Preparation of an ordered zeolite MFI film by epitaxial growth†

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Received (in Cambridge, UK) 19th October 2004, Accepted 22nd November 2004
First published as an Advance Article on the web 11th January 2005
DOI: 10.1039/b416072j

An ordered zeolite MFI film has been prepared on the substrate of a {001} basal face of high-quality large silicalite-1 crystals by epitaxial growth.

Zeolite films have been widely synthesized and attract considerable interest due to their potential applications as selective membranes, chemical sensors, and low dielectric constant materials.[1–3] In order to improve the performance of the zeolite films, much effort has been made to control the orientation of the crystals in the zeolite film. Appropriate orientation of the nanometre sized channels in the zeolite crystals can drastically affect the mass transport behavior within a zeolite film, and this is crucial for its application. Furthermore, a preferred crystal orientation can cause differences in the stresses which affect the mechanical stability of the films, and influence surface smoothness and transparency of the films which may be required for optical, photocatalytic or sensor applications.[4] However, it is still a challenge to prepare a zeolite film with not only one-dimensional (1D) but also two-dimensional (2D) and three-dimensional (3D) orientation for innovation materials. Several methods for the preparation of highly oriented zeolite films have been described.[4–8] Recently, Tsapatis and co-workers have prepared highly *b*-oriented MFI films using a high-degree orientation seed layer by secondary growth which is usually called the “seeded growth” method.[1] In this method, the role of the seed layer is dual. It not only leads to growth without nucleation but also prohibits or limits the incorporation of newly formed crystals. Due to the limitation of the size and shape of precursor seeds, it is difficult to prepare the highly oriented seed layer. Moreover, the absence of close-packed precursor seeds often leads to grain boundary defects of the film.

The purpose of this communication is to present a method employing the basal face of large silicalite-1 crystals (about 1 mm in width) instead of the seed layer to prepare an ordered MFI film which has not been reported up to now. There are two advantages to preparing zeolite films using the basal face of large silicalite-1 crystals instead of the seed layer. Firstly, it retained the merit and avoided the limitation of the seed layer used in the “seeded growth” method. Secondly, it is a direct approach to obtain the multidimensional orientation zeolite film. Here we first prepare a zeolite MFI film on the {001} basal face of a large silicalite-1 crystal because MFI-type zeolite films often show a preference for crystallographic *c*-axis orientation perpendicular to the plane of the substrate.[9]

The electronic supplementary information† gives information on the high-quality large silicalite-1 crystal with a size of 2 mm × 1 mm × 1 mm prepared by our group.[10,11] Fig. 1 presents the preparation of the substrate of the {001} basal face of the large silicalite-1 crystals. At first, a thick layer of UV glue (NCA 130, Beijing Lienhe Co.) is coated on a glass plate and then the large silicalite-1 crystals are arranged tightly with the *c*-axis of the crystals perpendicular to the plane of the glass plate. The UV glue layer is solidified under UV light for 10 min and the {001} basal face can be exposed after the crystals are mechanically polished vertically along the *c*-axis direction. Subsequently, the substrate is placed in a reaction solution vertically at the bottom of an autoclave. The reaction solution is prepared by adding tetraethylorthosilicate (TEOS) dropwise to an aqueous solution of tetrapropylammonium hydroxide (TPAOH, 1 M in water) with a composition of 40 SiO_2 : 8 TPAOH : 8000 H_2O : 160 EtOH. After a hydrothermal reaction for 12 h at 180 °C, the sample is taken out and cleaned with ultrasound. The morphology of the zeolite MFI films is observed with a field-emission scanning electron microscope (FE-SEM: JEOS JSM 6700). The XRD data are collected on a Siemens D5005 diffractometer with Cu–Kα radiation (λ =1.5418 Å). The step size is 0.02° and the count time is 4 s.

Fig. 2 shows the XRD patterns of the prepared substrate and treated sample after secondary growth. The XRD pattern of the substrate (Fig. 2a) shows only a couple of sharp peaks at 2θ = 13.2° and 26.6°, which correspond to the (002) and (004) indices of the MFI structure. This demonstrates the complete *c*-orientation of the prepared substrate. The XRD pattern in Fig. 2b indicates that the main peak positions of the zeolite film are almost the same as those of the substrate and only the intensities are slightly different. It suggests that the film is a complete *c*-orientation zeolite MFI film. The surface morphology of the zeolite MFI film is shown in Fig. 3a. It presents a complete *c*-orientation of the zeolite MFI film, which agrees with the result of XRD. Furthermore, the zeolite MFI film also shows a high-degree of *a*-orientation and *b*-orientation and is distinguished from the previously reported *c*-orientation zeolite MFI films which only show high *c*-orientation caused by the competitive

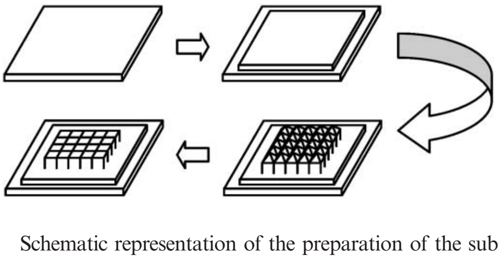

Fig. 1 Schematic representation of the preparation of the substrate.

