Preparation of *b*-oriented MFI zeolite membranes on porous α-alumina substrates precoated with mesoporous silica sublayer

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Zeolite membranes, with their unique molecular sieving, adsorption and molecular recognition properties, have shown excellent performances in many important applications such as gas separation, pervaporation, membrane reactors, and zeolite membrane-based novel optics, microelectronic, and sensor devices [1–4]. A particularly active field is that of MFI (Silicalite-1 and ZSM-5) membranes, mainly because of the crystal channel systems with pore diameter of 0.55 nm, which is near the sizes of many industrially important organic molecules. It has been demonstrated that the orientation of zeolite crystals can influence the membrane performance in most applications. Preferentially *b*-oriented MFI membranes are of great interest because they allow higher flux and faster response time of membrane based sensors [5–7]. Recently, Lai *et al.* reported the preparation of *b*-oriented MFI membranes by seeded growth of oriented particle monolayers and use of a certain structure-directing agent as crystal growth rate modifier to enhance the relative growth rate along the *b*-axis [5]. Considering of its simplicity, *in situ* crystallization technique has also been adopted to prepare *b*-oriented MFI membranes on nonporous substrates such as stainless steel, aluminum alloy and silicon [6, 7]. The formation of *in situ* grown MFI membrane was greatly dependent on the chemical nature of substrates. To our knowledge, there has been no test on the potential of the *in situ* crystallization technique for the preparation of *b*-oriented MFI membrane on porous substrates. In our study on the use of porous α-alumina substrate to prepare MFI membrane, we found that *b*-oriented membrane can be grown by *in situ* crystallization on porous α-alumina precoated with a mesoporous silica sublayer. Here, we report the investigation of the effect of the mesoporous silica sublayer on the orientation and morphology of MFI membrane.

Porous asymmetric α-alumina Cerantra® discs specially ordered from Narita Seitosho Co. Ltd., were used as substrates. These asymmetric α-alumina discs were fabricated by a novel technique developed in our group [8, 9]. The porosity and pore size can be modified by the processing conditions. The α-alumina discs, with porosity of 62.5%, consist of a thin fine-layer (150 μm) with 0.15 μm pores and a large-pore body with 150 μm pores. A mesoporous silica layer was deposited on the surface of the thin fine-layer by sol–gel dip-coating technique [10, 11]. Precursor silica sols were prepared by addition of CTAB (cetyltrimethylammonium bromide) to prehydrolized polymeric silica sols from TEOS (tetraethylorthosilicate), ethanol, water and HCl. The final molar ratios of the dipping sols were 1 TEOS:20 ethanol:5 H_2O:0.004 HCl:0.16 CTAB. After dip-coating, the samples were dried in a laminar flow cabinet at 25 °C for 12 hr and then calcined at 450 °C in air for 2 hr. Silica powders were obtained by casting the dipping sol in a glass Petri-dish, drying in the laminar flow cabinet and calcining under the same conditions as the dipped silica layer.

MFI membranes were prepared by *in situ* crystallization on uncoated and silica sublayer-coated substrates. TEOS, TPAOH (tetrapropylammonium hydroxide) and deionized water were used as raw materials for preparation of precursor sols. The molar ratio of the precursor sols was 1 TEOS:0.17 TPAOH:120 H_2O. The substrates with fine-layers were placed vertically in a Teflon-lined stainless steel autoclave which was kept in an oven at 180 °C. The membranes were calcined at 450 °C in air for 12 hr to remove the organic templates.

The crystal structures of zeolite membranes and powder were examined by X-ray diffraction (XRD) on a RIGACU RINT1100 diffractometer using Cu Kα radiation. The morphologies of the substrates and zeolite membranes were characterized using a scanning electron microscope (SEM, JEOL JSM-6100) at 15 kV. The porous texture of the calcined silica powder was measured using the N_2 adsorption/desorption isotherm at -196 °C with a GEMINI 2375 Micromeritics apparatus.

SEM micrographs of α-alumina substrates with and without a silica layer are shown in Fig. 1. The reflectivity of the silica layer surface is greater than that of the α-alumina surface, indicating the high smoothness of the precoated silica layer. The silica layer is approximately 2 μ thick. The N_2 adsorption/desorption isotherm of calcined silica powder indicates the lack of hysteresis and absence of any appreciable adsorption at relative pressures above 0.3, which suggests a unimodal porosity with no interpartical meso- or macroporosity [10]. The average pore sizes of the calculated silica powder are 24.5 Å and the special surface areas 1050 $m^2\ g^{-1}$.

The XRD pattern of the α-alumina substrate shows three strong peaks at $2\theta = 25.6°$, $35.1°$, and $37.8°$, respectively (Fig. 2). For the two zeolite membranes, new peaks at the 2θ ranges of 7–9° and 23–25° appear.

