

# Preparation of an MFI-type zeolite membrane on a porous glass disc by substrate self-transformation

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An MFI-type zeolite membrane containing boron has been prepared on the surface of a boron–silicon porous glass disc by substrate self-transformation in the vapor of ethylamine (EA) and H<sub>2</sub>O; both XRD and SEM show that the zeolite crystals on the surface of the porous glass disc were in random orientation; the thickness of the membrane layer was *ca.* 10–20 μm; permeation of O<sub>2</sub> and N<sub>2</sub>, and the chemical composition of the membrane were measured.

In the last decade, the study of zeolite membranes has become an important research topic in the area of inorganic membrane materials because of their uniform microporous structure, and high thermal and chemical stability. Many methods for preparing zeolite membranes on various substrates have been developed, including: hydrothermal crystallization;<sup>1</sup> *in situ* hydrothermal synthesis,<sup>2</sup> vapor phase synthesis,<sup>3</sup> sol–gel methods,<sup>4</sup> zeolite-filled (embedded) methods,<sup>5</sup> chemical growth,<sup>6</sup> galvanic metal deposition,<sup>7</sup> leakage-blocked method,<sup>8</sup> synthesis by microwave heating,<sup>9</sup> *etc.* Supports used include porous ceramic discs<sup>2</sup> or tubes,<sup>10</sup> porous glass discs<sup>11</sup> or tubes,<sup>12</sup> porous sintered stainless steel discs,<sup>13</sup> various kinds of metal discs,<sup>1</sup> glass discs or pipes,<sup>4</sup> Teflon slabs and sleeves,<sup>11</sup> single-crystal silicon wafers,<sup>1</sup> filter paper,<sup>14</sup> quartz plate, mica discs, cordierite discs, mullite, stainless steel networks<sup>1</sup> and liquid mercury.<sup>15</sup>

Zeolite ZSM-5 and ZSM-35 membranes were synthesized using the vapor phase method according to Dong *et al.*<sup>3</sup> in which a glass disc or pipe was put on the surface of aluminosilicate gels, or embedded in the gels. These syntheses were carried out at 473 K in amine vapor for 3–7 days. ZSM-35 membranes and ZSM-5 membranes were obtained in the vapor of *n*-propylamine(PrNH<sub>2</sub>)–H<sub>2</sub>O and diethylamine(Et<sub>2</sub>NH)–H<sub>2</sub>O or ethylenediamine(EDA)–triethylamine(Et<sub>3</sub>N)–H<sub>2</sub>O, respectively. Since this work, zeolite membranes have been synthesized *via* vapor phase methods by many researchers. Here, we report a novel finding related to the synthesis of an MFI-type zeolite membrane in the vapor phase. The zeolite membrane was prepared on the surface of a boron–silicon porous glass disc by substrate self-transformation in ethylamine (EA)–H<sub>2</sub>O vapor.

A porous glass disc (18.5 × 17.5 × 2.5 mm, Shanghai Silicate Institute), was used as the starting substrate. The chemical composition of the glass, as measured by chemical titration, was B<sub>2</sub>O<sub>3</sub> = 2.5 wt%, Al<sub>2</sub>O<sub>3</sub> = 0.37 wt%, SiO<sub>2</sub> = 96.68 wt%, Na<sub>2</sub>O = 0.44 wt%. The chemical composition of the membrane was determined with a Field Emission Auger Microprobe, MICROLAB 310F, (VG Scientific, Surface Analysis Company) using Mg-Kα radiation at an X-ray power of 300 W, under a vacuum of 3.0 × 10<sup>−8</sup> Mbar. The most probable pore diameter of the substrate was 7.5 nm. The disc was placed in a Teflon holder in a 35 ml stainless steel autoclave, containing *ca.* 10 ml of 50 wt% ethylamine aqueous solution. The porous glass disc was placed in a position so that the disc did not directly contact with the liquid mixture at both room and reaction temperature. The synthesis reaction was carried out in an oven at 180 ± 2 °C for 144 h. After cooling to room temperature, the disc was removed, and dried at 80 °C for 12 h. Both surfaces (A and B) of the disc were transformed to MFI

