Molecular design of AEC tri-block anionic surfactant towards rational synthesis of targeted thick-walled mesoporous silica

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Here we report a new synthesis strategy to synthesize thick-walled two dimensional hexagonal mesoporous silicas, using tri-block surfactant fatty alcohol ether carboxylate [AEC: C_{n}H_{2n+1}O(CH_{2}CH_{2}O)_{m}CH_{2}COONa] with two different hydrophilic head groups of (EO)_{x}-block and anionic carboxylate. The unique formation of double-layer silica wall arose from two types of hydrophilic head groups via the silica source condensation led to an obvious increase in the wall thickness. The successful carbon replication proved the existence of micropores formed by imbedded (EO)_{x}-block and electrostatic bonding of carboxylate head group and organic group of co-structure directing agent. The template-free mesoporous silica showed a high hydrothermal stability due to the thick wall.

Introduction

Well ordered mesoporous materials have been synthesized based on surfactant templating routes. It has been reported that the mesostructures, wall compositions and morphologies were controllable with abundance in variety. Tailoring the wall thickness is another important issue in the design and applications of mesoporous materials, because an increase in wall thickness will make the material more stable and applicable. However, the control of wall thickness of mesoporous materials is a challenge that remains unsolved.

Ryoo and his co-workers reported a synthesis method for the systematic control of the pore wall thickness of hexagonal mesoporous silicas, using non-ionic and cationic surfactant mixtures. Sayari et al. found that the pore wall thickening was accompanied by a significant pore size enlargement due to elongating the hydrothermal treatment in the post synthesis procedure. The wall thickness of hexagonal mesostructure has been increased with increasing the (EO)_{x}-block length of the Pluronic surfactant, (EO)_{x}-(PO)_{y}-(EO)_{x}, an increase in aging temperature led to an increase in pore size but a decrease in the pore wall thickness; and an increase in aging time resulted in thick wall. However, all of the reported methods were insufficient to provide a strategy for controlling pore wall thickness.

Here we report a new synthesis strategy to synthesize thick-walled two dimensional(2D)-hexagonal mesoporous silicas, using tri-block surfactant fatty alcohol ether carboxylate [AEC: C_{n}H_{2n+1}O(CH_{2}CH_{2}O)_{10}CH_{2}COONa] with two different hydrophilic head groups of (EO)_{x}-block and anionic carboxylate. The wall thickness of the mesoporous silicas in current work have been increased with increasing the (EO)_{x}-block length of the surfactant. The wall thickness of the mesoporous silicas, using tri-block surfactant fatty alcohol ether carboxylate [AEC: C_{n}H_{2n+1}O(CH_{2}CH_{2}O)_{m}CH_{2}COONa] with two different hydrophilic head groups of (EO)_{x}-block and anionic carboxylate, has been increased with increasing the (EO)_{x}-block length of the surfactant, resulting from the two types of silicate aggregation on both (EO)_{x}-block and carboxylate head groups of tri-block surfactant molecules. We have achieved the formation of tri-continuous mesostructure with thick wall by using AEC surfactant as a structure directing agent, N-trimethoxysilylpropyl-N,N,N-trimethylammonium chloride (the cation denoted here as TMAPS) as a co-structure directing agent (CSDA) and tetraethyl orthosilicate (TEOS) as a silica source, under a pH value of 6–7 (see Experimental section). As shown in Scheme 1, the AEC surfactants self-assemble to form a micelle. By operating at a pH higher than the isoelectric point of silica (pl ≈ 2), the silica species become anionic (I−); the silicate would be condensed in first hydrophilic layer of (EO)_{x}-block through hydrogen-bonding interaction (S−H−I) between the (EO)_{x}-block and silicate, incorporating the (EO)_{x}-block in the wall. In the second layer of hydrophilic part, the positively charged ammonium site of TMAPS interacts electrostatically with the negatively charged head group of the surfactant, through double decomposition of carboxylate and TMAPS. The alkoxysilane sites of TMAPS are co-condensed with TEOS, to be assembled subsequently to form the second layer silica framework. The cationic ammonium groups of TMAPS were covalently tethered by the trimethylene groups and thus incorporated into the framework. By adjusting the ionization degree of the surfactant and the CSDA/AEC molar ratios, a suitable pH value and a composition favorable for the formation of highly ordered hexagonal mesostructure can be achieved. When 3-aminopropyltrimethoxysilane (APS) is used as the CSDA, the mesostructure can also be formed via neutralization between the amino groups of APS and the carboxylic acid groups of the surfactant which subsequently interact with each other in an electrostatic way (not discussed here). Here, a 2D-hexagonal mesostructure has been synthesized with AEC tri-block anionic surfactant. It has been widely recognized that the three blocks in the tri-block molecules can...
self-assemble separately to form various multi-continuous and triple network phases, because of the difference in nature of each part. Double layered 2D-hexagonal mesostructure is one of the typical structures among them.

