

Nanosphere of Ordered Silica MCM-41 Hydrothermally Synthesized with Low Surfactant Concentration

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Nanospherical MCM-41 silica has been hydrothermally synthesized for the first time in the sodium hydroxide medium with low surfactant concentration. The average size of the nanosphere is about 105 nm.

The non-porous and porous silica beads of micrometer size have been widely used in many ways such as in packing material of chromatography, in catalysis, in bio-separation, etc. However, silica spheres of nanometer size have been urgently needed in above fields recently. For example, in capillary electrical chromatography (CEC)¹⁻³ the nanometer-sized silica beads⁴ may be coated with polymers and used as reversed-phase packings with controlled hydrophobic properties.

Grün et al.⁵ first reported the synthesis of spherical silica particles featuring an MCM-41 structure, whose size ranged from 400 to 1100 nm. Their synthesis procedure was a modification to Stöber's synthesis⁶ of monodisperse silica spheres by adding a cationic surfactant to the reaction mixture during the formation of MCM-41. Recently, Büchel et al.⁷ reported a novel method for synthesis of submicrometer-sized (~700 nm) solid core/mesoporous shell silica spheres. Their method was based on a combination of the Stöber approach,⁶ the Unger growth process,⁸ and the Kaiser approach.⁹ The spheres obtained by Büchel et al. were almost perfect in shape and no agglomeration took place. The pores were randomly distributed in the siliceous shell. However, synthesis of the mesoporous silica nanospheres has not been available in literatures.

The present paper describes a preparation of MCM-41 silica nanospheres ranging from 60 to 140 nm. Our method bases on a hydrothermal process with a low surfactant concentration and a sodium hydroxide medium. This concentration of surfactant is much lower than that of previous synthesis of MCM-41,^{5,7,10} although it is not lower than that used in synthesis of metal nanoparticles.¹¹

In the hydrothermal preparation, hexadecyltrimethylammonium bromide (CTAB) was used as cationic surfactants,¹² while tetraethyl orthosilicate (TEOS) served as the silica source. During preparation strong stirring was used to inhibit agglomeration of the formed beads. Aqueous sodium hydroxide was used as base. The mole ratio of starting reactants is 1TEOS: 0.125CTAB: 1197H₂O: 0.31NaOH. The synthesis procedure was as follows: (1) 3.5 cm³ of NaOH (2 mol dm⁻³) solution was mixed with 480 cm³ distilled water; (2) 1.0 g of surfactant was added into the solution with stirring and heating; (3) when the solution became homogeneous, 5 cm³ of TEOS were dropped, giving rise to a white slurry, then keeping the slurry at temperature of about 350 K; (4) after 2 h, the resulting product was filtered, washed with distilled water, dried at ambient temperature, followed by calcination in air at about 820 K for 4 h.

The X-ray diffraction pattern was recorded on a D/max-R

Rigaku diffractometer with Cu K α radiation. The sample was scanned from 1.4° to 9.6° (2 θ) with a step size of 0.02° and a count time of 1s at each point. The transmission electron micrographs (TEM) were obtained on a Hitachi-800 microscopy operated at 200 kV. For TEM analysis, specimen were prepared by dispersing the as-obtained powder in alcohol and then placing a drop of the suspension on a copper grid coated with a transparent graphite, followed by drying. Adsorption and desorption isotherm for nitrogen was obtained at 77 K using a Micromeritics ASAP-2010. The sample was outgassed at 573 K for 12 h before isotherm measurements. Specific surface area value was evaluated using the BET (Brunauer-Emmett-Teller) equation.

The XRD pattern (Figure 1) of the sample exhibits four sharp Bragg peaks, which can be indexed as (100), (110), (200) and (210) of MCM-41^{10, 13} (Figure 1, a). The repeat distance a_0 between two pore centers in MCM-41 can be calculated from

$$a_0 = (2/\sqrt{3})d_{100} \quad (1)$$

The pore diameter can therefore be calculated from a_0 by subtraction of 1.0 nm, which is an approximated value of the pore wall thickness.¹⁴ Using the obtained d_{100} value, the pore diameter is finally determined as 3.0 nm.

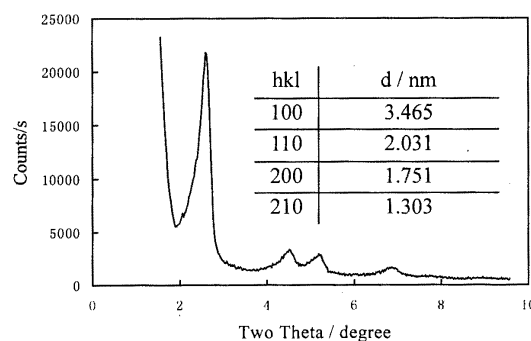


Figure 1. X-Ray diffraction pattern of the sample obtained after calcination at about 823 K for 4 h.

