A novel method for tailoring the pore-opening size of MCM-41 materials

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A novel pore tailoring method is proposed by which the pore-opening sizes of MCM-41 materials can be finely tuned without significant loss in pore volume and surface area.

The disclosure of the mesoporous molecular sieve MCM-41[1] has inspired a great deal of interest in catalysis, adsorption/separation and other fields,[2,3] in particular in processing bulk molecules.[4] Most excitingly, a recent study[5] shows that MCM-41 has a comparable cracking activity for long-chain hydrocarbons and even an increased activity for bulky hydrocarbons. This finding further shows the application potentials of MCM-41 in hydrocarbon processing such as in FCC (Fluid Catalytic Cracking) and Friedel–Crafts alkylation. However, for those catalytic reactions over MCM-41 materials studied so far, shape selectivity, which is of paramount importance, has not been observed. Normally, MCM-41 catalysts can lead to the thermodynamic equilibrium of the products owing to the existence of large mesopores.

Although the pore sizes of MCM-41 materials can be varied during synthesis by choosing various surfactants with different carbon chain lengths, the smallest pore size that can be obtained appears to be around 2 nm. It is obviously hard to observe any shape or size selectivity over these materials because the kinetic sizes of most of the products of catalytic reactions are smaller than this. Therefore, fine-tuning the pore diameter of MCM-41 by post modification is desirable and imperative to achieve shape-selective catalytic properties. In this study, we present a preliminary study on a novel pore modification method as schematically shown in Fig. 1. Through selectively removing the surfactant molecules occupied at both ends of the cylindrical pore (step A), we are able to tailor the pore-opening sizes of MCM-41 materials by deposing some modifying reagents such as tetraethylorthosilicate (TEOS) (step B). The main pore body can be protected against modification by the remaining surfactant molecules. In this way, the surface area and pore volume can be largely retained while the pore-opening sizes can be fine-tuned by the number of cycles of step B. Once the template is totally removed (step C), an ink-bottle-like pore-structured MCM-41 material results.

The parent mesoporous silica was prepared from the starting gel composition of 4.5 Na_2O : 30 SiO_2 : 5.6 CTMACl : 20 EtOH : 2500 H_2O, (CTMACl = cetyltrimethylammonium chloride), at 100 °C for 3 days. The mixture was filtered off and extensively washed with deionized water and acetone to remove any residual ions and surfactants. A typical pore modification run is described as follows. (1) 100 g of the as-synthesized sample were dried at 120 °C overnight before adding to 500 ml of toluene under stirring for 2 h; 1.5 g of acetic acid was then added to the above mixture under stirring for another 2 h. The mixture was filtered off, washed with toluene and dried at 120 ^{0}C. (2) Part of the sample (*ca.* 2 g) was loaded into a chemical vapor deposition (CVD) system[6] and heated to 200 °C. At this temperature, tetraethylorthosilicate (TEOS) was fed from a saturator by high purity helium gas with a flow rate of 50 ml min^{-1} for 18 h. Chemical reaction occurred between surface silanol groups and TEOS *via* SiOH + $Si(OEt)_4 \rightarrow SiOSi(OEt)_3$ + EtOH. (3) The helium carrier gas was then switched to a water saturator to allow the attached $-Si(OEt)_3$ species to hydrolyze to generate new silanol groups for the subsequent modification runs. (4) The modified sample was calcined at 540 °C to remove the remaining surfactant molecules. Samples before and after modification were characterized by physical adsorption of nitrogen, benzene and water vapor, thermogravimetric analysis (TGA), and X-ray diffraction (XRD).

Some preliminary characterization results for a sample whose pore openings had been modified three times using TEOS are given below. Fig. 2 compares the nitrogen adsorption/desorption isotherms of the MCM-41 samples before and after modification, along with their physical adsorption data. The inset to Fig. 2 shows the Haorvath–Kawazoe pore size distribution (PSD) curves. It is seen that the pore-modified MCM-41 sample exhibits a type I isotherm with a small hysteresis loop, different from the parent MCM-41 which shows

