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# Fabrication of MCM-41 mesoporous silica through the self-assembly supermolecule of $\beta$-CD and CTAB

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## Abstract

Using the self-assembly $\beta$-cyclodextrin ($\beta$-CD) and cetyltrimethylammonium bromide (CTAB) as structure-directing agents, high-quality ordered MCM-41 silicas have been prepared. Small-angle X-ray diffraction (SXRD), $N_2$ adsorption–desorption and scanning electron microscope (SEM) techniques were used to characterize the calcined samples. Results showed that the pore structure of the resulting mesoporous silica belonged to the two-dimensional hexagonal structure (space group *p6mm*). The high-quality hexagonal structure was formed as $n \leqslant 1$ ($n$ denotes molar ratio of $\beta$-CD to CTAB). $N_2$ adsorption–desorption curves revealed type IV isotherms, H4 hysteresis loops, for all samples, and H1 hysteresis loops for samples at $n = 0$, 0.1, 1 and 2, respectively. The pore size and the pore wall thickness of the samples increased with the increase in $n$ values, respectively.

*Keywords:* Mesoporous silica; MCM-41; Self-assembly; CTAB; $\beta$-CD

## 1. Introduction

Alcohols, as cosurfactants, can improve surface activity of a surfactant solution and make the critical micelle concentration (cmc) decrease. $\beta$-cyclodextrin ($\beta$-CD) is a cyclic oligosaccharide consisting of seven linked D-glucopyranose units. It has a toroidal or hallow, truncated, cone shape, with an apolar, hydrophobic interior and two hydrophilic rims, formed by the primary (narrow rim) and secondary (wide rim) OH groups. Cyclodextrins are known to form inclusion complexes with a variety of guest compounds [1]. Complexes between $\beta$-CD and aliphatic guests as new noncovalent amphiphiles have been reported [2]. The influences of $\beta$-CD, as host molecules, on cmc of the ionic surfactants aqueous systems with molecules such as decyltrimethylammonium chloride, docecyltrimehtylammonium chloride, tetradecyltrimehtylammonium chloride, hexadecylthimethylammonium chloride and octadecyltrimehtylammonium chloride as guest molecules were investigated by electroconductance at 298.15 K. The experimental results showed that, after addition of $\beta$-CD, the apparent cmc of these surfactants aqueous solution increased [3].

Surfactant-templated methods for the synthesis of mesoporous silica have attracted considerable attention since they produced structures with an extraordinary combination of high surface area, narrow pore size distribution and well-ordered pore organization [4,5]. Most recently, pore size and pore organization have been controlled through a choice of surfactant, introduction of a cosolvent, application of an external field, rigorous control of processing conditions such as temperature and evaporation rate during synthesis, use of a macroporous template or a combination of the above [6–14]. However, $\beta$-CD and cationic surfactant as mixed template to synthesize mesoporous silica of controlled pore size and pore wall thickness has not been reported, as we know.

Our interest in mesoporous materials which are able to increase pore size and pore wall thickness let us to use hybrid templates comprised of $\beta$-CD and cetyltrimethylammonium bromide (CTAB).

In this paper, we synthesized high-quality ordered MCM-41 silica through the self-assembly supermolecules

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of β-CD and CTAB as structure-directing agents. The pore size and pore wall thickness of the samples increased with increase in β-CD added in the synthesizing systems. The formation mechanism was also discussed.

## 2. Experimental

Tetraethoxysilane (TEOS) analytical-grade reagent, which contained 28.0% (w/w) $SiO_2$, and β-CD, which was twice recrystalized using water, were obtained from Tianjing Kemiou Chemical Reagent Co. Solid CTAB was analytical-grade reagent from Shanghai Ruijie Chemical Reagent Co. Aqueous ammonia, which contained 26.5% $NH_3$, was obtained from Laiyang Shuanghua Co.