zeolite crystals after this treatment in vapor. Calcination of the membrane was conducted in a crucible oven. One of the two surfaces of the disc (B) was polished before calcination. Permeability of gases on both the calcined zeolite membrane and the substrate was studied at room temperature with the supported membrane and substrate mounted in a special separator. The flow rate of the gas was measured with a soap bubble flowmeter, and the difference of the pressure between two sides of the disc kept at 0.1 MPa.

Fig. 1 shows typical XRD patterns of MFI-type zeolite on both sides of the disc after reaction [Fig. 1(a) and (b)]. The XRD patterns show that the zeolite crystals are in random orientation on the surfaces of the disc. The surfaces of the initial porous glass disc are amorphous [Fig. 1(c)].

SEM shows that the surfaces of the initial porous glass disc are rough and uneven [Fig. 2(a)]. After synthesis, both sides of the disc are covered by MFI zeolite crystals with random orientation [Fig. 2(b)–(d)], consistent with the XRD results. The size of the crystals is *ca.* 15–25 μm [Fig. 2(b)], and the thickness of the membrane layer is *ca.* 10–20 μm [Fig. 2(c) and (d)]. There are no zeolite crystals on the inner surfaces of the disc [Fig. 2(c) and (d)], indicating that the zeolite crystals only formed on the outer surfaces of the disc.

The chemical composition of the membrane, measured by surface analysis, is B<sub>2</sub>O<sub>3</sub> = 3.70 wt%, Al<sub>2</sub>O<sub>3</sub> = 0.55 wt%, SiO<sub>2</sub> = 95.25 wt%, Na<sub>2</sub>O = 0.50 wt%. The permeabilities of O<sub>2</sub> and N<sub>2</sub> through the substrate are 5.06 × 10<sup>−8</sup> and 5.56 × 10<sup>−8</sup> mol m<sup>−2</sup> s<sup>−1</sup> Pa<sup>−1</sup>, respectively. The calculated ideal selectivity of O<sub>2</sub>/N<sub>2</sub> (0.91) is very close to the Knudsen value (0.94), showing