**Experimental section**

**Chemicals**

C₁₂H₂₅O(CH₂CH₂O)₁₀CH₂COONa and C₁₂H₂₅O(CH₂CH₂O)₅CH₂COONa (Kao Chemicals Europe & Kao Chemical Corporation Shanghai), N-trimethoxysilylpropyl-N,N,N-trimethylanmonium chloride (TMAPS, Azmax), tetraethyl orthosilicate (TEOS, SCRC China), C₁₄H₂₉COONa (TCI), C₁₂H₂₅O(CH₂CH₂O)₁₀H and C₁₂H₂₅O(CH₂CH₂O)₄H (Sigma) were used without further purification. Anionic surfactants derived from amino acids (glutamic acid, alanine) were synthesized.

**Preparation of anionic surfactant**

In a typical synthesis of N-myristoyl-l-glutamic acid (C₁₄GluA), 120 mL of acetone, 19.2 g of sodium hydroxide, 49.3 g (0.2 mol) of myristoyl chloride, and 8.0 g (0.2 mol) of sodium hydroxide in 20 mL of water were added with stirring to a solution prepared from 35.5 g (0.24 mol) of l-glutamic acid in 140 mL of water, at 30 °C and pH 12 over a period of 20 min. The reaction mixture was stirred for 1 h additionally, cooled, and acidified to pH 1 with hydrochloric acid. The precipitated crystals of N-myristoyl-l-glutamic acid were purified by washing with petroleum ether.

Surfactants N-lauroyl-l-glutamic acid sodium salt (C₁₄GluNa), N-myristoyl-l-glutamic acid sodium salt (C₁₄GluNa), N-palmitoyl-l-glutamic acid sodium salt (C₁₆GluNa), N-myristoyl-l-Alanine sodium salt (C₁₄AlaNa), N-palmitoyl-l-Alanine sodium salt (C₁₆AlaNa) were prepared by neutralizing the acid form surfactant with one equivalent NaOH.

**Synthesis of mesoporous silicas using various anionic surfactants**

In a typical synthesis of anionic surfactant-template mesoporous silica, a mixture of 1.458 g TEOS and 0.515 g TMAPS (50 w% in methanol) was added to a mixture of 0.250 g C₁₄H₂₉COONa, 25 g deionized water and 0.1 g 1M NaOH at 70 °C with stirring. After the mixture had been stirred for 10 min, the reaction mixture was aged at 70 °C for 2 days. The precipitate was filtered, dried at 80 °C, and calcined for 6 h at 550 °C in air with a ramp of 1.5 °C/min to give surfactant-free mesoporous silica.

**Synthesis of mesoporous silicas using non-ionic surfactants**

In a typical synthesis route, 2.08 g of TEOS was added to a mixture of 0.627 g C₁₂H₂₅O(CH₂CH₂O)₁₀H, 30 g of 2 M HCl and 0.093 g dodecanol at room temperature with stirring. The resulting gel mixture was stirred for 1 day at room temperature and subsequently heated for 1 day at 100 °C. The precipitate was filtered, dried at 60 °C, and calcined for 6 h at 550 °C in air with a ramp of 1.5 °C/min to obtain template-free mesoporous silica.

**Synthesis of mesoporous silicas using AEC surfactant**

The synthesis route for well ordered mesoporous silica by using AEC surfactant as template was similar to that of the anionic surfactant-template mesoporous silica. A mixture of 0.109 g of TMAPS (50 w% in methanol) and 1.18 g TEOS was added to a mixture of 0.909 g (22 w% in water) of C₁₂H₂₅O(CH₂CH₂O)₁₀CH₂COONa, 20 g deionized water and 0.07 g 1 M HCl at 60 °C with stirring. The initial pH before addition of TMAPS and TEOS was measured to be 6.2. After 10 min, stirring was stopped and the reaction mixture was aged at 80 °C for 2 days. The precipitate was filtered, dried at 80 °C, and calcined for 6 h at 550 °C in air with a ramp of 1.5 °C/min to give template-free mesoporous silica.

