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Design of bimodal mesoporous silicas with interconnected pore systems by ammonia post-hydrothermal treatment in the mild-temperature range

Zhong-Yong Yuan, Jean-Luc Blin and Bao-Lian Su*

Laboratory of Inorganic Materials Chemistry, I.S.I.S, The University of Namur (FUNDP), 61 rue de Bruxelles, B-5000 Namur, Belgium. E-mail: bao-lian.su@fundp.ac.be

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Bimodal (4 and 8 nm) mesoporous silicas with interconnected three-dimensional structure were synthesized by mild-temperature post-synthesis hydrothermal treatment of MCM-41 mesoporous materials in ammonia solution.

In the course of the exploration of novel approaches for the preparation of mesoporous materials, our efforts were directed towards the rational design for bimodal mesoporous materials with three-dimensional networks. It has been known that a secondary mesoporous network can be generated during the post-synthesis hydrothermal dealumination of microporous zeolites by steaming at high temperature, which affects favorably the catalytic behavior by reducing transport limitations and coke toxicity. This is particularly important for zeolites exhibiting unidirectional systems of pores.[1] If the one-dimensional hexagonal mesopores of MCM-41 can be interconnected by inducing the above strategies for the generation of secondary mesoporosity it should be significant on the design and synthesis of novel mesoporous materials with controlled pore systems and their applications.

The occurrence of pores with a bimodal pore size distribution in mesoporous materials is important and useful for catalysis and for engineering of pore systems.[2] Several mesoporous silicas with bimodal pore size distribution have been reported recently. Wang *et al.*[3] reported two hysteresis loops at relative pressures P/P_0 of 0.24–0.45 and 0.8–1.0 in the N_2 adsorption–desorption isotherm of their mesoporous silica obtained from a mixture of cetyltrimethylammonium bromide and tetraetylorthosilicate at room temperature. Sun *et al.*[4] presented a method to cross-link the primary mesoporous particles with triblock copolymer surfactant to form a material with a secondary pore distribution. A hysteresis loop at P/P_0 of 0.8–0.98 was also observed besides a flat hysteresis loop at 0.4–0.55 in the isotherms. The larger mesopores are very big (about 20 nm) and their distribution is quite broad. Bagshaw[5] synthesized very interesting non-ionically templated [Si]-MSU-1 mesoporous silicas with bimodal pore systems in the pore size range 3.0–9.0 nm by adding sodium salt electrolytes in the mixture gel. The presence of two different mesophases (lamellar and hexagonal) in the network is the origin of the two pore size distributions. The occurrence of two different mesophases in one network could be an advantage but also a disadvantage for catalytic reactions requiring shape selectivity. Herein, we report the first study on the formation of bimodal mesoporous materials by mild-temperature post-synthesis hydrothermal treatment. Although the post-synthesis hydrothermal restructuring is a convenient synthesis route to expand the pore size of mesoporous silicates,[6-8] to our knowledge, no bimodal mesoporous system has been reported for post-hydrotreated materials.

Surfactant cetylpyridium chloride (CPCl) was selected to be used as a template in the preparation of the primary mesoporous silicas. The synthesis was performed at room-temperature under mild alkaline conditions. CPCl, ammonia (25% solution) and water were mixed under stirring, followed by the addition of tetraethoxysilane (TEOS) with further stirring for 2 h. The composition of the mixture was 1 TEOS : 9.2 NH_4OH : 0.5 CPCl : 130 H_2O. The resultant solid was recovered by filtration, washing and drying at 40 °C. Such primary mesoporous silicas presented an XRD pattern characteristic of the MCM-41 hexagonal structure (Fig. 1a), as well as typical TEM images for a hexagonal mesoporous array. Then, 0.6 g of the above dried primary sample was added to a solution of 2 ml NH_4OH (25% solution) and 30 ml water and sealed in an autoclave, followed by heating in an oven at 100 °C for 5 days. The final product was filtered off, washed and dried at 40 °C. Calcination to remove the organic species in the mesochannels was performed in air from room-temperature to 540 °C at a rate of 10 °C min^{-1} followed by a further calcination at 540 °C for 5 h. As shown in Fig. 1b, after post-synthesis hydrothermal treatment, the main XRD line is broadened and shifted to lower 2θ angle while the higher-order lines disappear, indicating a significant modification in the pore structure, besides lattice extension. If the primary solids were treated at a temperature lower than 100 °C, the final product did not show this type of change of the diffraction pattern upon activation.

