Microwave-induced Fabrication of MFI Zeolite Crystal Films onto Various Metal Oxide Substrates

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Thin films comprising oriented and micropatterned Si-MFI molecular sieves have been synthesized with metal oxide nanoparticles as a chemical glue by using microwave irradiation technique and soft lithography which can be applied to uniform coating of micropatterned molecular sieves.

Zeolite molecular sieves and mesoporous materials are promising candidates for designing nanoscopically engineered materials because of their well-defined pore structures, the possibility of tailored synthesis with useful optical, electronic, and magnetic properties.[1] Many strategies have been reported to synthesize nanostructured materials with various shapes, into membranes or in thin films form.[2] Thin films composed of crystalline one-axis-oriented zeolite molecular sieves are of particular interest for applications such as separations,[3] membrane reactors,[4] and sensing devices.[5] Several preparation methods such as direct in situ growth,[6] assembly of preformed zeolite crystals,[7] and seeding and regrowth procedure[8] have been developed. Stimulated by the great potential of nano- and microscopical array of zeolites, fabrication of micropatternd zeolite films have been reported by using the micromolding of zeolite nanocrystal,[9a] direct in situ hydrothermal method,[9b] and organic molecular linkers[9c] with preformed zeolite crystals. However, to the best of our knowledge, there are no reports for the in-site growth of micropatterned zeolite crystal comprising of different dielectric constants of undercoated metal oxide layers under microwave induced synthetic technique.

Microwave technique has advantages over the conventional hydrothermal method with rapid and homogeneous heating throughout the reaction vessel and the possibility of selective heating of specific materials.[10,11] As a result, this technique finds many applications in synthesis of inorganic materials; for the fast synthesis of zeolites[12,13] and for the morphology and size controls of nanoporous materials.[14] In addition, we recently found that the MFI zeolite crystals can stack in one direction to form a fibrous morphology which gives rise to several interesting physicochemical properties including lower packing density and higher hydrophobicity as a result of the combined effects of microwave synthesis and metal incorporation.[11a] On the basis of the above observations, we propose that M–OH groups of bulk MO_x surfaces could involve the strong interaction with the zeolite.

In the present studies, the reaction mixture was made by slowly adding tetraethyl orthosilicate (TEOS) to an aqueous solution of tetrapropylammonium hydroxide (TPAOH) under vigorous stirring. The molar composition of the reaction mixture was 1TEOS:0.2TPAOH:22 or $100H_2O$. The substrate surface was coated with a thin layer of various metal oxides with or without a micropattern (see Supporting Information). Subsequently, the mixture was heated for 90 min at 438 K under 600 W of microwave power using the microwave synthesis system (CEM Corp., MARS-5). For the hydrothermal reaction, the mixture was heated at 438 K for 24 h using a convection oven. The substrate was removed from the autoclave, washed with doubly distilled water, sonicated for 10 min, dried in an oven at 373 K for 10 h and calcined in air under static condition at 773 K.

We have postulated that the selective microwave activation (heating) of Ti–OH groups of bulk TiO_2 surfaces may lead to films of zeolite crystals on substrate. Accordingly, on the basis of the assumption that the selective microwave activation would be increased with the dielectric constant of the undercoating material, we have tried undercoatings of various metal oxides of a wide range of dielectric constants;[15] WO_3 ($\varepsilon = 300$), TiO_2 ($\varepsilon = 80$–170), α-Fe_2O_3 ($\varepsilon = 12$), and SiO_2 ($\varepsilon = 4.4$). The undercoatings were formed by spin-coating precursor solutions onto glass substrates followed by calcination at 500 °C for 2 h. The SEM images show that the undercoatings have coarse surfaces with particles of 20–80 nm in size (not shown). Zeolite precursor solutions of high and low silica contents ($H_2O/SiO_2 = 22$ and 100) were prepared.

Figure 1 shows the SEM images of the MFI-crystal films on substrates with various metal oxide undercoatings synthesized using a dilute silica solution ($H_2O/SiO_2 = 100$). All MFI crystals formed on substrates exhibit a rectangular shape with rounded edges regardless of types of metal oxide undercoatings. This figure clearly shows that only a few crystals are bound on the glass substrate while those with metal oxide undercoatings provide high-density thin films of MFI crystals. In all of the latter cases, the crystals are preferentially oriented with their *b* axes perpendicular to the substrate surfaces (see Supporting Information). One can also note that the α-Fe_2O_3 undercoating provides almost a monolayer film while the TiO_2 and WO_3 undercoatings