AEC surfactants with various (EO)ₓ-blocks were prepared by mixing two commercially available AEC surfactants with the same length of hydrophobic alkyl chain but different (EO)ₓ-blocks (C₁₂H₂₅O(CH₂CH₂O)₁₀CH₂COONa and C₁₂H₂₅O(CH₂CH₂O)₅CH₂COONa in different molar ratios, e.g. C₁₂H₂₅O(CH₂CH₂O)₇CH₂COONa could be achieved by adjusting the molar ratio of the two AEC surfactants to 2 : 3.
Synthesis of carbon replicas of mesoporous silicas

A two-step method was employed for the filling of sucrose. A specific example of the synthesis of carbon replica can be given as follows: 0.3 g of silica material was well-mixed with an aqueous solution consisting of 1.0 g of sucrose, 0.112 g of H$_2$SO$_4$ and 2.0 g of H$_2$O. The resultant mixture was dried at 100 °C in a drying oven for 6 h and then subsequently increased to 160 °C for another 6 h. The black silica powder containing partially decomposed sugar after the heating was mixed again with an aqueous solution consisting of 0.45 g of sucrose, 0.0448 g of H$_2$SO$_4$ and 2.0 g of H$_2$O. After heating to 160 °C in the drying oven again, the sugar was converted to carbon by heating the powder at 900 °C for 6 h under N$_2$ flow, with a ramp of 2.5 °C/min. The porous carbon was obtained after subsequent dissolution of the silica framework in 20 g 10% HF acid at room temperature.

Characterizations

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku X-ray diffractometer D/MAX-2200/PC using Cu Kα radiation (40 kV, 20 mA) at the rate of 1.0° 2θ/min over the range of 1–6° 2θ.

High-resolution transmission electron microscopy (HRTEM) was performed with a JEOL JEM-3010 microscope operating at 300 kV (Cs = 0.6 nm, resolution 1.7 Å). Images were recorded with a CCD camera (Gatan MultiScan CCD camera model 794, 1024 × 1024 pixels, pixel size 24 μm) at 50 000–120 000 times magnification under low-dose conditions.

The N$_2$ adsorption–desorption isotherms were measured at 77 K with a Quantachrome Nova 4200E porosimeter. The specific surface area, $S_{BET}$, was calculated from N$_2$ adsorption data in the relative pressure range from 0.04 to 0.2 using the Brunauer-Emmett-Teller (BET) method. The experimental value of the surface area may be higher than the true value. The mesopore volume, $V_p$, was estimated from the amount adsorbed at a relative pressure of 0.99. Pore size distributions (PSDs) were calculated from desorption branches of isotherms using the Barrett-Joyner-Halenda (BJH) method using the Kelvin equation for hemispherical meniscus and the statistical film thickness curve for silica.

Solid-state 13C MAS NMR spectra of the mesoporous materials were collected on a Varian Mercury plus-400 NMR spectrometer.

The wall thickness ($w$) of the mesoporous materials with 2D hexagonal mesostructures was calculated based on the experienced formula: $w = a_0 - \text{pore size} \left[ a_0 = 2d(10)/\sqrt{3} \right]$.

Results and discussion

1. Wall thickness comparison of mesoporous silica synthesized with different types of surfactants

Fig. 1A shows the XRD patterns of calcined mesoporous silicas synthesized with three types of surfactant: C$_{14}$H$_{29}$COONa with one anionic head group, C$_{12}$H$_{25}$O(CH$_2$CH$_2$O)$_{10}$H with one non-ionic (EO)$_x$ block head group, and AEC [C$_{12}$H$_{25}$O(CH$_2$CH$_2$O)$_{10}$CH$_2$COONa] with two types of head groups. All the samples show three well-resolved peaks in the range 2θ = 1.0–5.0° with a 1:√3:2 reciprocal spacing ratio, which are indexed as (10), (11) and (20) reflections, based on the 2D hexagonal $p6mm$ structure.

Meanwhile, d-spacings of [10] direction ($d_{[10]}$) might be observed and measured based on the TEM images (4.8 nm, 5.3 nm, 6.0 nm respectively), which are consistent with the results in XRD patterns shown in Fig. 1A. It is obvious that the d-spacing of [10] direction ($d_{[10]}$) in sample c is much larger than that of other samples despite the fact that all the samples have a similarity in pore diameter (Table 1).

