

Synthesis of Cubic $Ia\bar{3}d$ -like Mesoporous Silica at Low Temperature Using an Oligomeric Nonionic Surfactant

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A mesoporous silica having the cubic $Ia\bar{3}d$ structure similar to MCM-48 has been synthesized at low temperature using Brij 56 as surfactant in acidic media free of additives as evidenced by showing (211) and (220) reflection peaks in the XRD patterns and the same TEM images as MCM-48.

Mesoporous materials are ordered, highly porous silicates and aluminosilicates with pore sizes in the range of 2–10 nm. Although these materials exist in a variety of hexagonal, cubic, and other forms,^{1–5} the majority of publications in this area have been concentrated on the first reported 2d-hexagonal phase, MCM-41, FSM-16, or SBA-15. This may be due to the difficulty in synthesizing other phases.

These materials are synthesized using a liquid crystal templating mechanism, where the structure of the porous solid is determined by the aggregation of surfactant molecules such as $C_{16}H_{33}(CH_3)_3N^+$, which serves as a template for the formation of the pores. Recently, nonionic triblock copolymers, poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide), ($EO_nPO_mEO_n$ for brevity) have been used to synthesize large mesoporous siliceous materials exhibiting cubic $Ia\bar{3}d$ symmetry.^{6–8} Furthermore, such a high-quality, cubic $Ia\bar{3}d$ silica with large mesopores could be used as a template to fabricate new bi-continuous arrays of nanotube-type carbon (designated as CMK-9 mesoporous carbon), as well as rod-type carbon (CMK-1).^{7,8} Moreover, it has been reported that the ordered mesoporous materials with large cages were synthesized by using these nonionic triblock copolymers, e.g., cubic ($Im\bar{3}m$),^{9–11} cubic ($Fm\bar{3}m$),¹² etc. Zhao et al.⁵ reported the synthesis of cubic ($Im\bar{3}m$), cubic ($Pm\bar{3}m$), 3d hexagonal ($P6_3/mmc$), 2d hexagonal ($p6mm$), and lamellar symmetries, using nonionic alkylpoly(ethylene oxide) (PEO) oligomeric surfactants and poly(alkylene oxide) block copolymers in acid media. Compared with cationic surfactants, Brij type surfactants have advantages because they are inexpensive, less toxic, and more biodegradable.⁵ In addition, they are easy to remove by calcination because of higher combustibility and do not produce toxic nitrogen oxides. Here, we report a low-temperature synthesis procedure for obtaining the $Ia\bar{3}d$ structure using Brij 56 ($C_{16}H_{33}(OCH_2CH_2)_n$, $n \approx 10$) as a surfactant.

A typical synthesis was conducted as follows: 0.9 g of Brij 56 was dissolved in 69.1 g of distilled water at room temperature. The mixture turned homogeneous after stirred continuously at room temperature for 2 h, followed by addition of 9.9 g of HCl. The solution was cooled to 0 °C. Finally, 8 g of TEOS was added to the solution with vigorous stirring. The reactant molar composition was 0.035 Brij 56:100 H₂O:2.5–10 HCl:1 TEOS. The resulting mixture was subsequently allowed to react at 0 °C for 2 d under static conditions. The solid product

was filtered out and dried at 100 °C without washing. The surfactant was removed by calcination at 550 °C for 5 h. The influence of the synthesis temperature on the structure was examined. Figure 1 shows the XRD patterns of the samples synthesized with Brij 56 in the range of 0 to 80 °C. The sample synthesized at 0 °C followed by calcination (Figure 1a) showed (211) and (220) peaks, which are characteristic of the cubic $Ia\bar{3}d$ structure. The samples b–e synthesized at 15–60 °C showed the XRD pattern characteristic of disordered mesostructures. In contrast, the sample f synthesized at 80 °C possessed 2d-hexagonal structure. This could be accounted for by the g value,³ which decreases with increasing synthesis temperature as a result of the increase in mobility of the head group (ethylene oxide) and alkyl chain. Therefore, low temperatures, e.g. 0 °C, were favorable for the synthesis of the $Ia\bar{3}d$ structure.

We carried out investigation of the optimal conditions for the synthesis of cubic $Ia\bar{3}d$ mesostructure using the nonionic surfactant under strongly acidic conditions by varying the amount of H₂O and the HCl/TEOS molar ratios. To investigate the optimal amount of H₂O for synthesis, the H₂O/TEOS ratio was varied in the range of 50 to 150. Separation of (211) and (220) XRD peaks was observed by increasing the H₂O amount from 50 to 100. The XRD pattern became disordered when the molar ratio of H₂O/TEOS was higher than 125. Finally, the acid concentration was varied with keeping the H₂O/TEOS molar ratio constant at 100 to obtain the high-quality structure (Supporting Information). We have also tried to synthesize the cubic $Ia\bar{3}d$

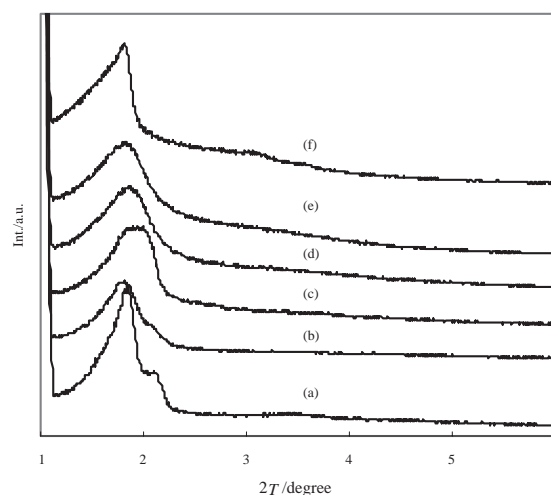


Figure 1. XRD patterns of samples synthesized at various temperature. 0 °C (a), 15 °C (b), 30 °C (c), 45 °C (d), 60 °C (e), and 80 °C (f). The molar ratio of the synthesis gel is 0.035 Brij 56:100 H₂O:2.5 HCl:1 TEOS.