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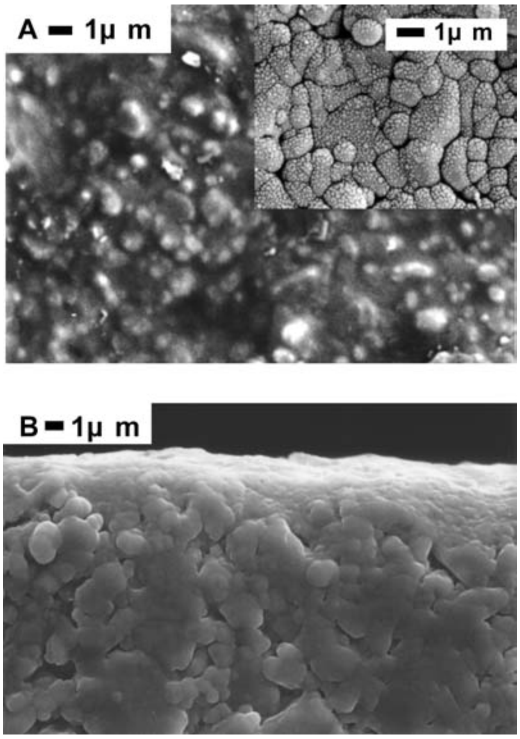

Figure 1 SEM photographs of surface (A) and cross-section (B) of silica sublayer coated substrate. Inset: SEM photographs of surface of α-alumina substrate.

These peaks correspond to the specific peaks of MFI zeolite. Compared to MFI powder, two MFI membranes display only single (0*k*0) peaks around 9 ° and 18 °. Meanwhile, the intensity ratios of (101) peak to that of (020) peak for the two silicalie-1 membranes are both about 0.09. This indicates the MFI crystals with their *b* axis perpendicular to the substrate surfaces are deposited on the α-alumina and silica sublayer surface. The shift of (020) and (040) peaks to lower angles demonstrates the larger Bragg spacing of the crystals on the α-alumina substrate. It is well known that aluminum can be leached from alumina substrate during zeolite crystal growth procedure [12, 13]. The appearance of (020) and (040) peaks at low angles indicates the incorporation of Al atoms into the crystal framework (Si—O band 1.61 Å and Al—O band 1.73 Å). On the other hand, the positions of (020) and (040) peaks of the silica sublayer supported membrane are equivalent to those of MFI powder at the bottom of autoclave. The XRD results suggest that a silica sublayer can reduce leaching of aluminum from the α-alumina substrate. A highly *b*-oriented MFI layer can be further observed in SEM micrographs (Fig. 3). MFI crystals on the silica sublayer supported membrane have a characteristic columnar shape and show a good intergrowth behavior. Otherwise, crystals on the α-alumina supported membrane are obviously discrete with varying crystal sizes. At the same time, a gel layer is observed on some areas of the surface, in which crystals are embedded.

For a long crystallization time, 10 hr, the intensity ratio of the (101) peak to the (020) peak increases rapidly from 0.09 to 0.6 for the α-alumina supported MFI membrane, confirming that the membrane loses its *b*-orientation (Fig. 4A). It can also be observed that gel is present among some crystals. For the silica sublayer supported MFI membrane, the intensity ratio of the (101) peak to the (020) peak decreases slightly from 0.09 to 0.08, which demonstrates that the MFI membrane can retain the *b*-orientation during crystallization. SEM micrograph in Fig. 4B shows the crystal size (*c* axis) grows from 8 μm in 6 hr to >15 μm after 10 hr. The increase in lateral size of crystals results in the loss of perfect morphology of the MFI crystals.

For the uncoated α-alumina substrate, the leached aluminum has dual roles during membrane growth, to facilitate the formation of the gel layer on the substrate and to retard zeolitization in this gel layer [12]. The SEM micrograph (Fig. 3A) indicates that the initial stage of membrane formation is the formation of a precursor gel layer on the α-alumina substrate. Subsequently, crystallization and growth take place inside the gel layer. Because the (010) face of the MFI crystals represents the largest flat surface, the preliminary crystals are most stable when they are settled on the substrate surface with *b*-direction [6, 7]. For a long crystallization time, the low-relative growth rate along the *b*-direction and the simultaneous slow consumption of nutrients in the neighboring gel layer are proposed to result in the secondary nucleation in the neighboring gel layer. As a result, the new crystals with random orientation

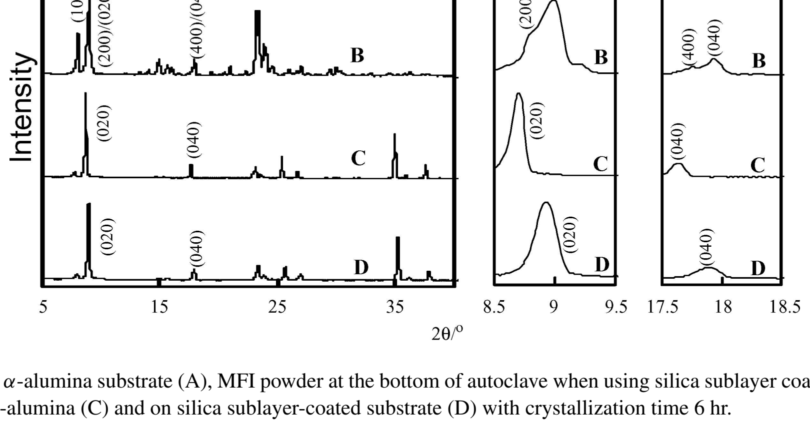

Figure 2 XRD patterns of α-alumina substrate (A), MFI powder at the bottom of autoclave when using silica sublayer coated substrate (B), and MFI membranes on uncoated α-alumina (C) and on silica sublayer-coated substrate (D) with crystallization time 6 hr.