As shown in Fig. 1B, the N$_2$ adsorption–desorption isotherms show type IV isotherms, typical for mesoporous materials, and feature sharp steps of capillary condensation in the relative pressure interval from 0.3 to 0.6. The PSD (Fig. 1C) confirms the existence of uniform mesopores with similar pore diameter of 3.4–3.8 nm. The structural properties of all samples were listed in...
Table 1. The wall thickness, \( w \), is evaluated using the relation \( w = \frac{a}{C_0} \), where \( a \) represents the unit cell parameter calculated from the positions of the peaks in XRD patterns, and \( d \) is the pore diameter defined as a position of the maximum on PSD.

It is interestingly to note from Table 1 that the wall thickness of mesoporous silica synthesized with AEC surfactant is much larger than that synthesized using surfactants with either (EO)\( x \)-block or carboxylate anionic head groups. This result shows that the two types of silicate aggregation on both (EO)\( x \)-block and carboxylate head groups of AEC surfactant led to an effective increase in the wall thickness. The specific surface area tends to decrease with increasing wall thickness.

As mentioned in introduction, the wall thickness of mesoporous silicas can be controlled by synthesis conditions such as temperature, pH values and aging time, etc. Other anionic and non-ionic surfactants have also been used to obtain ordered mesoporous silica with 2D hexagonal \( p6mm \) mesostructure. Here, we will show subsequently that the mesoporous silicas templated by non-ionic and anionic surfactants having the thickest wall have been chosen, for the purpose of comparison with AEC templated mesoporous silica.

Table 1 Structural properties of calcined mesoporous silicas shown in Fig. 1

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>( a )/nm</th>
<th>( S_{BET} )/m(^2) g(^{-1})</th>
<th>( V_p )/mm(^3) g(^{-1})</th>
<th>( d )/nm</th>
<th>( w )/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(<em>{12})H(</em>{25})O(CH(_2)CH(<em>2)O(</em>{10}))H</td>
<td>5.4</td>
<td>814</td>
<td>840</td>
<td>3.4</td>
<td>2.0</td>
</tr>
<tr>
<td>C(<em>{14})H(</em>{29})COONa</td>
<td>6.4</td>
<td>542</td>
<td>590</td>
<td>3.6</td>
<td>2.8</td>
</tr>
<tr>
<td>C(<em>{12})H(</em>{25})O(CH(_2)CH(<em>2)O(</em>{10}))CH(_2)COONa</td>
<td>7.2</td>
<td>472</td>
<td>520</td>
<td>3.8</td>
<td>3.4</td>
</tr>
</tbody>
</table>

\( a \) Notation: \( a \), unit cell parameter; \( S_{BET} \), BET specific surface area; \( V_p \), mesopore volume; \( d \), BJH pore diameter calculated on the basis of N\(_2\) desorption isotherm curves; \( w \), wall thickness.

Wall thickness of mesoporous silicas synthesized using various anionic surfactants. Fig. 3 shows the XRD patterns, N\(_2\) adsorption–desorption isotherms and pore size distributions of calcined mesoporous silicas synthesized using various anionic surfactants as template. From the XRD patterns (Fig. 3A), a typical 2D hexagonal \( p6mm \) mesostructure have been simply confirmed by the three well-resolved peaks with \( 1 : \sqrt{3} : 2 \) reciprocal spacing ratio. Meanwhile, all the samples show type IV isotherms (Fig. 3B) and the pore diameters (Fig. 3C) of mesoporous silica synthesized with these amino-acid headed surfactants have been obviously observed, ranging from 2.5 nm to 3.8 nm. The wall thickness has been calculated to be in the range of 1.8–2.8 nm (see Table 2). The wall thickness of the mesoporous silicas obtained from various anionic surfactant synthesis systems is different, mainly in respect that the synthesis conditions such as pH values, temperature, chemical compositions are different. Among these samples, the sample synthesized using C\(_{14}\)H\(_{29}\)COONa with the largest wall thickness has been chosen for comparison.
Wall thickness of mesoporous silicas synthesized using non-ionic surfactants. Various non-ionic surfactants have been used to synthesize mesoporous silicas with 2D hexagonal \textit{p6mm} mesostructure. Fig. 4 shows the XRD patterns, \(\text{N}_2\) adsorption–desorption isotherms and pore size distributions of these samples, and Table 3 summarizes the structural properties. Furthermore, surfactants with larger \((\text{EO})_x\)-block \((x > 11)\) have also been designed and used to synthesize mesoporous silica. However, no ordered 2D hexagonal \textit{p6mm} mesostructure can be well obtained based on the experimental results, owing to the larger hydrophilic head group in the surfactant molecule. It can be inferred that the wall thickness of the mesoporous silica synthesized with \(\text{C}_{12}\text{H}_{25}\text{O}(\text{CH}_2\text{CH}_2\text{O})_7\text{H}(\sim 1.4 \text{ nm})\) is much smaller than that of \(\text{C}_{16}\text{H}_{33}\text{O}(\text{CH}_2\text{CH}_2\text{O})_{10}\text{H}(\sim 2.0 \text{ nm})\) having the same alkyl chain length, due to the smaller \((\text{EO})_x\)-block. The mesoporous silica synthesized with \(\text{C}_{12}\text{H}_{25}\text{O}(\text{CH}_2\text{CH}_2\text{O})_{10}\text{H}\) and \(\text{C}_{16}\text{H}_{33}\text{O}(\text{CH}_2\text{CH}_2\text{O})_{10}\text{H}\) having the same \((\text{EO})_x\)-block length but different hydrophobic alkyl chain show the similar wall thickness of 2.0 nm and 1.9 nm. Therefore, the sample synthesized using \(\text{C}_{12}\text{H}_{25}\text{O}(\text{CH}_2\text{CH}_2\text{O})_{10}\text{H}\) with the largest pore wall thickness has been chosen for comparison.