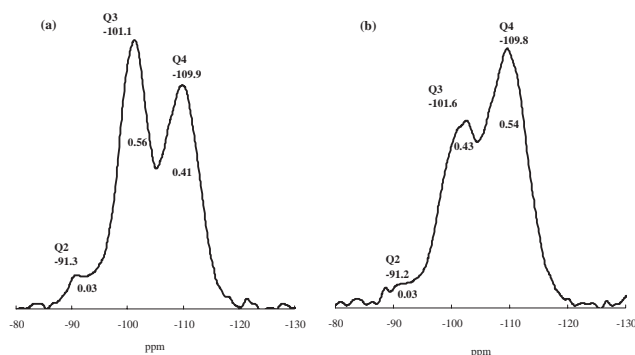


Figure 2. The ^{29}Si MAS NMR spectra of as-synthesized samples. (a) $\text{HCl}/\text{TEOS} = 2.5$ and (b) 10.

mesostructure by using other Brij type surfactants such as Brij 30, 52, 72, 76, 98, etc. However, only Brij 56 led to the cubic $Ia\bar{3}d$ mesostructure, probably because it has the balance between the hydrophobic alkyl part and the hydrophilic polyoxyethylene part, which would be favorable for the formation of this mesostructure.

Figure 2 shows ^{29}Si MAS NMR spectra of the as-synthesized samples with $\text{HCl}/\text{TEOS} = 2.5$ and 10, representing the degree of silica condensation. The sample synthesized with $\text{HCl}/\text{TEOS} = 10$ had more Q^4 sites ($\text{Q}^4/\text{Q}^2 + \text{Q}^3 + \text{Q}^4 = 0.54$) while that with $\text{HCl}/\text{TEOS} = 2.5$ had more Q^3 sites ($\text{Q}^3/\text{Q}^2 + \text{Q}^3 + \text{Q}^4 = 0.56$). This indicated that the condensation of silica in the sample of $\text{HCl}/\text{TEOS} = 10$ during the synthesis progressed more markedly than the other samples.

The increase of 2.3 to 2.7 nm in pore size with increasing HCl/TEOS ratio from 2.5 to 10 might be related to silica condensation progressive during synthesis. When the samples were synthesized with the synthesis gel having a HCl/TEOS ratio of 2.5 and 10, respectively, they showed almost the same size of the unit cell of $a_{211} = 13.9$ and 13.8 nm $a_{220} = 14.0$ and 13.8 nm, respectively. Because the sample synthesized at low acid concentration poorly condensed during synthesis, contraction occurred with the progress of condensation during calcination, but the highly condensed sample negligibly contracts on calcination to give a sample with larger pores.

The SEM image of the sample synthesized at $\text{HCl}/\text{TEOS} = 10$ is shown in Figure 3a. Clearly, truncated octahedral particles were formed. This is different from the previous

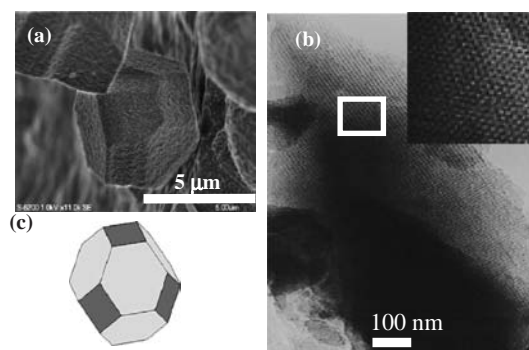


Figure 3. The SEM (a), the TEM image (b), in which incident electron is parallel with $[111]$, and the drawing of morphology (c) of the sample.

result¹⁴ that cube truncated by rhomb dodecahedron particles were synthesized by using sodium silicate, hexadecyltrimethylammonium bromide (HTABr) and various kinds of alcohol. The schematic drawing of the morphology of the as-synthesized samples is depicted in Figure 3c.¹⁵ It can be seen that the external surface of the particle was composed of six $\{100\}$ and eight $\{111\}$ planes. Further evidence for the cubic mesostructure is provided by the TEM images presented in Figure 3b. The TEM images were similar to those taken with three axes, $[100]$, $[110]$, and $[111]$ reported by Kaneda et al.,¹⁶ suggesting that the mesoporous silica has the $Ia\bar{3}d$ structure.

In conclusion, we have synthesized a cubic $Ia\bar{3}d$ structure mesoporous silica at low temperature using an oligomeric non-ionic surfactant, Brij 56, in strongly acidic conditions. Although it had smaller pore size, compared with the cubic $Ia\bar{3}d$ structure that was recently synthesized by other nonionic surfactants,^{7,8,11} it can be easily synthesized at low temperature without the addition of other silica sources⁸ or additive salts.¹¹

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