



Evolution from hollow nanospheres to highly ordered FDU-12 induced by inorganic salts under weak acidic conditions

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ABSTRACT

Sulfates have big influence on the structure and morphology of the mesoporous silicas synthesized under weak acidic conditions. The evolution from silica hollow nanospheres to doughnut-like nanoparticles, and to FDU-12 type mesoporous silicas with $Fm\bar{3}m$ symmetry can be induced by CuSO_4 during the condensation of TMOS around Pluronic F127 surfactant in weak acidic solution ($\text{pH} = 3.25$). It is noteworthy that doughnut-like nanoparticles can be obtained in the presence of lower amounts of CuSO_4 . Similar to CuSO_4 , other divalent sulfates, such as ZnSO_4 , NiSO_4 , and MgSO_4 can also induce the formation of $Fm\bar{3}m$ mesostructure. However, the presence of K_2SO_4 and Na_2SO_4 specially results in the formation of hollow nanospheres. Plausible mechanisms for the formation of FDU-12 and hollow nanospheres were also proposed.

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1. Introduction

Since their first appearance in 1990s [1], mesoporous silicas have attracted much research attention because of their innovative synthesis mechanisms, characteristic mesoscale pore structure and broad applications in catalysis, biotechnology, adsorption, and drug delivery [2–6]. Generally, mesoporous silicas are synthesized by self-assembly of the surfactant-type templates and inorganic precursors through electrostatic forces or hydrogen bonds under strong acidic or basic conditions [1,7–9]. However, the utilization of acidic or basic species brings forth some practical problems such as environmental destruction, difficulties in the *in situ* encapsulation, deterioration of the functional groups during synthesis, etc. Therefore, mild synthesis conditions should be highly desirable to avoid the use of harsh acid or base. Under mild conditions, the slow hydrolysis–condensation rates of precursors may provide possibilities to control the phase-separation behavior and the mesostructure evolution [10–13], *in situ* encapsulation of the active species such as transition metal atoms [14,15], enzyme [16] and cell molecule [17].

However, under weak acidic or basic conditions, it is difficult to synthesize typical mesoporous silicas due to the weak interactions between surfactant micelles and hydrolyzed silicon species [5]. Addition of inorganic salts may enhance the interactions and solve

this problem. It has been suggested that salts can decrease the critical micelle concentration (CMC) of the surfactants, increase the ionic strength of the synthesis solutions, and thus facilitate the self-assembly of the micelles and inorganic precursors [5]. This tangible role of salts in the formation of mesoporous silicas has been systematically studied by Yu et al., who successfully synthesized ordered mesoporous silicas in a wide range of acidity with the aid of inorganic salts [18–20]. It was found that the periodic mesoporous organosilicas could be obtained with the help of inorganic salts such as NaCl , KCl , Na_2SO_4 and K_2SO_4 [21]. Also, the morphology [22], microporosity [23], hydrothermal stability [24,25] and the induction time for the formation of mesostructure precipitation [26], etc. can be affected by inorganic salts.

It is known that mesoporous silicas like FDU-12 and SBA-16 have cubic supercages interconnected by multidirectional pore openings, allowing good accessibility for guest molecules [27–30]. Recently, cage-type mesoporous silicas were proved to be good matrix for encapsulation of chiral catalysts [31–34]. With the aid of inorganic salts (KCl), FDU-12 mesoporous silicas with highly ordered face-centered cubic $Fm\bar{3}m$ mesostructure were firstly synthesized using F127 as a template under strong acidic conditions [27]. Later on, many efforts have been devoted to the synthesis of FDU-12 type materials in strong acidic medium [35–39]. The successful synthesis of FDU-12 type materials under mild acidic conditions is rarely reported. In this paper, we reported the synthesis of FDU-12 mesoporous silicas under weak acidic conditions with the aid of inorganic salts. The influence of different sulfates like CuSO_4 , NiSO_4 , ZnSO_4 , MgSO_4 , K_2SO_4 and Na_2SO_4 on the

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structure and morphology of the materials was investigated in details. Subsequently, a mechanism was proposed to elucidate the role of inorganic salts in the structure and morphology formation of the materials.