2. Wall thickness control of mesoporous silica with different \((\text{EO})_x\)-block length of AEC surfactants

In a similar manner to the non-ionic surfactant synthesis system,\(^{17}\) it is reasonable that the wall thickness of the mesoporous silica increased with increasing \((\text{EO})_x\) length in this AEC surfactant templating system. Here, AEC surfactants \(\text{C}_{12}\text{H}_{25}\text{O}(\text{CH}_2\text{CH}_2\text{O})_x\text{CH}_2\text{COONa}\) with various \((\text{EO})_x\) length \((x = 5–10)\) are prepared by mixing\(^{24}\) two types of AEC surfactant \([\text{C}_{12}\text{H}_{25}\text{O}(\text{CH}_2\text{CH}_2\text{O})_{10}\text{CH}_2\text{COONa}\text{ and } \text{C}_{12}\text{H}_{25}\text{O}(\text{CH}_2\text{CH}_2\text{O})_5\text{CH}_2\text{COONa}]\) in different molar ratios. The XRD patterns of the mesoporous silicas synthesized using these AEC surfactants with different \((\text{EO})_x\)-block length are shown in Fig. 5A. All the samples show three well-resolved reflection peaks with a \(1: \sqrt{3}: 2\) reciprocal spacing ratio, which proves to be a typical 2D hexagonal \textit{p6mm} mesostructure. The \(d\)-spacing of the (10) reflection peak increased with an increase in the length of \((\text{EO})_x\)-block.

As shown in Fig. 5B, the \(\text{N}_2\) adsorption–desorption isotherms feature type IV isotherms and sharp steps of capillary condensation in relative pressure range of \(P/P_0 = 0.35–0.6\), indicating a narrow pore size distribution in mesopore scale. It can be observed from PSD (Fig. 5C) that all the samples show a similar mesopore diameter \(d\) of 3.7–3.8 nm based on the desorption isotherms due to the same length of hydrophobic alkyl chain \((\text{C}_{12}\text{H}_{25}\text{–})\). Details of the porosity of the samples are summarized in Table 4. The unit cell parameter \(a\) was increased from 6.5 nm to

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### Table 2

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>(a/\text{nm})</th>
<th>(S_{\text{BET}}/\text{m}^2\text{g}^{-1})</th>
<th>(V_p/\text{mm}^3\text{g}^{-1})</th>
<th>(d/\text{nm})</th>
<th>(w/\text{nm})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{C}_{14}\text{AlaNa})</td>
<td>4.6</td>
<td>764</td>
<td>400</td>
<td>2.5</td>
<td>2.1</td>
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<tr>
<td>(\text{C}_{16}\text{AlaNa})</td>
<td>5.0</td>
<td>680</td>
<td>510</td>
<td>3.2</td>
<td>1.8</td>
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<tr>
<td>(\text{C}_{12}\text{GluNa})</td>
<td>5.2</td>
<td>476</td>
<td>400</td>
<td>2.6</td>
<td>2.6</td>
</tr>
<tr>
<td>(\text{C}_{14}\text{GluNa})</td>
<td>5.7</td>
<td>495</td>
<td>510</td>
<td>3.5</td>
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<td>(\text{C}_{16}\text{GluNa})</td>
<td>5.9</td>
<td>459</td>
<td>650</td>
<td>3.8</td>
<td>2.1</td>
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<tr>
<td>(\text{C}<em>{14}\text{H}</em>{29}\text{COONa})</td>
<td>6.4</td>
<td>542</td>
<td>590</td>
<td>3.8</td>
<td>2.8</td>
</tr>
</tbody>
</table>

\(^{a}\) Notation: \(a\), unit cell parameter; \(S_{\text{BET}}\), BET specific surface area; \(V_p\), mesopore volume; \(d\), BJH pore diameter calculated on the basis of \(\text{N}_2\) desorption isotherm curves; \(w\), wall thickness.

