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Facile H$_2$O$_2$ Hydrothermal Synthesis of Bimodal Mesoporous Silica MCM-48 Spheres

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The ordered bimodal mesoporous silica MCM-48 spheres were facile synthesized by mild-temperature post-synthesis H$_2$O$_2$ hydrothermal treatment of as-synthesized MCM-48. The results showed that H$_2$O$_2$ is indispensable for simultaneously removing organic templates and forming ordered bimodal mesoporous silica MCM-48 spheres. The bimodal mesoporous MCM-48 was characterized by X-ray diffraction, transmission electron micrographs, FT-IR, and N$_2$ adsorption-desorption, and a possible mechanism was proposed for the formation of bimodal mesoporous MCM-48.

Key words: MCM-48, Bimodal mesoporous silica, Hydrothermal method, H$_2$O$_2$

I. INTRODUCTION

Since the discovery of M41S family in 1992 [1], drastic progress in the synthesis of ordered mesoporous silica materials has been carried out due to their wide potential applications in adsorption, catalysis, separation, sensor, drug delivery, and nanotechnology [2]. Especially, there is a great deal of interest in the synthesis of mesoporous silica materials with various framework structures, pore sizes, and morphologies [1, 3]. Recent studies showed that the external morphology of mesoporous silica materials was one of the major factors to influence their practical applications. For instance, mesoporous silica spheres used as matrix materials for chromatographic separations showed a superior separating ability than commercial porous silica [4], and the hollow mesoporous silicate spheres with a 3D pore-network exhibited excellent store and release properties of drug (e.g. aspirin) [5].

Among these mesoporous materials, the synthesis of hierarchical porous silica materials [6–13] as well as silica fine particles on a nanometer scale [14–16] has been studied extensively. The mesoporous materials with a bimodal pore size distribution exhibit important and valuable application in catalysis and porous systems [17], because the large and small pores play a cooperative role as gas or fluid paths and molecular adsorption sites or reservoirs, leading to highly functional catalyst supports and adsorbents. Up to now, most of the hierarchical porous materials are mainly synthesized by using mixing templates method. However, such mixing templates strategy does not necessarily result in the desired bimodal mesopores, because often the co-template just leads to a unimodal pore system. Although the post-synthesis hydrothermal restructuring is a convenient synthesis route to expand the pore size of mesoporous silicas [18], there is little report concerning the formation of bimodal mesoporous silica materials by post-synthesis hydrothermal treatment [8]. In this work, we study the first synthesis of bimodal mesoporous silica MCM-48 spheres with a cubic mesostructure using the H$_2$O$_2$ post-hydrothermal treatment when simultaneously removing the organic templates.

II. EXPERIMENTS

All commercial chemicals were used without further purification. A typical synthesis procedure for the as-synthesized mesoporous MCM-48 was as follows: 0.745 g (2.05 mmol) of cetyltrimethylammonium bromide (CTAB) was dissolved in 30 g of deionized water, and then stirred at 30°C until all CTAB was dissolved. To resulting solution, 15 mL of ethanol was added, and the mixture was further stirred for 5 min. After the addition of 4 mL of ammonia (27% aqueous solution, 56 mmol), and stand for 20 min, 1.2 mL (5 mmol) of tetraethylorthosilicate (TEOS) was added, and the mixture was stirred under 200–400 r/min for a further 10 h. The composition of the initial gel typically was 1.0TEOS/0.41CTAB/11.2NH$_3$ (27% aqueous solution)/53EtOH/344H$_2$O. The resultant white solid was separated by filtration, washed with distilled water and dried at 70–80°C overnight. Finally, in order to remove the organic templates, we adopted two different procedures: (i) the elimination of the surfactant by cal-
FIG. 1 Powder XRD patterns of (a) as-synthesized, (b) H$_2$O$_2$ hydrothermal treated, and (c) calcined MCM-48 samples.

FIG. 2 Representative TEM micrographs of (a) calcined and (b) H$_2$O$_2$ hydrothermal treated MCM-48 materials, showing the existence of bimodal mesopores.

FIG. 3 TEM image of mesoporous silica MCM-48 spheres.