We have also investigated the properties of nitrogen adsorption and desorption for the MCM-41 particles with sizes of around 100 nm. Nitrogen isotherms of the sample is shown in Figure 2, where the isotherms can be classified as the type IV isotherm according to the IUPAC nomenclature.¹⁵⁻¹⁶ A linear increase of absorbed volume at low pressures is followed by a steep increase in nitrogen uptake at relative pressure of $0.24 < p/p_0 < 0.34$, which is due to capillary condensation inside the mesopores. The long plateau at higher relative pressures indicates that pore-filling is restricted to the inflection point at $p/p_0 = 0.30$. It is interesting to note in this figure that second steep increase occurs in nitrogen uptake and an adsorbed hysteresis loop appears at the relative pressure of $0.9 < p/p_0 < 1.0$. The

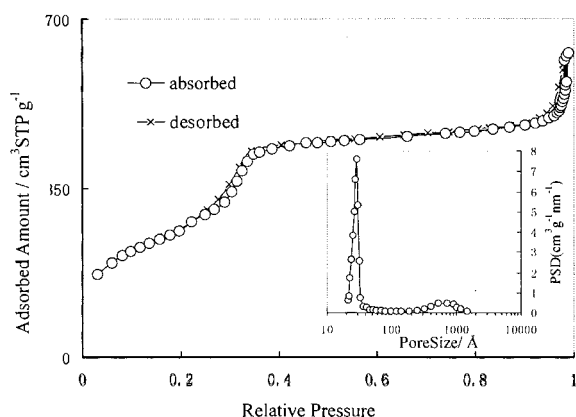


Figure 2. Nitrogen sorption isotherms obtained at 77 K and pore size distributions of the sample.

inset figure gives the pore size distribution evaluated by Barret–Joyner–Halenda (BJH) method. The results indicate that the beads possess two peaks of the pore size distribution. One narrow peak is at 3 nm and another dispersion peak is around 70 nm. A summary of all parameters obtained by nitrogen sorption and by XRD is shown in Table 1. It is seen that the results obtained by the two methods are well consistent.

Table 1. Material properties of nanospheres of MCM-41^a

specific surface area m ² /g	specific pore volume cm ³ /g	average pore diameter (XRD) nm	average pore diameter (N ₂ -sorption) nm
965	0.84	3.00	3.49 (3.04 ¹ , 70 ²)

^aSpecific surface area: BET equation; pore diameter (XRD): $d_{100} * 2/\sqrt{3} - 1.0$ nm (pore wall thickness); specific pore volume: single point volume at $p/p_0 = 0.98$; average pore diameter (N₂-sorption): $4V_p/a$, by BET. ¹: pore size at maximum of pore volume in the mesopore range; ²: pore size at maximum of pore volume in the macropore range.

The morphologies and microstructure of the obtained MCM-41 samples are clearly revealed by TEM. Figure 3a shows a typical TEM image of the samples, where nano-sized particles with round sphere or elongated sphere can be seen. The sizes of the particles range from 70 to 140 nm. HRTEM image of the sample (Figure 3b, scale bar, 44 nm) shows the existence of highly ordered hexagonal array and streak structural features, which revealed the mesoporous structure of the samples. The hexagonal array feature noted by arrow in Figure 3b is the view of the particles with its *c* axis perpendicular to the paper plane; and the streak structural feature noted by arrow head in the figure is assigned to that with *c* axis of the particles parallel to the paper plane and with *b* axis perpendicular to the paper plane. Detailed TEM investigation here shows that nominal diameters of the interstices among the nanometer spheres range from 50 to 120 nm, in accordance with the pore size distribution revealed by second peak in the isotherms (Figure 2).

In summary, nanospheres of MCM-41 silica were for the first time hydrothermally synthesized by using the sodium hydroxide medium and extremely low concentration of the surfactant. The nanospheres are ranging from 70 to 140 nm in diameter. Pores with sizes averaging 3 nm with narrow pore size distribution and sizes averaging 70 nm with broad pore size distribution are found in this materials. These two pore size distribution are assigned to the mesopore of the beads and the

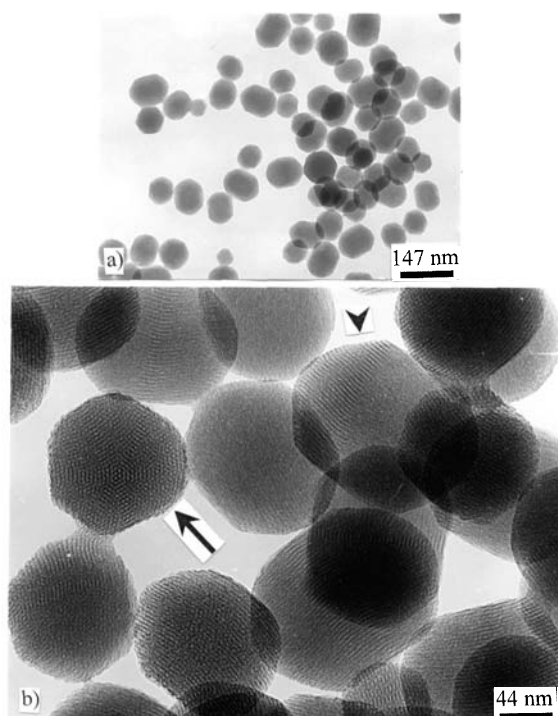


Figure 3. a) The TEM image of the calcined materials; scale bar: 147 nm, b) The HRTEM image of the calcined materials, scale bar: 44 nm.

interstices among the nanometer spheres respectively. Homogeneity, thermal stability and high specific surface area might make these silica beads suitable as adsorbents for novel applications, such as in CEC.

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