Fig. 2 shows the N_2 adsorption–desorption isotherms of the hydrotreated and calcined samples. Two distinct capillary condensation steps can be clearly seen at P/P_0 values of about 0.45 and 0.7, respectively. BJH model analysis of this material provides one narrow peak centered at 4 nm in the pore size distribution and another broad peak in the region of 5–14 nm with an evident maximum at 8 nm, showing a dual mesoporous distribution. The desorption branch also displays two distinct steps. This suggests that two pore systems with different diameters are present to form a three-dimensional pore structure.[5] The BET surface area is 750 $m^2\ g^{-1}$, while the pore volume is as high as 1.43 $cm^3\ g^{-1}$ (1320 $m^2\ g^{-1}$ and 1.29 $cm^3\ g^{-1}$, respectively, for the primary MCM-41 material). The decrease of the surface area and only slight increase in pore volume indicate the possible interconnection of the pore systems.

Confirmation of a double pore system was clearly supported by the TEM images (Fig. 3). Many large 'holes' can be seen in Fig. 3, interweaved with the parallel mesochannels with size comparable to the first pore size distribution of 4 nm in the N_2 analysis data. These larger holes are disordered and mixed in the

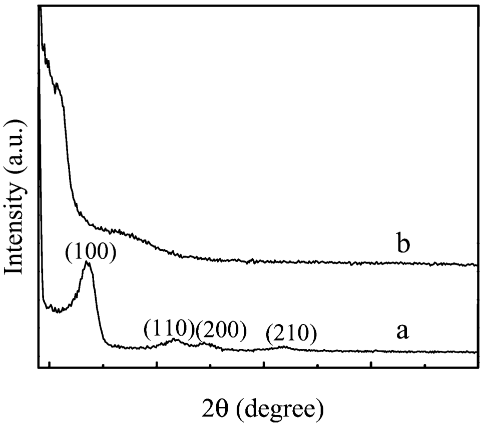

Fig. 1 XRD patterns of mesoporous silicas: (a) untreated and uncalcined, and (b) post-treated at 100 °C and calcined at 540 °C.

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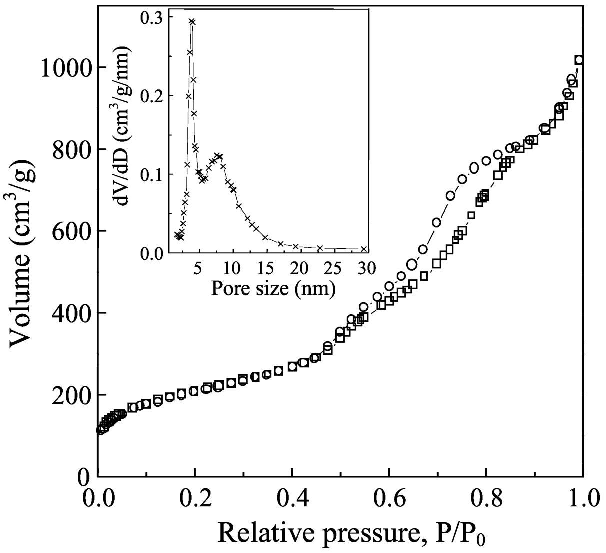

Fig. 2 Nitrogen adsorption–desorption isotherms of the hydrotreated and calcined sample and its pore size distribution plot (insert).

smaller mesopores, and they can be regarded as the secondary pores in the pore size distribution region of 5–14 nm. These two pore systems are obviously interconnected (as shown schematically in Fig. 3). Further evidence for the connectivity of the dual pore systems by HRTEM using Pt wires as a contrast agent[9] has been performed.