III. RESULTS AND DISCUSSION

The as-synthesized and H$_2$O$_2$ hydrothermal treated mesoporous silica exhibited similar XRD patterns characteristic of the MCM-48 cubic structure (space group Ia3d) with a high-intensity peak and two additional higher order peaks (Fig.1 (a) and (b)), which can be indexed as (211), (220), and (332) diffraction peaks, respectively. The well-resolved peaks indicate that as-synthesized mesoporous MCM-48 possesses higher order structure. After eliminating surfactant by calcination or H$_2$O$_2$ post-synthesis hydrothermal treatment, the main XRD lines are broadened and shifted to higher 2$\theta$ values (Fig.1 (b) and (c)), indicating a consequence of the network shrinkage and poor order. Obviously, the lattice distance contraction of calcined sample is larger than that of the H$_2$O$_2$ hydrothermal treatment. In practice, the surfactant elimination procedure affects the position of the (211) reflection (and consequently the $a_0$ parameter), which appears shifted to higher 2$\theta$ values for calcined sample. Compared to calcined MCM-48 sample, the (220) reflection peak of the H$_2$O$_2$ hydrothermal treated is clearly observed, indicating the presence of the ordered MCM-48 cubic structure after the surfactant elimination by H$_2$O$_2$ hydrothermal treatment, as indicated by TEM image (Fig.2(b)) which shows a wormlike mesoporous array. Interestingly, the sphere morphology with a diameter of about 350-400 nm was observed from the TEM image of H$_2$O$_2$ hydrothermal treated MCM-48 (Fig.3).

The information derived from the N$_2$ adsorption-desorption isotherms (Fig.4) is in agreement with the XRD patterns. The isotherm for calcined MCM-48 is a typical reversible type IV adsorption-desorption isotherm (Fig.4(a)). The sharpness of the isotherm in range of 0.20<$P$/P$_0$<0.35 corresponds to mesoporous...
size. The hysteresis loop in $N_2$ adsorption-desorption isotherm at low relative pressure ($P/P_0$~0.20) reflects its uniform mesopores, which limits the emptying and filling of the accessible volume [19]. The BJH model analysis of this material provides one quite narrow pore size distribution centered at 24 Å (Fig.4(b)), indicating the existence of uniform mesopores. The presence of bimodal pore systems in the $H_2O_2$ hydrothermal treated MCM-48 is illustrated by the $N_2$ adsorption-desorption isotherm (Fig.4(c)). The curve shows two well-defined adsorption steps. The first, at an intermediate relative pressure ($0.20<P/P_0<0.35$), is characteristic of type IV isotherm and can be related to capillary condensation of nitrogen inside the intra-nanoparticle mesopores. Its sharp curvature suggests the existence of uniform and cylindrical small mesopores ($\sim 2.5$ nm). The second step, at a high relative pressure ($P/P_0>0.45$), corresponds to the filling of the large mesopores among the primary nanoparticles. An important distinction between the calcined and $H_2O_2$ hydrothermal treated MCM-48 is the presence of the hysteresis loop for $H_2O_2$ hydrothermal treated MCM-48 at higher relative pressure ($P/P_0>0.45$) which is a consequence of nitrogen filling the textural mesopores. Interestingly, the BJH model analysis of this material provides one narrow peak centered at 25 Å in the pore size distribution and another broader peak in the region of 3~5 Å with an evident maximum at 3.6 Å, showing a dual mesoporous distribution (Fig.4(d)). Desorption branch also displays two distinct steps which suggest that two pore systems with different diameters are present [20].

TEM image also demonstrated the existence of a double pore system (Fig.2(b)). It was found many larger “holes” are disordered and mixed in the smaller mesopores, and these large holes can be regarded as the secondary pores. It was also found there is obvious interconnection between the secondary pores and smaller mesopores. The obvious low surface area and slightly low pore volume of the $H_2O_2$ hydrothermal treated MCM-48 (1060 m$^2$/g and 0.95 cm$^3$/g), when compared to the calcined MCM-48 (1729 m$^2$/g and 1.06 cm$^3$/g), can be understood of taking into account the thickness of the respective pore walls (estimated from XRD and porosity data). It is noteworthy that the strengthening of the MCM-48 pore wall could favour high thermal and/or hydrothermal stability. Furthermore, the decrease of the surface area and slightly decrease of pore volume imply existence of the possible interconnection of the pore systems.

