The Upper Temperature Limit in Cooperative Assembly of Ordered Mesoporous Materials

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Several examples for high temperature (95 °C, higher than the cloud point of pure surfactant) synthesis of highly ordered hexagonal mesoporous silica structures by employing triblock copolymers such as P65 ($EO_{20}PO_{30}EO_{20}$) as structure-directing agents have been presented. Such understanding may increase the range of surfactants and the temperature regime under which ordered mesoporous materials can be cooperatively assembled.

Recently, considerable research efforts have been made in the field of mesoporous materials because of their emerging uses in catalysis, adsorption, sensors, and separations.[1–3] For different applications, the fabrication of mesoporous materials with controllable pore size, porosity, structure together with adjustable inorganic wall compositions is important. Recent advances in the formation mechanism of mesoporous materials reveal that such mechanism depends much on the surfactants employed and the experimental conditions of synthesis.[4] It is noted that in the big family of surfactants, only a few have been used as templates to synthesize highly ordered mesoporous materials. Recently, we proposed that the critical micelle concentration (CMC) of surfactants may be used approximately to predict the quality of cooperatively assembled mesostructures:[5,6] surfactants with low CMC values may result in high quality mesoporous materials; therefore, the use of "salting-out" inorganic salts[7] may lead to highly ordered mesoporous materials.

Although increasing temperature may dramatically decrease the CMC especially for nonionic block copolymer surfactants,[8] the system may finally reach the cloud point (CP) of surfactants, decreasing the association ability of surfactant molecules. The potential of cooperative self-assembly of mesostructures at high temperature is not extensively examined. Kipkemboi et al. proposed that when the reaction temperature is close to or reaches the surfactant CP, the silica mesostructure formed was of bad quality.[9] Synthesis of ordered mesoporous materials above this limit (>CP) has not been studied.

Here we report the synthesis of highly ordered mesoporous silica structures at very high temperature (95 °C) by employing triblock copolymer P65 [$EO_{20}PO_{30}EO_{20}$, BASF, CP = 82 °C in 1 wt% solution. EO is poly(ethylene oxide) and PO is poly(propylene oxide)] as a structure-directing agent. It is revealed that high concentration of H^+ and a small amount of ethanol released by the hydrolysis of tetraethyloxysilane (TEOS) during synthesis may greatly increase the CP of surfactant (>100 °C), thus the CP of surfactant in aqueous solutions cannot be regarded as an upper limit for the synthesis of mesostructures at high temperatures. Moreover, our results suggest that the cooperative assembly of highly ordered mesoporous materials may also occur at very high temperatures, which may be useful to synthesize new mesostructured materials whenever a high temperature sol-gel process is available.

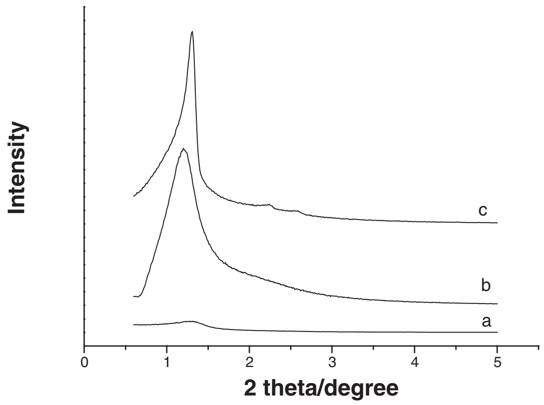

Figure 1. XRD patterns of calcined mesoporous silica prepared by using P65 template at different reaction temperatures: a, b and c for temperature 55 °C, 75 °C and 95 °C, respectively.

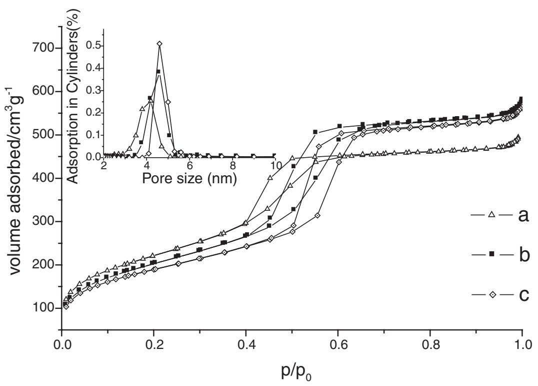

Figure 2. Nitrogen adsorption-desorption isotherm plots and pore size distribution curves (inset) of calcined mesoporous silica prepared by using P65 template at different reaction temperatures. a, b and c for temperature 55 °C, 75 °C and 95 °C, respectively.

In a typical preparation, 1 g of P65 was dissolved in 30 g of 2 M HCl at desired temperature (55–95 °C). To this solution, 2.08 g of TEOS was added with vigorous stirring for 24 h (TEOS:P65:HCl:H_2O=1:0.0003:6:166, molar ratio). The mixture was aged at 100 °C overnight without stirring. The solid product was filtered and air-dried at RT. Calcination was carried out at 550 °C in air for 5 h.