In a typical synthesis, a mixture of CTAB, β-CD, $H_2O$ and ammonia aqueous was vigorously stirred until a transparent solution was obtained. This solution was then added to TEOS. The emulsion was vigorously and regularly stirred for 4 h at 338.2 K. The molar ration of the mixture was $\beta$-CD:CTAB:TEOS:$NH_3$:$H_2O = n$: 1:5:100:4000. The solid product was recovered by filtration, washed with distilled water and dried at room temperature. The mixed surfactants were removed by calcination at 823.2 k for 6 h.

Powder small-angle X-ray diffraction (SXRD) data were obtained on a D/max-rB model with a Cu target at 40 kV and 120 mA, using a speed of 0.2°/min and a step of 0.01°.

Scanning electron microscopy (SEM) experiments were performed on a S520 model SEM.

Nitrogen adsorption–desorption measurements were carried out on an Omnisorp 100 CX gas adsorption

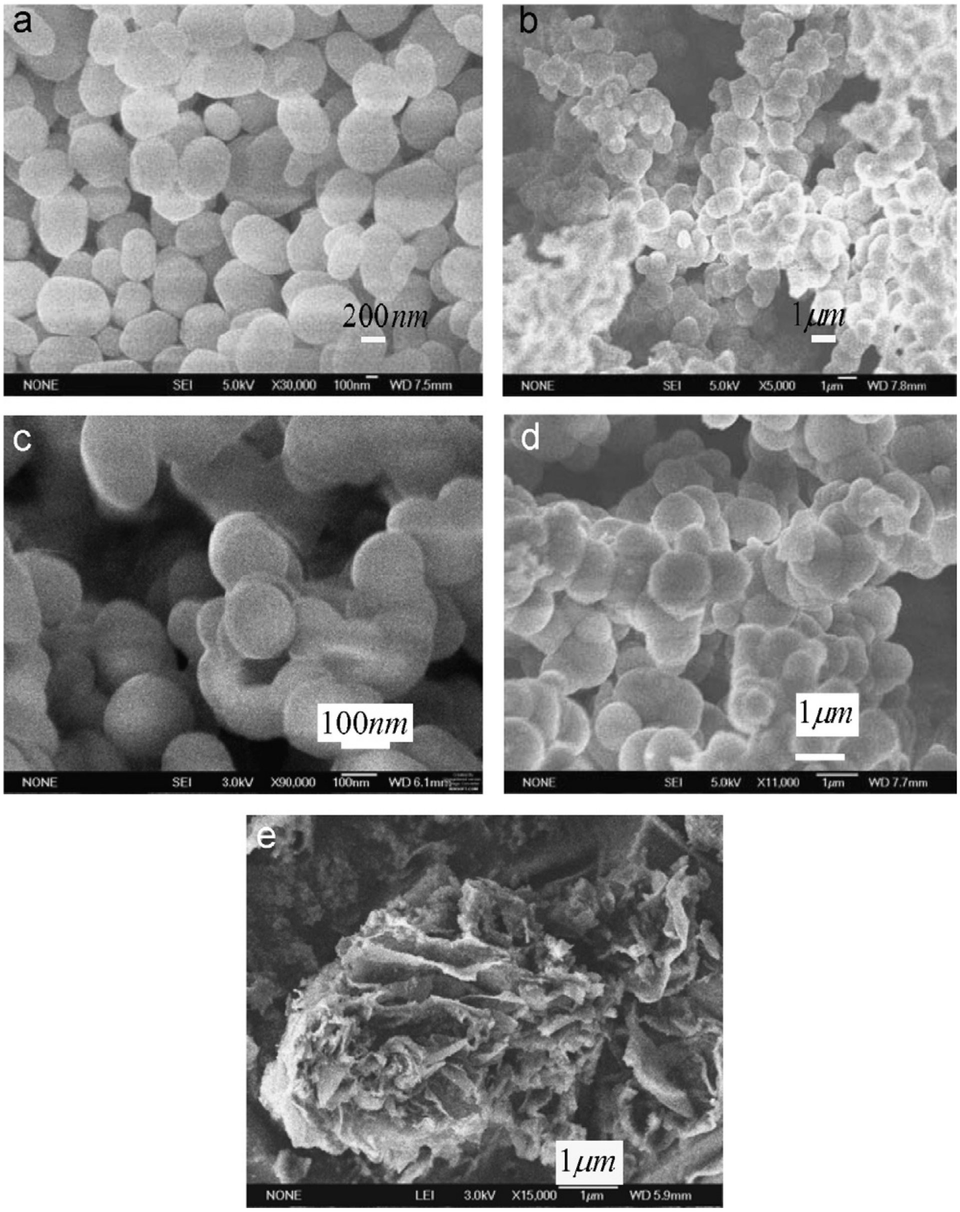

Fig. 1. SEM photography of mesoporous silica at different molar ratios of β-CD to CTAB, as (a) 0, (b) 0.1, (c) 1.0, (d) 2.0 and (e) 5.0.

analyzer from Coulter Co. Every sample was degassed at 350 °C for 12 h under a pressure of $10^{-5}$ Pa or below.

## 3. Results and discussion

Fig. 1 gives SEM photos of the synthesized mesoporous silica at different molar ratios of $\beta$-CD to CTAB. The particles with elliptic shapes of about 600 and 300 nm diameter, were obtained in the absence of $\beta$-CD. The particles translated to uniform spheres in the presence of $\beta$-CD as $n = 0.1$, 1.0 and 2.0, and to irregular shape as $n = 5.0$, where $n$ denotes the ratio of $\beta$-CD to CTAB. The size of particles changed with varying the additive of $\beta$-CD, and reached the smallest size of about 200 nm as $n = 1.0$.