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† Electronic supplementary information (ESI) available: information on the large silicalite-1 crystals and the polished face of the crystal. See http://www.rsc.org/suppdata/cc/b4/b416072j/

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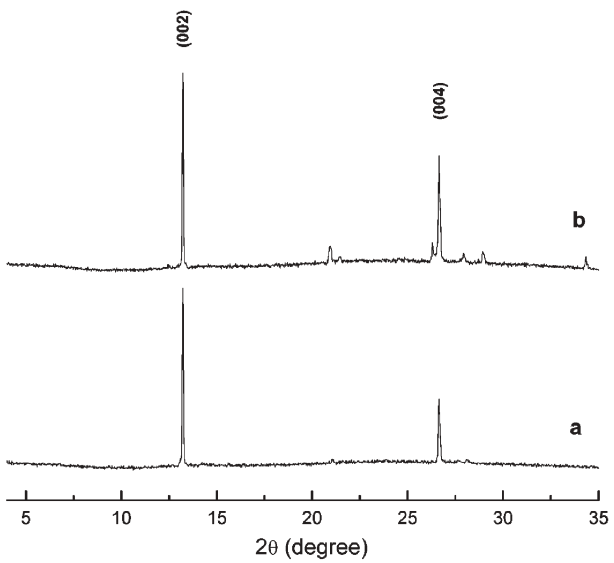

Fig. 2 XRD patterns of (a) the substrate, (b) the substrate after a 12 h hydrothermal treatment.

growth model.[9] This result may be explained by the use of the large MFI crystal basal face as the substrate which provides the complete orientation seed layer and the occurrence of epitaxial growth. Generally, the same crystal structure types have the best fit and the lowest energy barrier through which epitaxial growth is easily carried. At first, the substrate of the {001} basal face of the large silicalite-1 crystals supplies a complete *c*-orientation seed layer, which suppresses the nucleation in the reaction solution. Substrate-generated nuclei with the same lattice structure occur and then the crystals grow along the former orientation of the basal face of the large MFI crystal. Fig. 3b shows that there is no separation between the substrate and the film which suggests the epitaxial growth from the substrate of the {001} basal face of the large silicalite-1 crystals. Fig. 3c shows the SEM image of the surface of the substrate of the {001} basal face of the large silicalite-1 crystals after a 3 h reaction. It presents a layer of many small crystals grown from the substrate. They have the same tent shape as the top part of a typical MFI crystal. After a 6 h reaction, the small crystals grow larger and form an ordered crystal layer along the three dimensions (Fig. 3d). With an increase in crystallization time, an ordered over-growth zeolite MFI film is formed with a thickness of 10 μm (Fig. 3b). In addition, using the substrate prepared from the calcined large MFI crystals, the same results can be obtained. It indicates that the direction of the crystal substrate controls the oriented growth of new crystals.

In summary, the present study explored a novel method to prepare an ordered zeolite MFI film firstly. We believe that the ordered zeolite MFI film with a precise pore orientation has a potential application in optical devices over sufficiently large scales.[1,12] More importantly, it provides more information for the investigation on the mechanism of the "seeded growth" method which is an important method to prepare zeolite films.

We are grateful for the financial support of the State Basic Research Project (G2000077507), and the National Nature Science Foundation of China (grant nos. 29873017, 20273026 and 20101004).

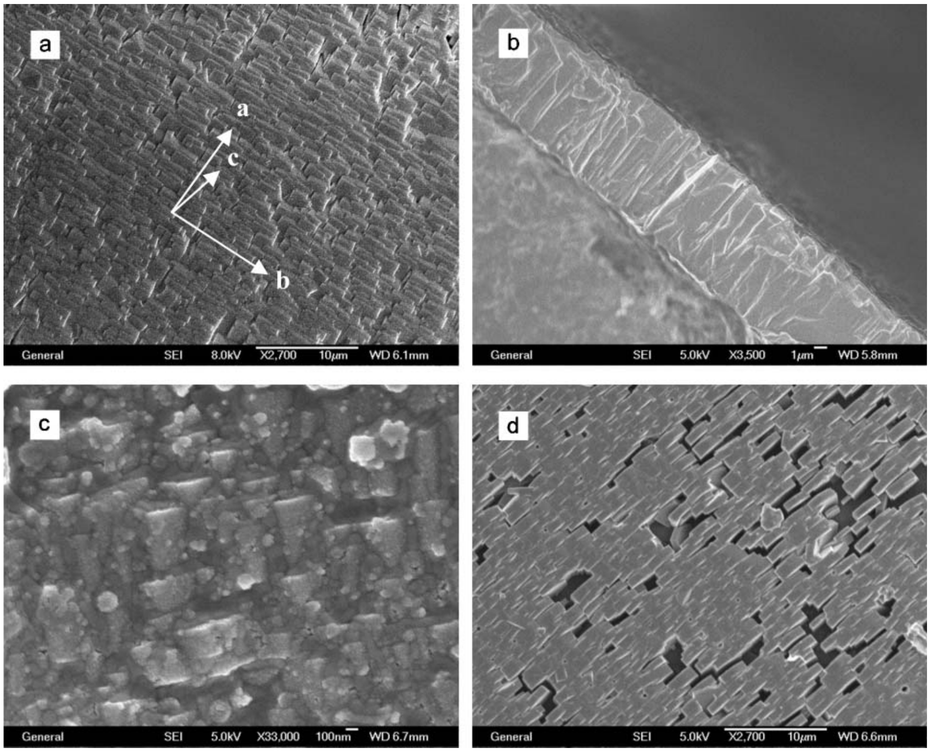

Fig. 3 FE-SEM images of the surface of the zeolite MFI {00l} basal face reacting in a solution with a composition of 40 SiO_2 : 8 TPAOH : 8000 H_2O : 160 EtOH after (a) 12 h, (b) cross-section image of (a), (c) 3 h and (d) 6 h crystallization at 180 °C.

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