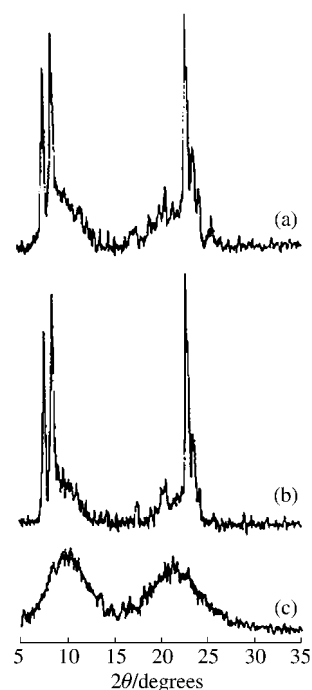
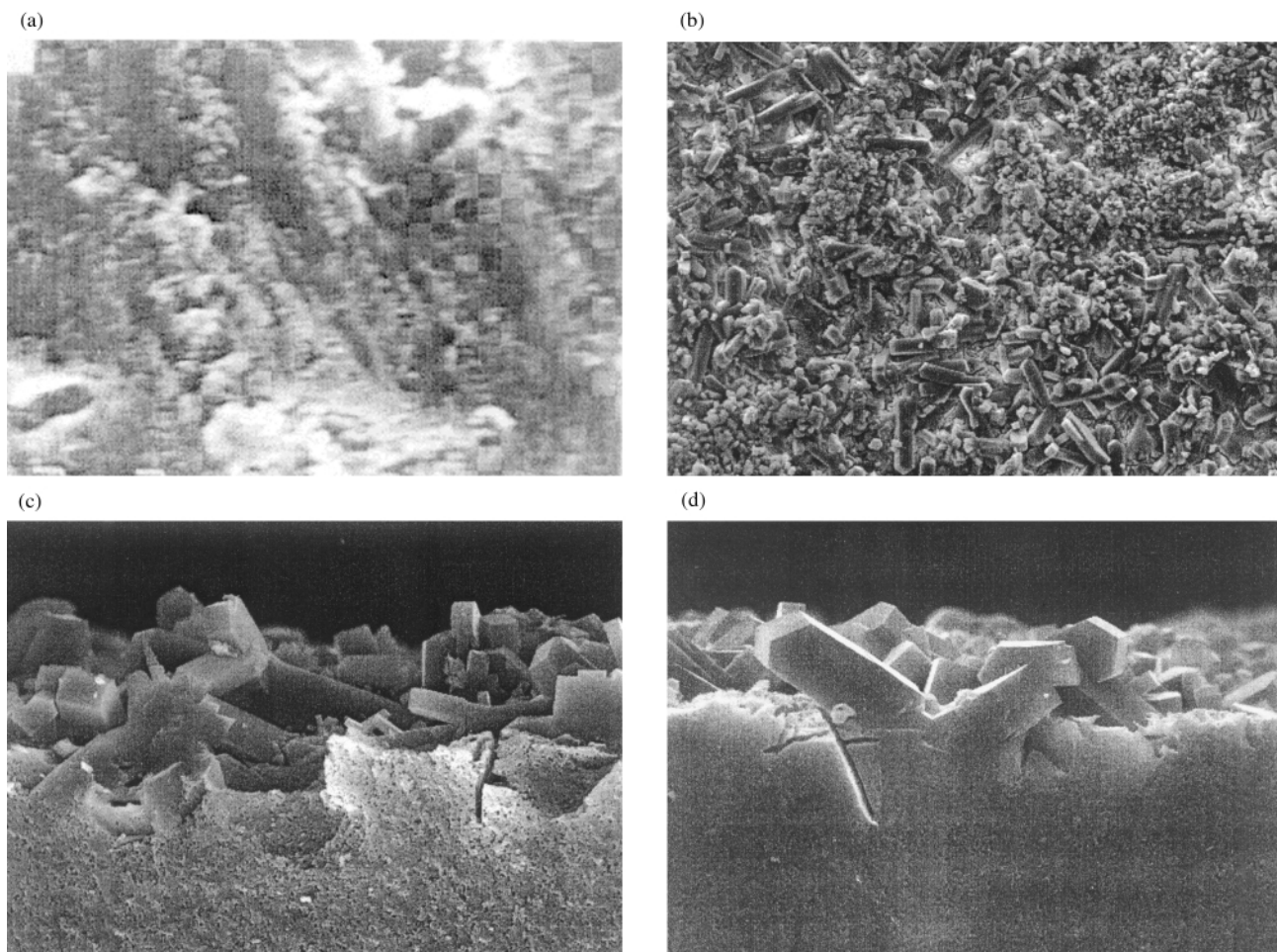


Fig. 1 XRD patterns: (a) surface A of the membrane, (b) surface B of the membrane and (c) surface of the initial porous glass disc.



**Fig. 2** SEM photographs: (a) the surface of the initial porous glass disc; magnification 1950 $\times$ , (b) plane view of surface A of the membrane, (c) cross-section of surface A of the membrane, (d) cross-section of surface B of the membrane, before polishing.

that the substrate shows no preferential selectivity for the penetration of  $O_2$  and  $N_2$ . On the calcined boron-containing MFI-type zeolite membrane, the permeabilities of  $O_2$  and  $N_2$  are  $0.095 \times 10^{-8}$  and  $0.15 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ , respectively. The calculated ideal selectivity of  $O_2/N_2$  (0.63) is obviously lower than that for Knudsen behaviour and for the substrate. The fact indicates that the membrane selectively permeates  $N_2$ .

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