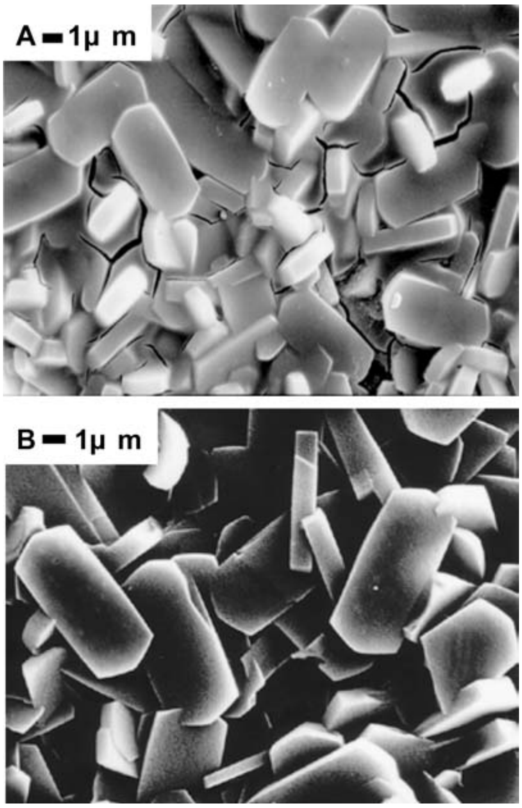

Figure 3 SEM photographs of MFI membranes on α-alumina (A) and on silica sublayer coated substrate (B) with crystallization time 6 hr.

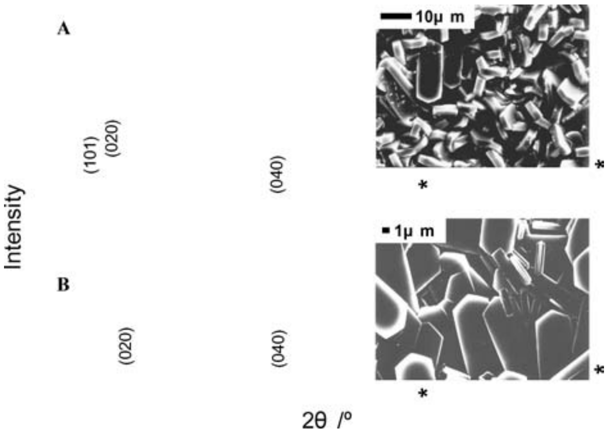

Figure 4 SEM photographs and corresponding XRD patterns of MFI membranes on α-alumina (A) and on silica sublayer coated substrate (B) with crystallization time 10 hr. (*peaks from α-alumina substrate.)

are incorporated inside the preliminary crystal layer. In addition, the rough surface of uncoated α-alumina substrate is suggested to lead to the tilt of some MFI crystals from the substrate surface during crystallization. Thus, a randomly oriented membrane with discrete crystals is obtained at this growth stage. The investigation of the further growth of the MFI membrane on the uncoated α-alumina substrate is in progress. Under the same experimental conditions, we have not observed the gel layer on the silica sublayer-coated substrate. Recently, a membrane formation model had been proposed for the growth of b-oriented MFI membranes by *in situ* crystallization on nonporous metal substrates [7]. This model suggests that the chemical property of the substrate surface is important for the adsorption of preliminary sub-micron crystals, possibly formed via aggregation of nanoslabs in bulk solution, with appropriate numbers to cover the substrate surface. It is well known that sol–gel silica membrane has surfaces covered by Si—OH groups [14]. For the silica sublayer-coated substrate, these Si—OH groups could provide strong chemical bonding between the silica sublayer surface and the (010) face of sub-micron crystals which leads to sufficient coverage of the substrate surface with preliminary crystals. In addition, we cannot exclude the possibility that surface smoothness of the silica sublayer also plays an important role in the formation of b-oriented MFI membrane. The elimination of intrinsic defects on porous substrate by the silica sublayer provides a smooth surface for the adsorption and growth of the sub-micron crystals with their (010) faces parallel to the substrate surfaces.

In summary, continuous b-oriented MFI membrane can be prepared on porous α-alumina substrates precoated with mesoporous silica sublayers. Only randomly oriented MFI membranes with poor crystal intergrowth are obtained on the uncoated α-alumina substrate during crystallization. Both the chemical bonding between the silica sublayer surface and the preliminary sub-micron crystals and the surface smoothness are believed to have significant effects on the formation of b-oriented MFI membrane on the silica sublayer coated substrate.

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