### Table 3

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>(a/\text{nm})</th>
<th>(S_{\text{BET}}/\text{m}^2\text{g}^{-1})</th>
<th>(V_p/\text{mm}^3\text{g}^{-1})</th>
<th>(d/\text{nm})</th>
<th>(w/\text{nm})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{C}<em>{12}\text{H}</em>{25}\text{O}(\text{CH}_2\text{CH}_2\text{O})_7\text{H})</td>
<td>5.0</td>
<td>780</td>
<td>938</td>
<td>3.6</td>
<td>1.4</td>
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<tr>
<td>(\text{C}<em>{16}\text{H}</em>{33}\text{O}(\text{CH}_2\text{CH}<em>2\text{O})</em>{10}\text{H})</td>
<td>5.7</td>
<td>796</td>
<td>997</td>
<td>3.8</td>
<td>1.9</td>
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<tr>
<td>(\text{C}<em>{12}\text{H}</em>{25}\text{O}(\text{CH}_2\text{CH}<em>2\text{O})</em>{10}\text{H})</td>
<td>5.4</td>
<td>814</td>
<td>840</td>
<td>3.4</td>
<td>2.0</td>
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\(^{a}\) Notation: \(a\), unit cell parameter; \(S_{\text{BET}}\), BET specific surface area; \(V_p\), mesopore volume; \(d\), BJH pore diameter calculated on the basis of \(\text{N}_2\) desorption isotherm curves; \(w\), wall thickness.

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![Fig. 4](image-url) XRD patterns (A), \(\text{N}_2\) adsorption–desorption isotherms (B) and pore size distributions (C) of calcined mesoporous silicas synthesized with various non-ionic surfactants, \(\text{C}_{12}\text{H}_{25}\text{O}(\text{CH}_2\text{CH}_2\text{O})_7\text{H}\) and \(\text{C}_{16}\text{H}_{33}\text{O}(\text{CH}_2\text{CH}_2\text{O})_{10}\text{H}\).
7.2 nm with lengthening the (EO)_x-block and the corresponding pore wall thickness of these samples was thickened from 2.8 nm to 3.4 nm with enlarging (EO)_x-block length from x \( \frac{1}{2} \) 5 to 10. The effective and accurate control in the thickness of the mesoporous silica has been achieved by choosing and designing the amphiphilic block of the AEC surfactant molecular structure.

Table 4  Structural properties of calcined mesoporous silicas shown in Fig. 5

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>a/Å</th>
<th>( S_{\text{BET}} )/m² g⁻¹</th>
<th>( V_p )/mm³ g⁻¹</th>
<th>d/Å</th>
<th>w/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}<em>{12}\text{H}</em>{25}\text{O} (\text{CH}<em>{2}\text{CH}</em>{2} \text{O})_5 \text{CH}_2\text{COONa} )</td>
<td>6.5</td>
<td>664</td>
<td>760</td>
<td>3.7</td>
<td>2.8</td>
</tr>
<tr>
<td>( \text{C}<em>{12}\text{H}</em>{25}\text{O} (\text{CH}<em>{2}\text{CH}</em>{2} \text{O})_6 \text{CH}_2\text{COONa} )</td>
<td>6.6</td>
<td>473</td>
<td>590</td>
<td>3.7</td>
<td>2.9</td>
</tr>
<tr>
<td>( \text{C}<em>{12}\text{H}</em>{25}\text{O} (\text{CH}<em>{2}\text{CH}</em>{2} \text{O})_7 \text{CH}_2\text{COONa} )</td>
<td>6.8</td>
<td>518</td>
<td>690</td>
<td>3.8</td>
<td>3.0</td>
</tr>
<tr>
<td>( \text{C}<em>{12}\text{H}</em>{25}\text{O} (\text{CH}<em>{2}\text{CH}</em>{2} \text{O})_8 \text{CH}_2\text{COONa} )</td>
<td>7.0</td>
<td>558</td>
<td>720</td>
<td>3.8</td>
<td>3.2</td>
</tr>
<tr>
<td>( \text{C}<em>{12}\text{H}</em>{25}\text{O} (\text{CH}<em>{2}\text{CH}</em>{2} \text{O})_9 \text{CH}_2\text{COONa} )</td>
<td>7.1</td>
<td>528</td>
<td>660</td>
<td>3.8</td>
<td>3.3</td>
</tr>
<tr>
<td>( \text{C}<em>{12}\text{H}</em>{25}\text{O} (\text{CH}<em>{2}\text{CH}</em>{2} \text{O})_{10} \text{CH}_2\text{COONa} )</td>
<td>7.2</td>
<td>472</td>
<td>520</td>
<td>3.8</td>
<td>3.4</td>
</tr>
</tbody>
</table>