2. Experimental section

2.1. Reagents

All materials were analytical grade and used as received without further purification. Triblock poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) co-polymer Pluronic F127 ($M_{av} = 12,600$, $EO_{106}PO_{70}EO_{106}$) was commercially available from Sigma-Aldrich Company Ltd. (USA). Tetramethoxysilane (TMOS), inorganic salts and other reagents were obtained from Shanghai Chemical Reagent Company of Chinese Medicine Group.

2.2. Synthesis

In a typical synthesis, 1.00 g of triblock copolymers F127, 1.00 g of 1,3,5-trimethylbenzene (TMB) and a desired amount of inorganic salt (sulfate) were dissolved in 60 mL of deionized water. The solution was stirred at 13.5 °C for 4 h. 3.04 g (20 mmol) of TMOS was added to the above surfactant solution (the pH value of the surfactant solution was listed in Table 1 and in some cases it was adjusted utilizing desired amount of H_2SO_4). After stirring at 13.5 °C for 24 h, the mixture was transferred into a Teflon-lined autoclave and aged statically at 100 °C for another 24 h. The precipitate was filtered off, rinsed repeatedly with deionized water and dried at ambient temperature. The as-synthesized sample was calcined in air at 550 °C for 10 h with a heating rate of 2 °C min^{-1} . The samples were denoted as $M(x)-y$, where M is the formula of inorganic salt, x is the mmol of inorganic salt and y is the pH value of the surfactant solution. For example, $CuSO_4(20)-3.60$ denotes a sample synthesized with 20 mmol of $CuSO_4$ as additive in a surfactant solution at pH value of 3.60.

2.3. Characterization

X-ray diffraction (XRD) patterns were recorded on a Rigaku RINT D/Max-2500 powder diffraction system using $Cu K\alpha$ radiation of 0.154 nm wavelength. Transmission electron microscopy (TEM)

was performed using a FEI Tecnai G² Spirit at an acceleration voltage of 120 kV. Field-emission scanning electron microscopy (FES-EM) was undertaken on a FEI Quanta 200F microscope and a HITACHI S-4800 microscope operating at an accelerating voltage of 1–30 kV. The nitrogen sorption experiments were performed at –196 °C on a Micromeritics ASAP 2020 system. Prior to the measurement, the samples were outgassed at 120 °C for at least 6 h. The Brunauer–Emmett–Teller (BET) specific surface areas were calculated using adsorption data in the relative pressure range of $P/P_0 = 0.05–0.25$. Pore size distributions were calculated from the adsorption branch using the Barrett–Joyner–Halenda (BJH) and Horvath–Kawazoe (HK) method. The total pore volumes were obtained from the amount adsorbed at a relative pressure (P/P_0) of 0.99.

3. Results and discussion

3.1. From hollow nanospheres to doughnut-like nanoparticles, and to FDU-12 induced by $CuSO_4$

At the same pH value (the pH value of the synthesis medium was adjusted to 3.25 using H_2SO_4 aqueous solution before the addition of TMOS), $CuSO_4(x)-3.25$ were synthesized with different $CuSO_4$ amount. The XRD patterns of the samples are displayed in Fig. 1. No diffraction peaks are observed in the XRD patterns of $CuSO_4(0)-3.25$ and $CuSO_4(5)-3.25$ synthesized in the presence of lower amounts of $CuSO_4$ (Fig. 1A). For the samples synthesized with $CuSO_4$ amounts of 10, 20 and 40 mmol, two diffraction peaks can be observed in the XRD patterns (Fig. 1B). It is noteworthy that the ratios of the *d*-spacings of the two diffraction peaks are very close to $(8/3)^{0.5}$. This suggests that these two diffraction peaks can be indexed to [1 1 1] and [2 2 0] reflection of the cubic $Fm\bar{3}m$ phase, which is characteristic of FDU-12 type materials [27]. When $CuSO_4$ amount is further increased to 60 mmol, no diffraction peaks can be observed in the XRD pattern of $CuSO_4(60)-3.25$ (Fig. 1A). The XRD result shows that the mesoporous silicas with $Fm\bar{3}m$ mesophase could be formed with $CuSO_4$ amount in the range of 10 to 40 mmol under weak acidic conditions.