The powder X-ray diffraction (XRD) patterns of calcined mesoporous silica prepared in the presence of P65 at different temperature (55–95°C) are shown in Figure 1. With increasing temperature, the first diffraction peak becomes much stronger and much narrower; moreover, at the highest temperature employed (95 °C), two additional peaks are observed, suggesting

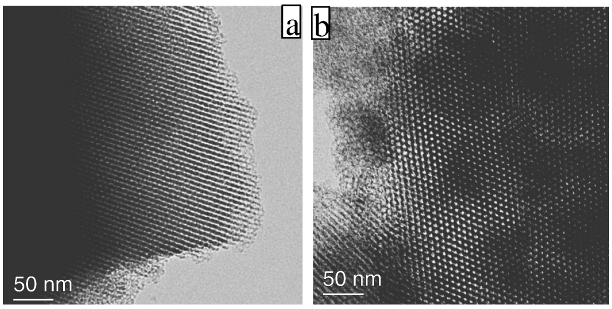

Figure 3. TEM images of calcined hexagonal mesoporous silica synthesized by using P65 as a template at 95 °C along (a) [100] direction and (b) [001] direction.

that the mesoscale order is much improved with increasing temperature. The silica material synthesized by P65 at 95 °C can be attributed to a two-dimensional hexagonal structure (*p6mm*) with a cell parameter of 86.4 and 77.7 Å for as-synthesized and calcined materials, respectively. Representative N_2 adsorption-desorption isotherms and the corresponding pore size distribution curves (analyzed by using BdB model)[10] of calcined mesoporous materials synthesized at different temperatures are shown in Figure 2. All calcined materials yield type IV isotherms with type-H_1 hysteresis loops. From the pore size distribution curves, it is calculated that the full wave at half maximum (FWHM) is 9.5, 8.9, and 6.5 Å for materials synthesized at temperature 55, 75, and 95 °C, respectively, indicating that the pore size distributions become more uniform at higher temperatures, in good accordance with the XRD results. The pore size increases a little at high temperature (37.4, 43.2, 47.3 Å for temperature 55, 75, and 95 °C, respectively).[11] The transmission electron micrograph (TEM) results confirm that mesoporous materials prepared by P65 template at 95 °C are highly ordered hexagonal structures (Figure 3).

The above results reveal that the quality of mesoporous materials templated by P65 at high temperature is much better than that at low temperature. This can be explained by the temperature-CMC-mesostructure correlation as we proposed before.[7] However, the structure-directing agent P65 utilized in our synthesis has a CP of 82 °C in 1 wt% water solution.[12] Obviously, the fact that highly ordered mesoporous materials can be synthesized by using P65 templates at 95 °C suggests that the CP of surfactant in water cannot be simply regarded as an upper limit in the synthesis of mesoporous materials.[9] Cooperative assembly of silica mesostructures involves a complex system. In our synthesis, strong acidic conditions and the ethanol released by the hydrolysis of TEOS are found to greatly increase the CP of P65. At the same concentration of 3 wt% (the reactant ratio in synthesis), the CP of P65 is found to be ≈65 and ≈85 °C in water and 2 M HCl solutions (The measurement of CP is according to reference[13]), respectively, suggesting that the strong protonation of EO groups may greatly decrease the ability of liquid-liquid phase separation at high temperatures. Moreover, after adding 1.84 g (0.04 mol, similar to the amount of ethanol released by TEOS in synthesis) ethanol into 30 g of 3 wt% P65 water solution, the CP of P65 in the final solution is found to be ≈75 °C. Finally, the CP of P65 in a system similar to our synthesis condition is found to be larger than 95 °C (~30 °C higher than normal CP in water solutions) because of the combination of the H^+ and ethanol effect. More importantly, the successful synthesis of highly ordered mesoporous silica structures at high temperature (≈95 °C) may increase the range of surfactants and the temperature regime under which ordered mesoporous materials can be cooperatively assembled. While the use of inorganic salts may decrease the synthesis temperature at the low end,[7] the use of strong acidic condition and a certain amount of organic solvents may increase the temperature at the other end. Such understanding may be useful to fabricate new mesostructured materials once a high temperature sol-gel process is employed and combined with the self-assembly potential of surfactants.

Similar results have also been obtained for P85 ($EO_{26}PO_{39}EO_{26}$) and B40-2500 [$EO_{17}BO_{14}EO_{17}$, where BO represents poly(butylene oxide)]. Highly ordered hexagonal mesoporous silica materials are obtained at high temperatures (>90 °C) by utilizing these templates (see Table 1 for the CP of surfactants, synthesis temperature and the physicochemical properties of the resultant calcined silica structures.)

Table 1. The CP of block copolymers, synthesis temperature and the physicochemical properties of the resultant calcined silica structures

Block copolymers	*CP*[a] /°C	*CP*[b] /°C	*T* /°C	*V* /cm^3g^{-1}	*S* /m^2g^{-1}	*D* /nm
$EO_{20}PO_{30}EO_{20}$	≈82	>95	95	0.92	683	4.7
$EO_{26}PO_{39}EO_{26}$	≈85	>95	95	1.09	587	6.8
$EO_{17}BO_{14}EO_{17}$	≈80	>95	95	0.95	787	4.8

[a]In 1 wt% aqueous solution. [b]In a system similar to our synthesis conditions; *T*: reaction temperature; *V*: pore volume; *S*: surface area; *D*: pore diameter.

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