\( ^a \) Notation: a, unit cell parameter; \( S_{\text{BET}} \), BET specific surface area; \( V_p \), mesopore volume; d, BJH pore diameter calculated on the basis of N₂ desorption isotherm curves; w, wall thickness.

Fig. 5  XRD patterns (A), N₂ adsorption–desorption isotherms (B) and pore size distributions (C) of calcined mesoporous silicas synthesized by AEC with different length of (EO)ₙ-block: \( \text{C}_{12}\text{H}_{25}\text{O} (\text{CH}_{2}\text{CH}_{2} \text{O})_5 \text{CH}_2\text{COONa} \) (a), \( \text{C}_{12}\text{H}_{25}\text{O} (\text{CH}_{2}\text{CH}_{2} \text{O})_6 \text{CH}_2\text{COONa} \) (b), \( \text{C}_{12}\text{H}_{25}\text{O} (\text{CH}_{2}\text{CH}_{2} \text{O})_7 \text{CH}_2\text{COONa} \) (c), \( \text{C}_{12}\text{H}_{25}\text{O} (\text{CH}_{2}\text{CH}_{2} \text{O})_8 \text{CH}_2\text{COONa} \) (d), \( \text{C}_{12}\text{H}_{25}\text{O} (\text{CH}_{2}\text{CH}_{2} \text{O})_9 \text{CH}_2\text{COONa} \) (e), \( \text{C}_{12}\text{H}_{25}\text{O} (\text{CH}_{2}\text{CH}_{2} \text{O})_{10} \text{CH}_2\text{COONa} \) (f).

Fig. 6  (A) XRD patterns of carbon inverse replica synthesized using calcined \( \text{C}_{14}\text{H}_{29}\text{COONa} \) (a), \( \text{C}_{12}\text{H}_{25}\text{O} (\text{CH}_{2}\text{CH}_{2} \text{O})_{10} \text{H} \) (b), \( \text{C}_{12}\text{H}_{25}\text{O} (\text{CH}_{2}\text{CH}_{2} \text{O})_{10} \text{CH}_2\text{COONa} \) (c) surfactant templated mesoporous silica as a hard template. (B) N₂ adsorption–desorption isotherm, pore size distribution of sample c. (C) TEM image of sample c.
3. Carbon replica of AEC surfactant templated mesoporous silica

As mentioned above, the organic and inorganic co-condensation in our synthesis system mainly happens between the two types of head groups, organic part of CSDA and silica source. Therefore, it is conceivable that micropores formed by imbedded (EO)x-block and electrostatic bonding of carboxylate head group and quaternary ammonium group will come into existence in the process of the formation of double-layer silica wall. The presence of these micropores is further verified through the successful synthesis of carbon inverse replicas using nanocasting method proposed by Ryoo et al.25

As shown in Fig. 6A (c), the XRD pattern of the carbon replica shows a main reflection peak at 2\(\theta\) = 1.6\(^{\circ}\), which indicates the presence of an ordered mesostructure. It is difficult to index the peak and further determine the space group because no other peaks have been observed. However, from the HRTEM image (Fig. 6C) taken with the electron beam parallel to the channel axis, 2D hexagonal \(\text{p}_{6}\text{mm}\) structure has been obviously observed. The sharp peak at 3.4 nm for the replica in the pore size distribution (Fig. 6B) is in agreement of the wall thickness (~3.4 nm) of the silica template. As expected, \(\text{C}_{13}\text{H}_{25}\text{O(CH}_2\text{CH}_2\text{O)}_{10}\text{H}\) templated mesoporous silica has directed the formation of carbon replica due to the existence of micropores formed by (EO)x-block embedded in the silica wall, while no carbon mesostructure has been replicated by the anionic surfactant templated mesoporous silicas [Fig. 6A (a and b)]. These results demonstrate the effectiveness of the strategy of using two types of head groups in series to initiate double-layer silica condensation with incorporation from the (EO)x-block and organic part of CSDA.

