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Oriented growth of MCM-22 zeolite films

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MCM-22 zeolite films have been grown with layers vertical to the substrate under hydrothermal synthesis conditions, and characterized by X-ray diffraction and scanning electron microscopy.

In situ synthesis of zeolites and molecular sieves on various supports is of significant importance in utilizing the well defined intracrystalline pores for membrane separation, membrane catalysis and molecular sensing. A variety of zeolites and molecular sieves, *e.g.* ZSM-5 or silicalite-1,[1,2] zeolite A[3,4] and UTD-1,[5] have been grown into films and membranes. Most zeolite films and membranes are obtained with random crystal orientation, and better performances are expected for an oriented zeolite film or membrane.[6,7] Particularly for zeolites with one- or two-dimensional pore systems, the accessibility of zeolite pores in a film depends on crystal orientation. Zeolite MCM-22, which is a good catalyst in a variety of reactions,[8,9,11] has an unusual layered structure and dual two-dimensional pore systems.[10] Here we report the oriented growth of MCM-22 films under static hydrothermal synthesis conditions.

The synthesis mixture was prepared using silica sol (25wt% SiO_2), sodium aluminate, hexamethyleneimine (HMI), sodium hydroxide and deionized water. 0.8 g sodium hydroxide and 1.7 g sodium aluminate was dissolved in 135 g deionized water, then 10.3 g HMI and 50.2 g silica sol were added with stirring. The molar composition of the resultent mixture was $13.5Na_2O:5Al_2O_3:100SiO_2:4500H_2O:50HMI$. After stirring for 1 h at 303 K, the mixture was transferred into a Teflon-lined autoclave, and a glass plate was immersed vertically in the mixture. Crystallization was carried out at 423 K for 96 h. The powder product and the glass plate were separated, washed with deionized water, and then dried at 353 K. Calcination was carried out at 813 K for 10 h with a temperature ramping rate of 2 K min^{-1}. The products were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM).

The XRD pattern of the as-synthesized powder sample [Fig. 1(a)], characterized by both sharp and broad peaks, agrees well with that of the as-synthesized MCM-22 sample, and the XRD pattern of the calcined powder sample [Fig. 1(b)], with only sharp peaks, is consistent with that of MCM-22.[12] Although the detailed structure of as-synthesized MCM-22 is unclear, it is clear that as-synthesized MCM-22 and the MCM-22 sample have the same *a*-parameter, but the *c*-parameter of MCM-22 is smaller than that of as-synthesized MCM-22. As-synthesized MCM-22 exhibits two separated XRD peaks at 2θ 6.5 and 7.2° for (002) and (100), respectively, whereas the two reflections overlap into one peak in MCM-22. Compared with the XRD patterns of as-synthesized MCM-22 and MCM-22 powder samples, no other phases except for as-synthesized MCM-22 and MCM-22 are present in the as-synthesized and calcined films [Fig. 1(c) and (d)]. The broad and sharp peaks of the as-synthesized film are unambiguously from as-synthesized MCM-22, and the sharp peaks of the calcined film are from MCM-22. The as-synthesized MCM-22 film gives an intense peak for (100) but very weak peaks for (001), (002), (101) and (102), which indicates that the MCM-22 crystals are grown with a preferred orientation. As the layers of MCM-22 are linked together along the [001] direction, the MCM-22 layers in the film are vertical to the substrate.

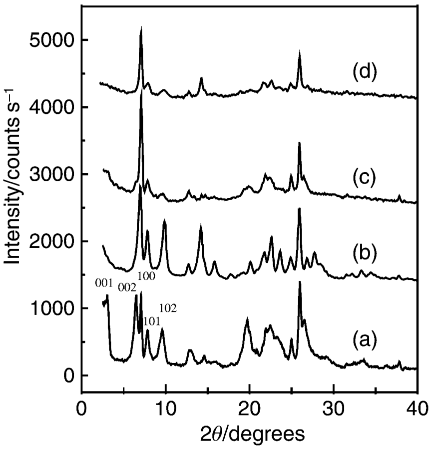

Fig. 1 XRD patterns of the as-synthesized MCM-22 powder (a), MCM-22 powder (b), as-synthesized MCM-22 film (c) and MCM-22 film (d).

SEM micrographs of MCM-22 crystals and the MCM-22 film are depicted in Fig. 2. MCM-22 crystals show stacked-thin-disk morphology. Most particles are aggregates of MCM-22 crystals intergrown in the [001] direction as illustrated in Fig. 2B. Sometimes intergrowth also occurs in the [100] direction. The MCM-22 film shows continuous intergrowth of MCM-22 crystals. The aligned-thin-sheet surface morphology, similar to that of MCM-22 crystals, further demonstrates that the MCM-22 layers are vertical to the substrate. The film has some cracks along the layer direction. Because as-synthesized MCM-22 lacks interlayer linkages and the *c*-parameter is larger than that of MCM-22, the formation of these cracks is ascribed to the contraction of the *c*-parameter during calcination. A cross-section micrograph (Fig. 2D) shows that the film has a thickness of *ca.* 5 μm. Only a monolayer of MCM-22 crystals is grown on the substrate and these crystals are largely normal to the substrate.

