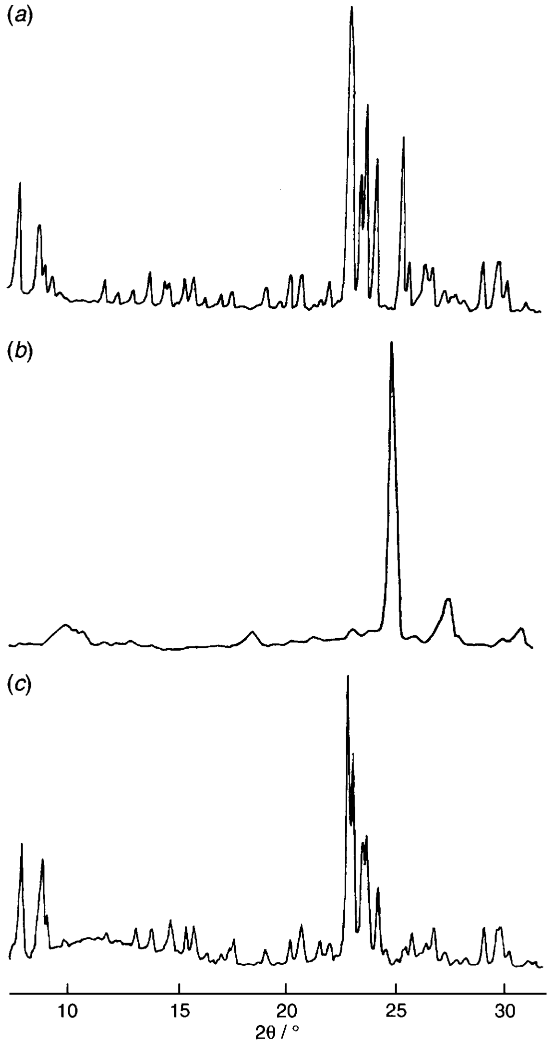

Fig. 2 X-Ray diffraction patterns of (*a*) the zeolite composite membrane, (*b*) α-Al_2O_3 substrate and (*c*) silicalite powder

and EtOH (Tianjin Chemical Reagents Factory) according to a molar ratio of 8–30 : 4–15 : 100 : 250–300. The mixture was sealed and aged in air under ambient conditions for a few weeks. Then the gel was coated onto the inner surface of an α-Al_2O_3 ceramic tube (o.d. 10 mm, i.d. 6 mm, length 250 mm, average pore diameter 1 μm) which had been wetted with an aqueous solution of NaOH and TPABr. The as-treated tube was sealed in an autoclave with some water and heated to 353 K for 8 h leading to hydrolysis. The subsequent crystallization was performed at 453 K for 36 h. The product was washed with deionized water, dried at 423 K for 2 h and calcined at 823 K for 4 h. This procedure was generally repeated 2–3 times so as to obtain a defect-free composite membrane.

Fig. 1(*a*) clearly shows that the gel layer was firmly attached onto the entrance of the pores of the support and did not fill the pores. This is due to the presence of an aqueous solution in the pores. Upon contacting the aqueous solution, the sol moved forward into the pores with alcohol diffusing into the aqueous solution. However, this movement was stopped rapidly when most of the alcohol in the sol had been abstracted into the aqueous solution, as the remaining components in the sol were hydrophobic. Hence a gel layer was formed near the entrance of the pores after hydrolysis, which was converted to a zeolite film under hydrothermal conditions as shown by Fig. 1(*b*).

The product was characterized as a silicalite by XRD (performed with D/Max-rB X-ray diffractometer with the following operation parameters: Cu-Kα radiation, graphite monochromator, DS/SS : 1°, RS : 0.3 mm); the X-ray diffraction pattern of the composite membrane [Fig. 2(*a*)] was a combination of those of the α-Al_2O_3 substrate [Fig. 2(*b*)] and silicalite powder [Fig. 2(*c*)].

Permeation of N_2 on this silicalite composite membrane was performed at several temperatures (the measuring apparatus similar to that in reference 5) and results are given in Table 1. The permeability of N_2 was found to increase with increasing temperature. This result would not have been obtained if some cracks had existed, for which the opposite behaviour would be observed.

Table 1 N_2 permeability of the composite membrane

T/K	10^7 Permeability/ mol m^{-2} s^{-1} Pa^{-1}
433	0.92
473	0.96
513	1.01
553	1.06

Separation properties of the membrane are under investigation.

We thank the National Natural Science Foundation of China for financial support.

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Received, 13th February 1996; Com. 6/01059H