IR spectra of all three samples are shown in Fig.5. The broad band in the range of 3700~3000 cm$^{-1}$ is assigned to a superposition of several stretching modes of Si–OH or H$_2$O group vibration. The band around 1630 cm$^{-1}$ is attributed to the bending vibrations of water molecules. The bands at 1215, 1090, 800, and 470 cm$^{-1}$ are assigned to symmetric or asymmetric Si–O–Si stretching vibrations. The band at 960 cm$^{-1}$ is generally assigned to Si–O stretching vibration of
Si–O–R+ groups in the as-synthesized state and to Si–OH in the calcined state as well. The band in the range of 3000–2800 cm⁻¹ is due to adsorbed substances containing CH groups [21]. Compared to the as-synthesized MCM-48 (Fig.5(a)), after calcination or H₂O₂ hydrothermal treatment, the bands between 2921 and 2852 cm⁻¹ (stretching vibrations of CH₂ and CH₃ groups) completely disappear, indicating that organic moiety was completely decomposed. Interestingly, the H₂O₂ post-hydrothermal treatment can also completely remove organic template, which can be attributed to oxidation decomposition of the surfactant molecules under H₂O₂ hydrothermal treatment condition.

The TGA curve of the as-synthesized MCM-48 sample exhibits an initial weight loss (2.47%) at an onset temperature of about 50 °C, corresponding to the removal of the adsorbed water molecules. The second weight loss (49.07%) occurs between 150 and 320 °C and corresponds to the decomposition of the CTAB surfactant species. The third weight loss (7.81%) occurs between 350 and 600 °C and corresponds to the coke calcination and loss of silanol groups (Fig.6(a)). The TGA curve of the H₂O₂ treated MCM-48 sample displays an initial weight loss (2.45%) at an onset temperature of about 50 °C, corresponding to the removal of the adsorbed water molecules. Over 100 °C, only slight weight loss (4.21%) is observed (Fig.6(b)), indicating that the organic templates were removed completely after H₂O₂ post-hydrothermal treatment.

Only after the H₂O₂ hydrothermal treatment did a bimodal mesoporous size distribution arise, which we think H₂O₂ should play an important role. Because H₂O₂ was decomposed to product O₂ and H₂O, O₂ molecules should be penetrated inside the nanochannels more easily than water, and such swelled channels, leading to the pore size expansion from 24 Å to about 25 Å. On the other hand, since the thermal stability of surfactant CTAB is higher (melting point of more 230 °C), the surfactant molecules may be difficult to decompose under 100 °C hydrothermal condition, but it could be decomposed by O₂ oxidation after H₂O₂ hydrothermal treatment, giving rise to some small species which may result in further pore expansion [22] or degradation of part channels. Therefore, the H₂O₂ amount should exceed 60 mL for 0.5 g as-synthesized MCM-48 solid in order to completely remove organic templates and simultaneously form ordered bimodal mesoporous MCM-48 materials. Also, since some surfactant species could be leached out during hydrothermal treatment, the silica walls would tend to collapse inward, making the mesochannels interconnected. However, it should be noted that the creation of the secondary and larger mesopores by the H₂O₂ post-hydrothermal treatment is quite random. It should also be noted that if the H₂O₂ is replaced by ammonia, no similar bimodal mesoporous distribution was observed under the hydrothermal condition. As a result, the oxidation action of H₂O₂ hydrothermal treatment is necessary to prepare mesoporous MCM-48 with bimodal porous systems.

IV. CONCLUSION

We report a novel preparative procedure yielding narrow distributed bimodal mesoporous MCM-48 spheres by using H₂O₂ post-hydrothermal treatment method. The bimodal mesopores are framework pores and mesochannels interconnected. It is believed that H₂O₂ plays an important role in simultaneously removing organic templates and forming ordered bimodal mesopores. Taking into account the quick and convenient preparation of the bimodal mesoporous materials under mild hydrothermal condition, it is expected that this material has a large range of possible applications such as catalysis and sorption.

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