There existed three diffraction peaks, (100), (110) and (200) in the XRD patterns (as Fig. 2). Thus, the pore structure of the synthesized mesoporous silica was in a hexagonal array regardless of the presence of $\beta$-CD. The $d$ values and half-peak width ($H_{1/2}$) of the (100) diffraction peak in Fig. 2 are listed in Table 1. The changes of the values of $d$ and $H_{1/2}$ became sharp from $n = 2.0$ to $n = 5.0$. The data in Table 1 revealed that the half-peak width of $d_{100}$ was becoming small when the molar ratio of $\beta$-CD to CTAB was equal to 0.1. When the $n$ value was below 2.0, three diffraction peaks of (100), (110) and (200) occurred. And two diffraction peaks of (100) and (110), and only one peak of (100), appeared as $n = 2.0$ and 5.0, respectively. These results indicated that the high-quality hexagonal structure was formed as $n \leqslant 1.0$, and the ordering of the pore structure increased with the additive $\beta$-CD in the reaction system with $n > 0.1$, and decreased when $n$ value further increased especially as $n \geqslant 2.0$.

The distances between two adjacent pore centers ($a$ values) (calculated according to the formula $a = 2d_{100}/3^{1/2}$) are also given in Table 1. The values of $a$ increased with increase in $n$.

The $N_2$ adsorption–desorption isotherm for the samples showed a type IV for all samples (as Fig. 3). These results indicated that the pore size of the synthesized silica was in the range of mesoscale [15]. This conclusion was consistent with that from XRD (Fig. 2). On the other hand, the BET surface area decreased with the increase in $n$ value (Table 1), and especially decreased sharply from 899 to 519 $m^2/g$ as $n$ changes from 2.0 to 5.0. The maximum BET surface area was 1374 $m^2/g$ in absence of $\beta$-CD.

H1 hysteresis loop appeared for samples as $n = 0$, 0.1, 1.0 and 2.0, respectively, and capillary condensation

