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Room temperature synthesis of mesoporous aluminosilicate materials

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Abstract

Mesoporous aluminosilicate materials with the MCM-41 structure and atomic Si/Al ratio of 8 have been synthesized at room temperature using aluminum chloride hexahydrate and tetraethyl orthsilicate as the sources of materials. The products were characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), nitrogen adsorption and ^{27}Al magic-angle-spinning (MAS) NMR. XRD results show that thermal stability of the product can be improved when aluminosilicate MCM-41 is synthesized following a procedure of pH adjustment from 11∼12 to 5∼6 with hydrochloric acid. NMR analysis clearly shows that both 4- and 6-coordinate aluminum is present in the calcined products. High-resolution electron micrograph first exhibits the presence of nanocrystallites, which could be regions of segregated alumina, in amorphous aluminosilicate phase.

Keywords: A. Sol–gel processes; B. Electron microscopy; B. X-ray methods; D. Silicate

1. Introduction

A new family of mesoporous materials, designated as MCM-41, has been attracting worldwide interest since their first synthesis in 1992 [1,2] due to their potential as catalysts, adsorbents, and host matrixes [3]. These applications are a consequence of their unique structure, which exhibits a regular array of uniform pore openings. However, the MCM-41 materials constructed with pure-silica framework are of limited use for various applications because of the lack of acid sites and ion-exchange capacity. Much attention has therefore been devoted to isomorphous substitution of Al [4–6] as well as Mn, V, Cr, and Ti [7–11], in the silicate network. However, up to now, all reported syntheses of these materials were performed under hydrothermal conditions (100∼150°C). According to Huo et al. [12], the acid-side synthesis of purely siliceous MCM-41 at room temperature has the advantage of shorter synthesis time and lower surfactant concentrations as compared with the basic high-temperature synthesis. We describe here the synthesis and characterization of high-quality aluminosilicate MCM-41 with Si/Al = 8 at room temperature by adjusting the pH of the reaction gel from basic to acidic conditions.

2. Experimental

A typical synthetic procedure is outlined as follows: a required amount of aluminum chloride hexahydrate was dissolved in the mixed solution of cetyltrimethylammonium bromide ($C_{16}H_{33}Me_3NBr$, CTMAB) and NaOH (solution A). Tetraethyl orthosilicate (TEOS) was added slowly to solution A while stirred. The resulting mixture with a molar composition of 1TEOS: $0.125AlCl_3$($6H_2O$:0.12CTMAB: 0.6NaOH:$111H_2O$ was stirred for 2h at room temperature in the range of pH≈11–12. After that, the pH value of the resultant mixture was adjusted to 5∼6 by the addition of 1M hydrochloric acid. The stirring was continued for 3 h at room temperature, and then the solid products were collected by filtration, followed by washing with distilled water. The resultant gels were dried in air at 90°C overnight, and then calcined at 540°C at a heating rate of 1°C/min for 24 h in air. Elemental compositions

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determined by X-ray fluorescence (XRF) shows that the Si/Al molar ratio of the calcined sample with pH adjustment is 8.6, in close agreement with the composition of the gel mixture.

3. Results and discussion

Using the above procedure, high quality aluminosilicate MCM-41 can be generated. Powder XRD results of the samples synthesised in the present work are depicted in Fig. 1. The XRD pattern of calcined sample Fig. 1a consists of one very strong peak and two weak peaks at 2.25, 3.94, and 4.55°, respectively. The first peak at 2.25° corresponds to a d spacing of 3.93 nm. The whole shape and the respective peak positions of the XRD pattern are the same as those of MCM-41 [4–6] using the same surfactant under hydrothermal conditions. For the calcined MCM-41 sample synthesized without pH adjustment in Fig. 1b (i.e. obtained after the addition of TEOS and stirring the aluminosilicate gel mixtures for 5 h at room temperature), only a single intense reflection is observed at 2.25°. The peaks are shifted to higher 2θ angles in comparison with the as-synthesized sample (Fig. 1b). This result indicated that calcination leads to a contraction of unit cell accompanied by the condensation of Si–OH groups. Such a large lattice contraction (about 15%) upon calcination of MCM-41 sample is similar to those reported previously by other researchers [13]. On the contrary, the lattice contraction for the other sample synthesized by pH adjustment to 5∼6 is less than 5%, which is in agreement with those reported by Kim et al. [13] who prepared the aluminosilicate mesoporous materials following a procedure for pH adjustment to 10.2 repeated three times during hydrothermal synthesis of MCM-41. The much decreased lattice contraction implies that the thermal stability of MCM-41 obtained at room temperature has been markedly improved by adjusting the pH of the aluminosilicate gel mixture from 11∼12 to 5∼6. Because lower pH speeds up the kinetics of silica polymerization, the improvement of the thermal stability is believed to be due to the increased degrees of silanol group condensation in MCM-41 resulted from equilibrium shifts for the silicate polymerization.