When the hydrothermal treatment temperature is lower than 100 °C, well-defined XRD patterns with hexagonal structure, comparable to that of the primary mesoporous silica, could be observed in the treated materials while the positions of the diffraction peaks shifted to lower angle with an increase of the hydrothermal temperature. The pore size distributions of these samples treated at temperatures lower than 100 °C show single and narrow peaks with the peak maxima increasing from 2 to 4 nm. This is different to previous results that no observable changes of the pore sizes were found when samples (synthesized in the presence of acid or alkali) were subjected to hydrothermal treatment below 100 °C.[7] If the hydrothermal temperature is higher than 110 °C, XRD and N_2 adsorption analyses revealed that the order of the mesostructure has been virtually totally lost.

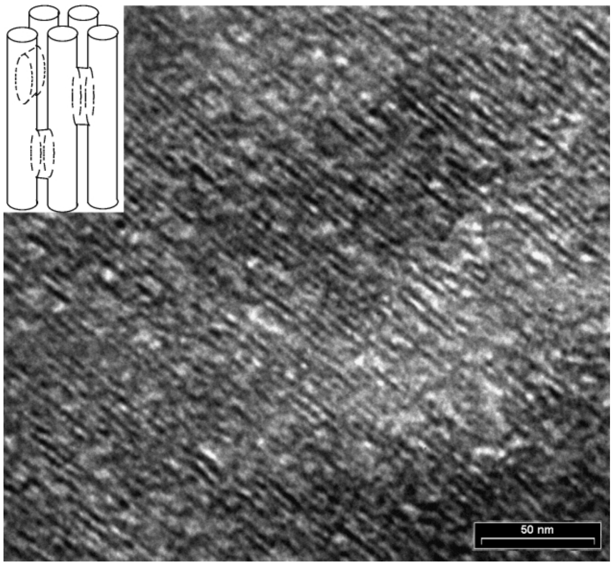

Fig. 3 Typical TEM image of hydrotreated samples showing the existence of double-mesopores. A model of pore systems is schematically shown in the insert.

Additionally, the pore structure characteristics are also affected by the treatment time. A gradual increase in the *d*-spacing and the pore size occurs in the initial stage of hydrothermal treatment, and the pore size distributions of the obtained samples are all unimodal. Only after a hydrothermal treatment of more than three days did a bimodal pore size distribution arise. In the initial stage of hydrothermal treatment lattice expansion is the main effect. Ammonia should play an important role in such a pore expansion process. Due to the volatility of ammonia, ammonia molecules should be penetrate inside the nanochannels more easily than water, and such swelled channels leads to the pore size expansion from 2.3 to about 4 nm. Since the thermal stability of surfactant CPCl is low (melting point of 86 °C), part of the surfactant species in the mesochannels may start to decompose after hydrothermal treatment for three days. Some neutral, solubilizing species, such as pyridium, may be formed which may result in further pore expansion[8] or degredation of part of the channels. Also, since some surfactant molecules would be leached out during hydrothermal treatment, the silica walls would tend to collapse inward, making the mesochannels interconnected. The above factors, supported by the colour change of the surfactant/silicate composites and elemental analysis data, cause the presence of the secondary mesoporous distribution. The porosity of these two types of mesopores can be controlled by varying the treatment time as well as the concerntration of ammonia. However, it should be noted that the creation of the secondary and larger mesopores by the ammonia post-hydrothermal treatment is quite random, similar to the dealumination process by steam treatment where Al atoms are randomly removed from the zeolite structure. It should also be noted that if the surfactant CPCl is replaced by cetyltrimethylammonium surfactant, no similar phenomenon of bimodal mesoporous distribution was observed under the present experimental conditions. The combination of the selection of low thermal-stable cetylpyridium surfactant and the action of ammonia hydrothermal treatment is necessary to prepare mesoporous silicas with bimodal porous systems.

The results briefly outlined here provide us with a new method for an alternative synthetic strategy to fabricate novel materials with tailorable pore systems and also provide further understanding of the formation mechanism of mesoporous materials. A rational design should be feasiable for the preparation of desirable pore systems by the flexible utilization of convenient techniques. Further investigation of a complete mechanism for formation of bimodal mesoporous systems and their modification by surface functionalizations, as well as their possible applications is currently in progress.

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