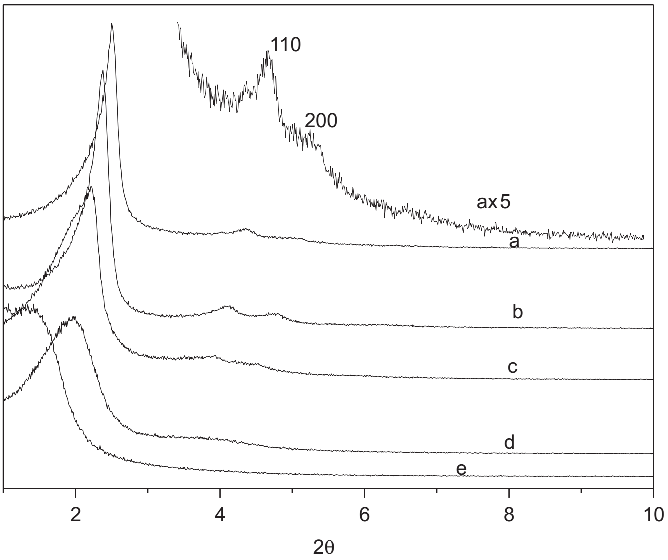

Fig. 2. SXRD of mesoporous silica at different molar ratios of $\beta$-CD to CTAB as (a) 0, (b) 0.1, (c) 1.0, (d) 2.0 and (e) 5.0.

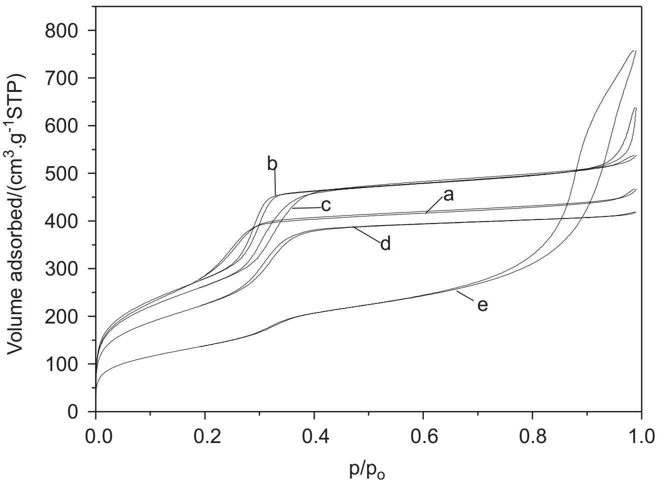

Fig. 3. $N_2$ adsorption–desorption of mesoporous silica at different molar ratios of $\beta$-CD to CTAB as 0 for (a) 0, (b) 0.1, (c) 1.0, (d) 2.0 and (e) 5.0.

Table 1
Pore structure and surface properties parameters of hexagonal mesoporous silica

| Samples | $N^a$ | $d_{100}$ (nm) | $H_{1/2}$ (nm) | $a_o$ (nm) | $S_{BET}$ ($m^2/g$) | $d_{BJH}{}^b$ (nm) | Pore wall thickness$^c$ (nm) |
|---|---|---|---|---|---|---|---|
| a | 0 | 3.5 | 0.26 | 4.1 | 1374 | 2.3 | 1.7 |
| b | 0.1 | 3.7 | 0.22 | 4.3 | 1237 | 2.6 | 1.7 |
| c | 1.0 | 4.0 | 0.28 | 4.6 | 1014 | 2.7 | 1.9 |
| d | 2.0 | 4.5 | 0.32 | 5.2 | 899 | 2.7 | 2.5 |
| e | 5.0 | 6.8 | 0.84 | 7.8 | 519 | 2.7 | 5.1 |

[a] Molar ratio of $\beta$-CD to CTAB.
[b] Calculated from adsorption portion of $N_2$ adsorption–desorption isotherm.
[c] Pore wall thickness: $a_o$ minus most probable pore size.

appeared in the relative pressure ($p/p_0$) range of 0.2–0.4 as shown in Fig. 3. And H4 hysteresis loop was seen for the all samples with $p/p_0$ range of 0.9–1 for $n = 0$, 0.1, 1.0, and 2.0, and 0.7–1 for $n = 5.0$. H1 and H4 hysteresis loops were attributed to the primary pores of mesoporous silica and to the voids between particles, respectively. The primary pores and voids consisted of ''framework-confined'' and ''textural'' mesoporosities, which were defined and differentiated as in Pinnavaia et al. [16,17]. The framework-confined mesoporosity was the porosity contained within the uniform channels of the templated framework. The textural mesoporosity was the porosity arising from noncrystalline intraaggregate voids and spaces formed by interparticle contacts.