The formation of oriented zeolite films and membranes is closely related to the nucleation and crystal growth of zeolites. It has been demonstrated that completely oriented LTA-type zeolite films can be prepared by the intergrowth of oriented seed crystals.[6] Oriented zeolite films and membranes, *e.g.* of MFI-type[13,14] and AFI-type,[15] have also been prepared by direct hydrothermal syntheses. Zeolite crystals tend to orient with the largest crystal faces parallel to the smooth substrate, whereas crystal growth is preferred in the direction with the largest crystal growth rate vertical to the substrate. For thin disks, MCM-22 crystals would laterally lie on the smooth substrate. Thus, the vertical growth of MCM-22 film is not due to the orientation of the MCM-22 crystals. The high growth rate of the MCM-22 layer structure, indicated from the thin-disk-like crystal morphology, appears to be responsible for the vertical growth.

For MCM-22, shape-selective reactions occur in the channels and supercages, whereas the surface active sites can reduce the selectivity.[11] The low outer surface area vertically oriented MCM-22 film, for which the two pore systems are easily

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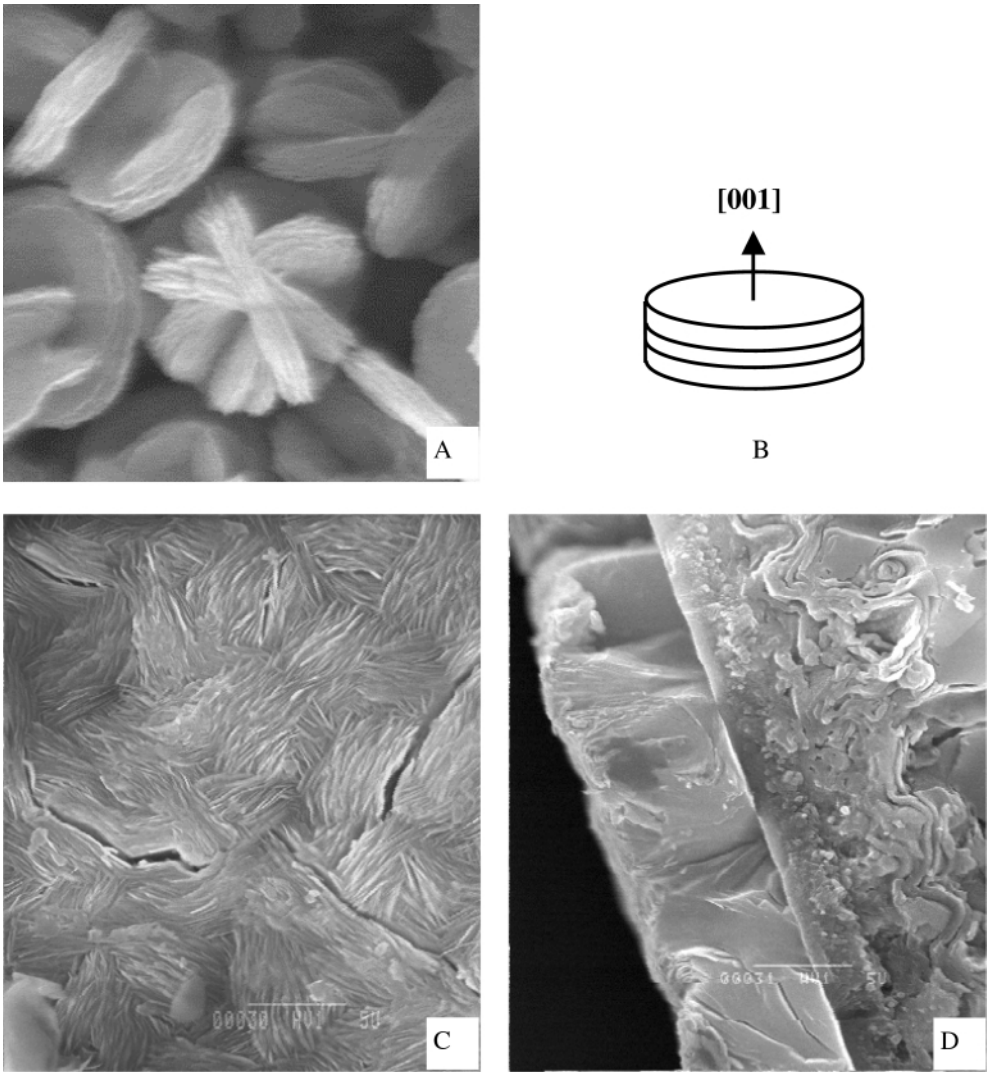

Fig. 2 SEM micrograph of the MCM-22 powder sample (A), the schematic intergrowth of MCM-22 crystals (B), and SEM photographs of the surface (C) and cross section (D) of the oriented MCM-22 film.

accessible to reactants may be a highly selective catalyst for some reactions.

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