TEM observation (Fig. 2) of calcined sample with pH adjustment shows the regular hexagonal array of uniform channel characteristic of MCM-41. A representative electron diffraction pattern (Fig. 2), with the MCM-41 in the same orientation, confirms the periodicity of the structure. After the TGA/DTA experiment of the calcined MCM-41 up to 840°C, the XRD results show that the hexagonal structure of the calcined MCM-41 is still present.

The calcined MCM-41 with pH adjustment is further characterized by a N_2 adsorption isotherm (Fig. 3). A big jump of adsorbed N_2 volume at relative pressure 0.2∼0.3 confirms the presence of the typical mesoporosity of the calcined MCM-41 material. The pore size distribution, which was calculated from the adsorption curve using BJH model, shows an average pore size of about 2.5 nm and half-height width of 0.4 nm. The wall thickness of about 2.04 nm was estimated with the d spacing value of the (100) reflection (4.54 nm in Fig. 1a)

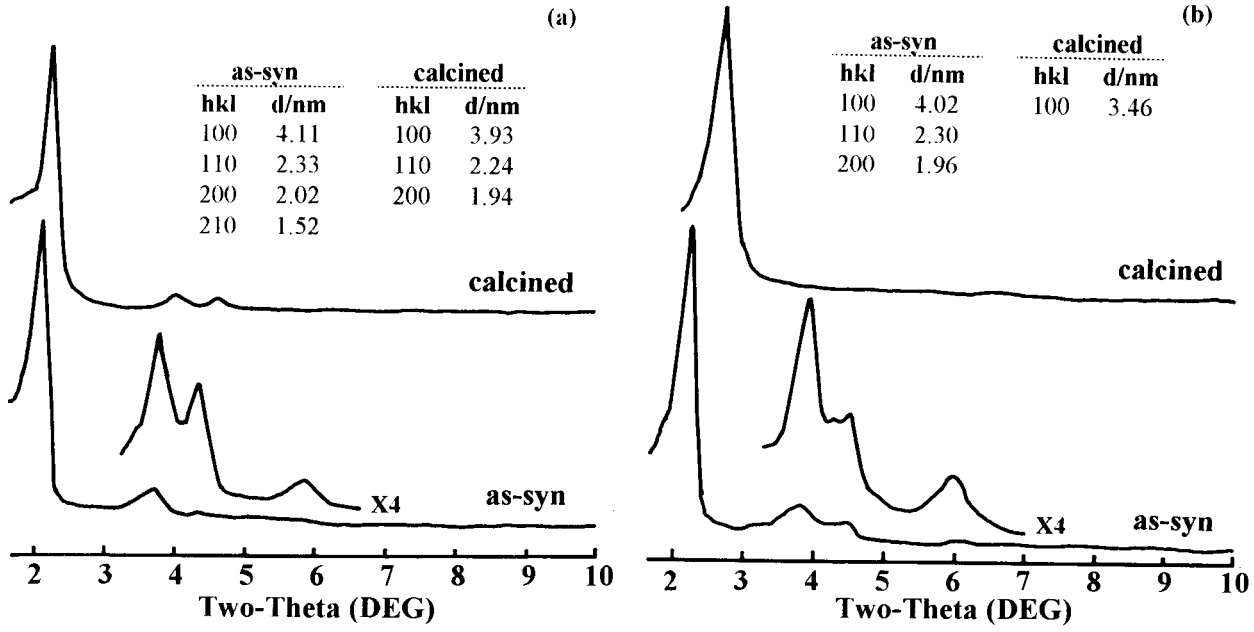

Fig. 1. XRD patterns of MCM-41 samples obtained using a Cu$K\alpha$ X-ray source: (a) aluminosilicate MCM-41 synthesized following a procedure for pH adjustment to 5∼6 with hydrochloric acid; (b) aluminosilicate MCM-41 synthesized without pH adjustment. The as-synthesized samples were washed with distilled water and dried in oven at 90°C. The calcination of the samples was performed in air at 540°C for 24 h.