4. Functionalization and hydrothermal stability

The functionalized mesoporous silica with quaternary ammonium group inside micropore surface has been obtained by refluxing the mixture of as-synthesized mesoporous silica, ethanol and HCl at 90 °C for 12 h. Based on the XRD pattern shown in Fig. 7A, the three well-resolved peaks with a \(1 : \sqrt{3} : 2\) reciprocal spacing ratio can be indexed to (10), (11) and (20) reflections with unit cell parameter \(a = 7.5\) nm, indicating that the well ordered 2D hexagonal \(\text{p}_{6}\text{mm}\) mesostructure is maintained after extraction. \(\text{N}_2\) adsorption–desorption isotherm shows a type IV isotherm typical for mesoporous materials, and pore size distribution confirms that the pore diameter of the extracted mesoporous silica is 3.9 nm (Fig. 7B), similar to that of the calcined material (~3.8 nm). Furthermore, the wall thickness of the material has been calculated to be ~4.6 nm, much larger than that of calcined mesoporous silica (~3.4 nm). This result indicates that the micropores in the silica wall shrank in a large rate during calcinations, leading to a decrease in the wall thickness.

The solid-state \(^{13}\text{C}\) MAS NMR spectrum (Fig. 7C) of the AEC surfactant templated mesoporous material after extraction

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Fig. 7 XRD pattern (A), \(\text{N}_2\) adsorption–desorption isotherm, pore size distribution (B) and solid-state \(^{13}\text{C}\) MAS NMR spectrum of extracted mesoporous silica synthesized with \(\text{C}_{13}\text{H}_{25}\text{O(CH}_2\text{CH}_2\text{O)}_{10}\text{H}\text{CH}_2\text{COONa}\).

Fig. 8 XRD patterns of the mesoporous silicas obtained by fluxing the calcined samples in boiling water for 24 h. The materials were templated by \(\text{C}_{13}\text{H}_{25}\text{O(CH}_2\text{CH}_2\text{O)}_{10}\text{H}\) (a), \(\text{C}_{14}\text{H}_{29}\text{COONa}\) (b) and \(\text{C}_{13}\text{H}_{25}\text{O(CH}_2\text{CH}_2\text{O)}_{10}\text{CH}_2\text{COONa}\) (c), respectively.
confirms a complete remove of the surfactant molecule, and the four peaks observed at 8.5, 17.0, 53.1 and 68.4 ppm can be assigned to C1, C2, C4 and C3 of TMAPS, respectively. The quaternary ammonium or amino group functionalized mesoporous silica will exhibit potential applications in many fields such as sensors and catalyst, and the enhanced wall thickness makes the material more stable in hydrothermal conditions and thus more applicable.

The XRD patterns of the mesoporous silicas obtained after calcination and subsequently heated for 24 h in boiling water are shown in Fig. 8. The structures of samples synthesized with non-ionic surfactant C12H25O(CH2CH2O)10H and anionic surfactant C14H29COONa completely disappeared, as no X-ray diffraction peaks can be detected. However, the mesoporous silica templated by AEC surfactant C16H25O(CH2CH2O)10CH2COONa after boiling in water shows a high XRD reflection peak, which indicates a high order of mesostructure and high hydrothermal stability. This result shows that due to the formation of double-layer silica wall, the wall thickness and stability of mesoporous silica has been significantly improved.

**Conclusion**

Highly ordered 2D hexagonal $p6mm$ mesoporous silica with a thick wall has been successfully synthesized by using molecular design of an AEC surfactant. The wall thickness of the mesoporous silicas reached 1.2–1.7 times of that synthesized with other non-ionic and anionic surfactants. Moreover, the pore wall thickness can be controlled by design of surfactant molecule, i.e. different (EO)$_2$-block length. In addition, amino or quaternary ammonium groups functionalized mesoporous silicas with high hydrothermal stability can be synthesized by using AEC surfactant. It is promising to provide a new strategy for controlling properties of porous materials using molecular design of AEC tri-block anionic surfactant. This could open up new uses for mesoporous silica in applications such as catalysis, adsorption and separations, nanocasting and nanodevices.

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**References**