The most probable pore size with the BJH model was obtained as Fig. 4 and listed in Table 1. There existed two peaks for the sample ''*e*''. The first one was corresponding to the primary pore, and the second one to the voids. These results were agreement with those obtained from $N_2$ adsorption–desorption curves.

As we can see from Table 1 and Fig. 4, the most probable pore size with the BJH model was in the range 2.3–2.7 nm, and it increased with increase of $\beta$-CD. The pore wall thickness was becoming also increased as increasing the additive $\beta$-CD, and it increased sharply from 2.5 to 5.1 nm as $n$ changes from 2.0 to 5.0.

From the obtained results above, we can see that the morphology and the porous structure of the samples were changing with $\beta$-CD added, especially the change became strong for $n$ values 2.0–5.0. $\beta$-CD was only used as template to fabricate mesoporous silica, but no porous structure was found [18,19]. Thus, $\beta$-CD and CTAB self-assembly supermolecule was formed in our reacting

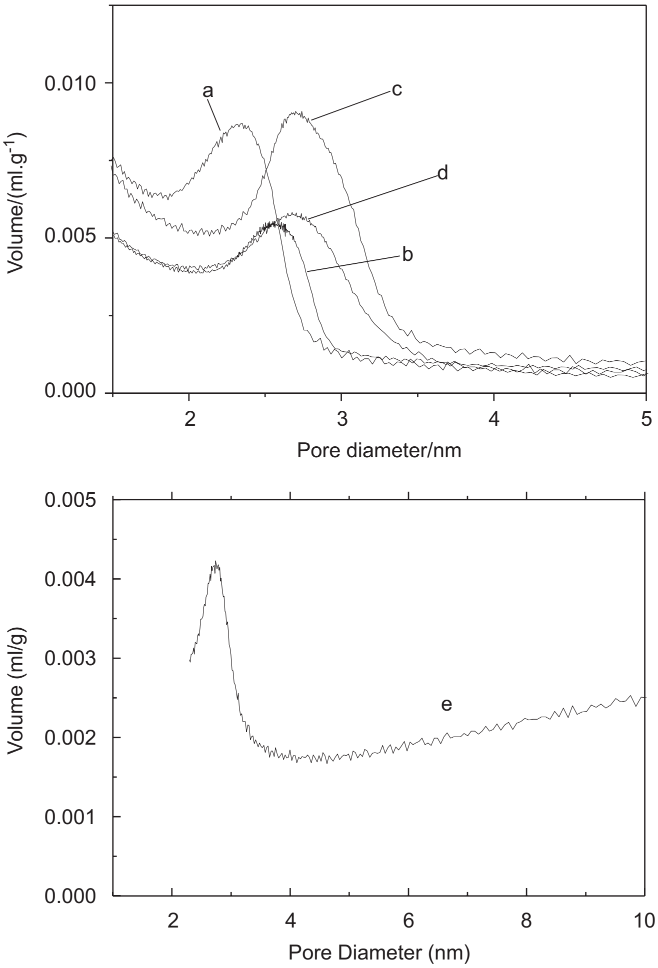

Fig. 4. Pore size distribution curves of mesoporous silica at different molar ratios of $\beta$-CD to CTAB as (a) 0, (b) 0.1, (c) 1.0, (d) 2.0 and (e) 5.0.