and the pore diameter determined for the MCM-41 materials. Nitrogen adsorption experiments yielded a BET surface area of 611m^2/g, which is rather lower than that of the purely silicate MCM-41 materials. Although the present procedure can improve the degree of silanol group condensation, because of the high aluminium content of the solid, dealumination, which results in deterioration of the quality of MCM-41 materials, played a significant role during template removal.

Further evidence of the eduction of alumina from the molecular sieve framework is provided by ^{27}Al MAS NMR spectrum of the sample after calcination shown in Fig. 4. The spectrum contains a single resonance from 4-coordinate Al at about 53.669 ppm and a weak signal at about −5.459ppm from 6-coordinate, indicating both tetrahedral framework aluminum and octahedral extra-framework aluminm were present.

High-resolution electron micrograph of the calcined sample with pH adjustment exhibits some ordered

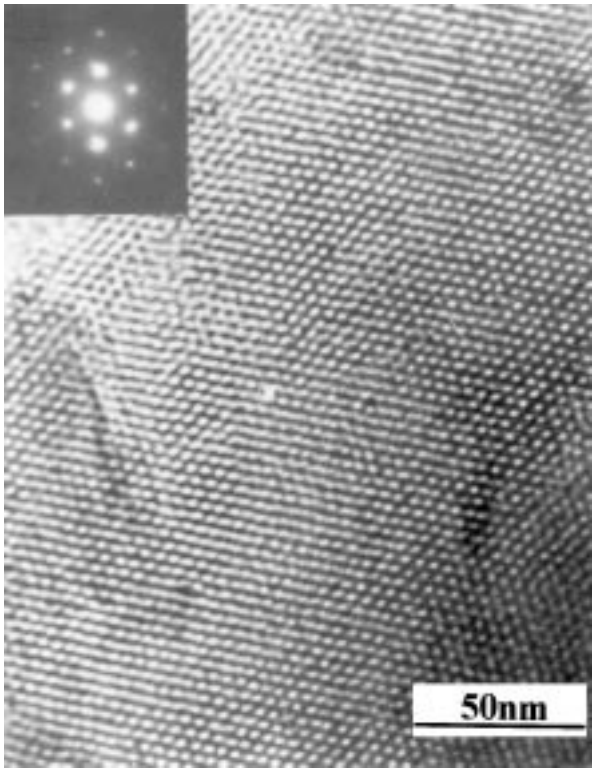

Fig. 2. Representative transmission electron micrograph of calcined MCM-41 synthesized with pH adjustment was obtained with a JEOL JEM-200CX. Inset: selected-area electron diffraction pattern.

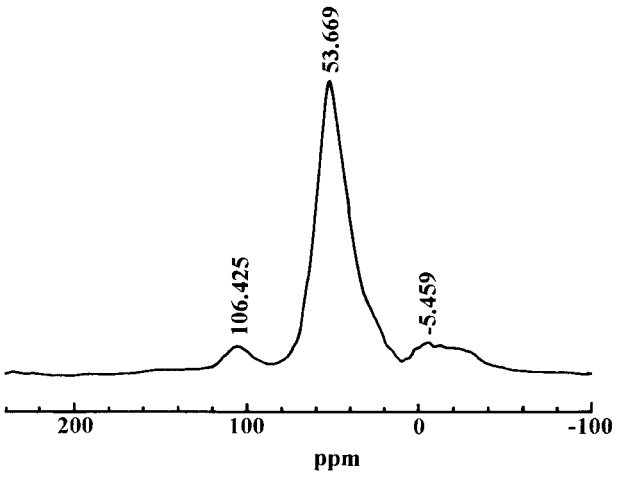

Fig. 4. ^{27}Al MAS NMR spectra of calcined aluminosilicate MCM-41 sample synthesized with pH adjustment as recorded using a MSL-300 spectrometer.