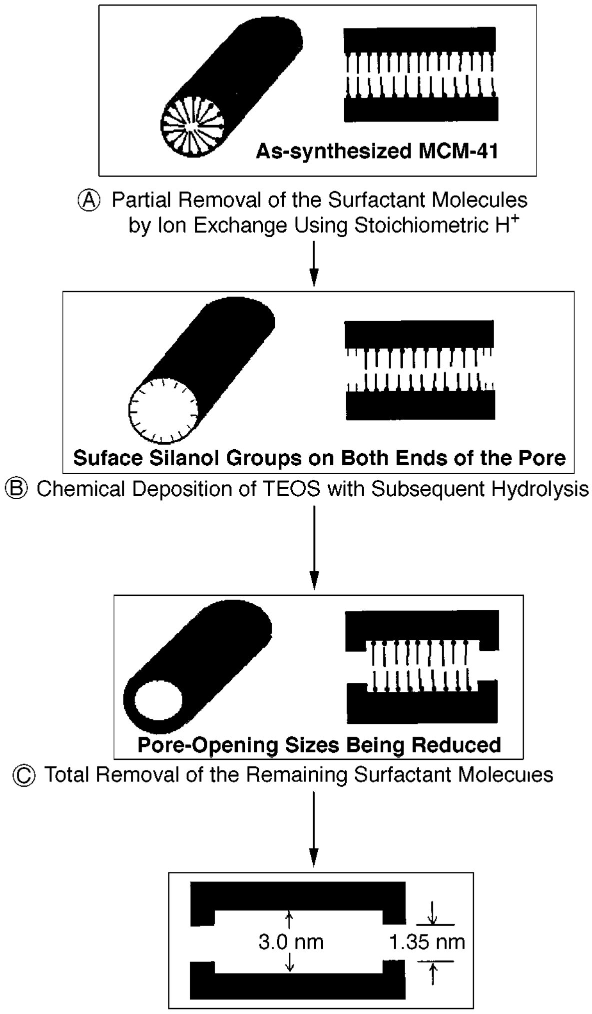

Fig. 1 Schematic model for tailoring the pore-opening size of MCM-41.

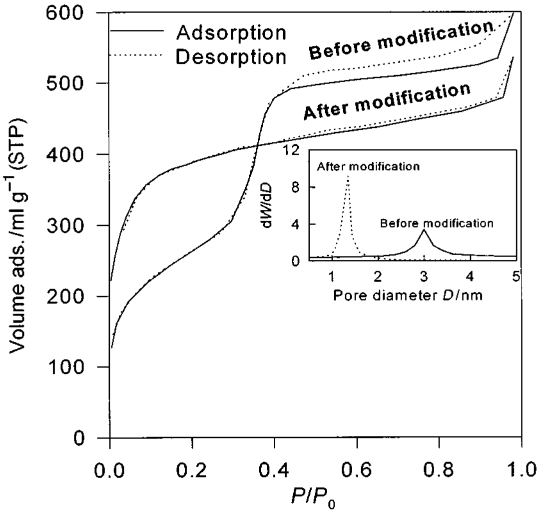

Fig. 2 Nitrogen adsorption/desorption isotherms and other physical adsorption data of the MCM-41 samples before and after pore modification.

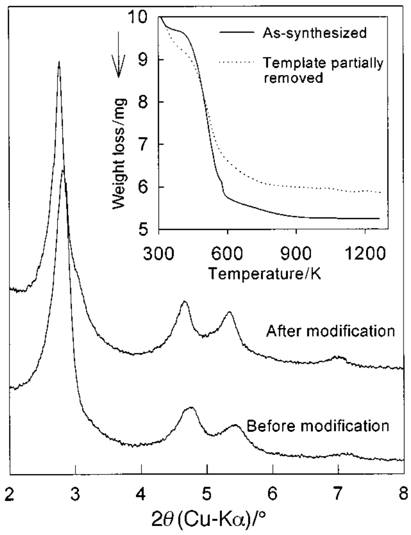

Fig. 3 XRD patterns of MCM-41 samples before and after modification and TGA curves of the parent and the template partially removed MCM-41 sample.

a type IV isotherm. The enhanced adsorption volume in the low relative pressure region indicates that the narrowed pore entrances (to the micropore size) enhanced the adsorption potential near the pore mouth region. The effective pore size, BET surface area, pore volume, benzene and water adsorption capacity had been reduced from 3.0 to 1.35 nm, 1120 to 886 m^2 g^{-1}, 0.86 to 0.69 ml g^{-1}, 8.3 to 6.5 mmol g^{-1} and 39 to 34 mmol g^{-1}, respectively, after three modification runs. These adsorption parameters support our hypothesis shown in Fig. 1 because of the fairly small reduction in porosity after modification (If the whole of the pores were modified, the pore volume would be decreased by about 80%, assuming the thickness of one silica layer to be 0.3 nm). However, the characteristic hysteresis loop for ink-bottle pore structures as documented[7] was not significant on the modified sample, presumably due to the short equilibrium time (60 s) used in our experiments. Further pore structure characterization work, along with shape-selective catalytic properties, are now being undertaken and a full paper will be published soon.

The XRD and TGA data shown in Fig. 3 further confirm our pore modification model. The XRD patterns of the MCM-41 samples before and after modification are essentially identical, demonstrating that the hexagonal pore structure was maintained after modification. The degree of template removal calculated from the TGA curves is *ca.* 15% based on anhydrous silica, indicating that most of the surfactant molecules remained inside the channels after being extracted by acetic acid solution in toluene. The 15% of the removed template is believed to be that occupying both ends of the pore.

To conclude, an effective, novel pore modification method has been proposed and the preliminary characterization data confirm our suggested modification model. This method allows for the tailoring of pore opening sizes of surfactant-templated mesophases without significant loss in pore volume and surface area.

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