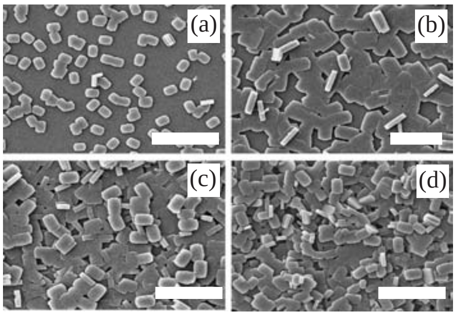

Figure 1. SEM images of as-made Si-MFI/Metal oxide/glass under MW for 90 min: (a) glass (b) Fe_2O_3 (c) TiO_2, and (d) WO_3 in a $H_2O/SiO_2 = 100$ at 438 K. Scale bar is 10 µm.

yield double or triple layers of zeolite crystals. Zeolite crystal films grown on various substrates by hydrothermal reactions have been extensively studied.[16] The similar results are also obtained from our hydrothermal reactions; the films are composed of multiple layers of zeolite crystals. The crystals are larger than those from the microwave reactions and have well developed crystal surfaces and edges (see Supporting Information). In addition, the films are all alike regardless of the nature of the substrate materials, which is in contrast to the films from microwave reactions.

The surface coverage of the films from microwave reactions of low silica content solution increases with the increase of the dielectric constant of the substrate material. This observation can be attributed to the crystal binding on the substrate is achieved by the microwave activation of the substrate materials and that the amount of microwave energy absorbed by the substrate is increased with the dielectric constant. The nature of the substrate materials influence the number of MFI layers formed on it. The Fe_2O_3 undercoating gives practically a monolayer thin film while TiO_2 and WO_3 substrates produce double or multiple layers. The high temperature and pH conditions probably cause dissolution of some part of the undercoating materials during the process. The dissolved material might become a part of the product in the form of dopant as an extraneous small particles on the surface inducing multilayer formation just like in the crystal stacks in our previous work.[12a] However, the amount of metal species in zeolite crystals are too low to detect it.

The concept of microwave selective heated surface, which is the sites for the fabrication induced by the selective absorption of microwave energy, is proposed for the synthesis of nanoporous materials. This process appears to be self-assembly process through the dehydration reaction involving adjacent zeolite crystallites by selective absorption of microwave. On the basis of the above-mentioned results, it is clear that the nature of substrate material in the microwave synthesis of MFI thin films decides the film thickness and adhesion.

We have exploited this property to form patterned MFI thin films on a patterned substrate. The TiO_2 patterns on a glass substrate were formed by applying the soft lithography technique with TiO_2 sol solution.[16] In Figures 2a–2d, we show a SEM images of the MFI thin film on a patterned TiO_2 substrate obtained by the above described microwave synthesis. After a 10 min of sonication treatment, the MFI crystals on the bare SiO_2 glass surfaces fell off, while there remained MFI crystal films that replicate the pattern of TiO_2 undercoating layer. Weaker attraction forces between bare glass and colloidal MFI crystals as compared to strong forces with patterned high dielectric TiO_2 undercoat under microwave irradiation condition resulted in the preferential growth of oriented crystals on patterned TiO_2 glass. As comparison with micropatterned zeolite crystals of the spin-coated films reported by Huang et al.,[9a] and the hydrothermal direct in situ coating reported by Wan et al.,[9b] zeolite coating under microwave induced heating have good benefits such as small and uniform size distribution, preferential orientaion, and good crystallinity of crystal, which remains the good adhesion between zeolite crystals and undercoated dielectric materials at the early stage of crystallization. This result demonstrates that by combining the contact printing and microwave synthesis technique a variety of patterned zeolite crystal films can be produced, which may find applications in many nanoscale fabrications onto metal species with various dielectric constants.

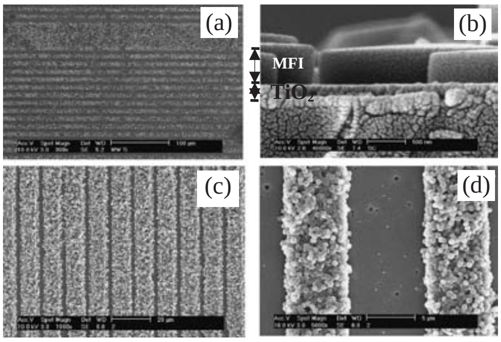

Figure 2. SEM images of (a) Si-MFI/TiO_2/glass under MI for 30 min in a $H_2O/SiO_2 = 100$, (b) cross section image of (a), (c) Si-MFI/TiO_2/glass under MI for 90 min in a $H_2O/SiO_2 = 22$, and (d) enlarged scale of patterned area of (a).

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