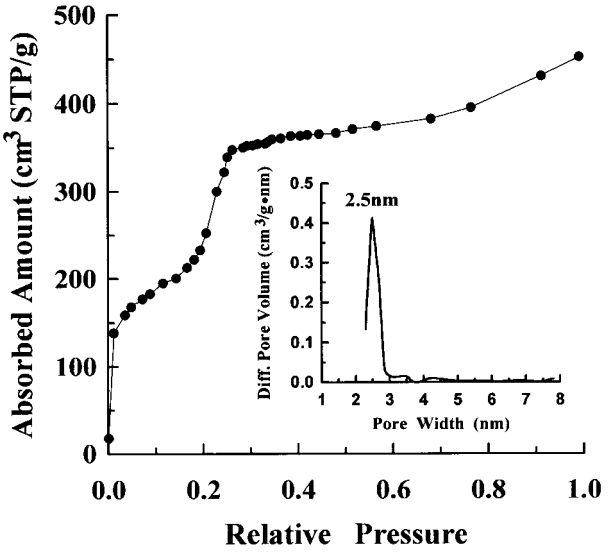

Fig. 3. Adsorption isotherm of nitrogen at 77 K on calcined sample synthesized with pH adjustment. The inset is the pore size distribution curve (max at 2.5 nm) calculated from the adsorption using the Barrett–Joyner–Halenda formula.

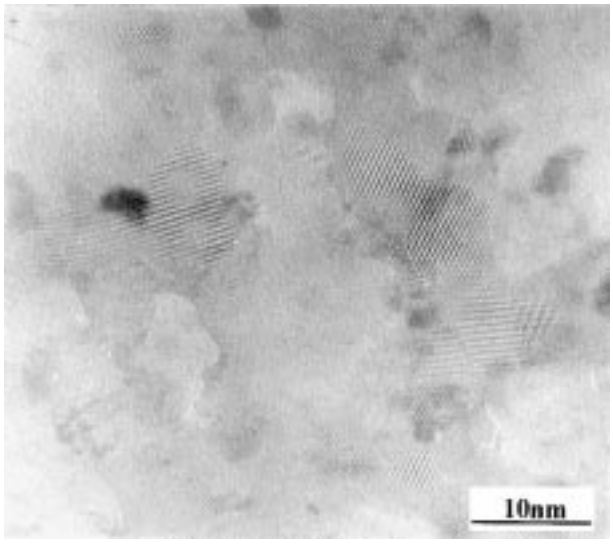

Fig. 5. Representative HRTEM image of calcined aluminosilicate MCM-41 sample synthesized with pH adjustment. This image was obtained on a JEOL JEM-200CX at accelerating voltage of 200 kv with atomic resolution (less than 0.2 nm). Arrows indicate position of ring nanocrystallite.

crystalline microdomains (from ca 2 to 10 nm), with a characteristic ring-nanocrystallite morphology (Fig. 5). The nanocrystallites could be regions of educed alumina, because under the lower calcined temperature condition only crystalline alumina may be present in the silica–alumina system. This result is consistent with the phenomenon suggested by XRD and ^{27}Al MAS NMR spectrum.

4. Summary

In conclusion, it is clearly demonstrated that high quality aluminosilicate mesostructured materials, having the hexagonal array of the pores, could be synthesized at room temperature with pH adjustment from 11∼12 to 5∼6 with hydrochloric acid. Because lower pH speeds up the kinetics of silica polymerization, the thermal stability of MCM-41 material is improved. Nanocrystallites, which could be regions of segregated alumina, were observed in aluminosilicate mesoporous materials for the first time.

Acknowledgements

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