The TEM and SEM images of $CuSO_4(x)-3.25$ are shown in Fig. 2. Aggregated hollow nanospheres with particle size of around 25 nm are clearly observed in the TEM image of $CuSO_4(0)-3.25$ (Fig. 2a). The SEM image of $CuSO_4(0)-3.25$ shows fused nanospheres (Fig. 2a, inset). It is difficult to estimate the particle size from SEM image because of the aggregation of nanospheres. TEM image of $CuSO_4(5)-3.25$ (Fig. 2b) exhibits nanospheres with hollow interior, which have a uniform particle size of about 30 nm. In the SEM image of $CuSO_4(5)-3.25$, many doughnut-like nanoparticles with average diameter of around 30 nm can be observed (Fig. 2b, inset). It is worth mentioning that silicas with doughnut-like morphology have been rarely reported. TEM images of $CuSO_4(10)-3.25$ (Fig. 2c), $CuSO_4(20)-3.25$ (Fig. 2d) and $CuSO_4(40)-3.25$ (Fig. 2e) all confirm the presence of ordered $Fm\bar{3}m$ pore structure, which are consistent with the XRD results. TEM image of $CuSO_4(60)-3.25$ (Fig. 2f) shows the disordered wormhole-like pore arrangement [40], indicating that the presence of large amount of $CuSO_4$ is detrimental to the formation of ordered mesostructure. Hexagonal disk crystals can be easily found in the SEM images of $CuSO_4(10)-3.25$ (Fig. 2c, inset) and $CuSO_4(20)-3.25$ (Fig. 2d, inset). Average width and thickness of the hexagonal disk crystals is about 7 and 3 μm , respectively. Irregular large particles and spherical particles co-exist in the SEM images of $CuSO_4(40)-3.25$ (Fig. 2e, inset) and $CuSO_4(60)-3.25$ (Fig. 2f, inset).

Fig. 3 gives the nitrogen sorption isotherms of $CuSO_4(x)-3.25$. The textural parameters of these samples are compiled in Table 1. All samples show type IV isotherm patterns. For $CuSO_4(0)-3.25$

Table 1
Textural and structural properties of calcined samples.

Sample	pH value ^a	d_{111}^c (nm)	Surface area ^d (m^2/g)	Pore volume ^e (cm^3/g)	Pore diameter ^f (nm)
$CuSO_4(0)-3.25$	3.25 ^b	–	839	1.54	19.5
$CuSO_4(5)-3.25$	3.25 ^b	–	949	1.52	24.1
$CuSO_4(10)-3.25$	3.25 ^b	13.0	1001	0.90	11.5
$CuSO_4(20)-3.25$	3.25 ^b	15.2	801	0.68	13.2
$CuSO_4(40)-3.25$	3.25 ^b	15.7	785	0.70	13.8
$CuSO_4(60)-3.25$	3.25	–	619	0.60	16.0
$CuSO_4(20)-3.60$	3.60	14.8	935	0.78	13.4
$ZnSO_4(20)-4.26$	4.26	17.2	1203	1.09	15.6
$NiSO_4(20)-3.90$	3.90	16.4	1134	1.18	15.9
$MgSO_4(20)-3.83$	3.83	16.3	1012	0.87	15.7
$K_2SO_4(20)-6.33$	6.33	–	530	2.41	13.5
$Na_2SO_4(20)-5.88$	5.88	–	596	1.58	13.2
$K_2SO_4(20)-3.80$	3.80 ^b	–	562	1.31	14.3

^a The pH value of the surfactant solution.

^b The pH value of the surfactant solution was adjusted using 0.1 mol/L of H_2SO_4 .

^c Calculated from the small angle XRD profiles.

^d BET surface area.

^e Obtained from the volume of N_2 adsorbed at $P/P_0 = 0.99$.

^f Calculated using the BJH model based on the adsorption branch of the isotherm.

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