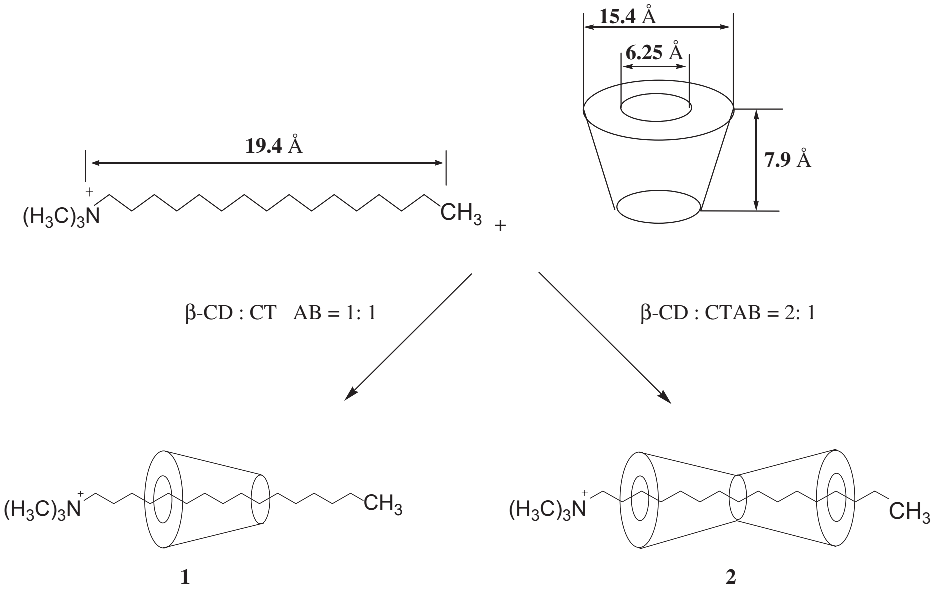

Fig. 5. Schematic of the formation of inclusion complex of CTAB and $\beta$-CD.

systems. The inclusion complex formation between a homologous series of n-alkyltrimethylammonium bromides and $\beta$-CD has been investigated by using conductometric technique [20]. The results have been found that DETAB and DOTAB form only the 1:1 complexes, while TTAB forms 1:1 and 1:2 TTAB/CD complexes. 1:1 and 1:2 complexes between DOTAB and $\alpha$-CD have been determined by NMR technique [21]. In the 1:2 complex two $\alpha$-CD molecules adopt the head-to-head structure. The 1:2 complex between cetylpyridinium chloride and $\alpha$-CD has also been determined by Chang et al. [22]. Thus, 1:1 and 1:2 complexes between CTAB and $\beta$-CD may form in our researching systems as Fig. 5. The change of the morphology and the porous structure of the mesoporous silica can be explained: the inclusion complexes **1** and **2** form and the micelles change when $\beta$-CD was added in the systems. The electrostatic repulsion among $CTA^+$ ions in micelles decrease, which is like the action of alcohol solubilized only in the palisade layer of micelles. These resulted in the change of the morphology and pore structure in mesoporous silica as $n$ changes from 0 to 2.0. However, when $n = 5.0$, the micelles consisted of the inclusion complex **2** and $\beta$-CD, the morphology and pore structure of the sample changed sharply from $n = 2.0$ to 5.0.

The mesporous silica was synthesized using the micelles as templates, which was reported with pentanol as cosurfactant [23]. The size of the micelles increased with increase in the amount of $\beta$-CD. Thus, the distances between two adjacent pore centers and the pore size of the mesoporous silica increased with addition of $\beta$-CD. Because one molecule of $\beta$-CD contains 16 "OH" groups, and "OH" group is advantages for the hydrolysis of TEOS, the pore wall thickness of the synthesized samples increased with the increase of the amount of the $\beta$-CD in the reacting systems, especially for $n$ change from 2.0 to 5.0.

In conclusion, we have described a self-assembly by supermolecular templating route to fabricate mesoporous silica, and have shown that the textural characteristics of these materials with a narrow pore size distribution. The pore size and the pore wall thickness of the samples can be increased by adding $\beta$-CD. Thus, the preparation of mesoporous materials with control of the pore size and the pore wall thickness is in progress.

## 4. Conclusions

1. 1:1 and 1:2 complexes between CTAB and $\beta$-CD have formed as a self-assembly templates in the reacting systems.
2. Morphologies of the samples changed from elliptic shape to spheres and to irregular shape with addition of $\beta$-CD.
3. Pore size and pore wall thickness of the samples increased with increase in $\beta$-CD.
4. There existed a type IV adsorption isotherm, H1 and H4 hysteresis loops in $N_2$ adsorption–desorption curves. The Brunauer-Emmett-Teller surface area was between 519 and 1374 $m^2/g$, and the most probable pore size with Barrett-Joyner-Halenda diameter increased with the increase of the molar ratio of $\beta$-CD to CTAB. The result is in agreement with that of SXRD.

## Acknowledgment

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