Templated Synthesis of Mesoscopic Tube Silicates Using Aqueous Mixtures of Naphthalenediol and Ammonium Surfactants

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An aqueous mixture of cetyltrimethylammonium bromide (CTAB) and 2,3-dihydroxynaphthalene (2,3-DHN) gives a viscous solution of rodlike nanoaggregates as confirmed by transmission electron microscopy. These supramolecular assemblies are first used as templates for the sol–gel synthesis, providing an aqueous route for tube silicates.

Porous materials with nanosized cavities and channels have a wide range of important applications to molecular separations, such as ion exchange, and heterogeneous catalysis. Molecular-assembly-templated sol–gel synthesis provides effective routes for the preparation of these inorganic nanomaterials, as exemplified by lamellar and mesoporous silicates, which are templated by synthetic bilayer membranes[1,2] and cylindrical micelles,[3–5] respectively. Nonagglomerated, large silica nanotubes with diameters of 4–50 nm are also prepared using tubular nanoassemblies prepared from synthetic bilayer membranes[6] and organogels.[7,8]

Another important family of mesopore silicates has wormhole and tube structures[9–12] that possess catalytically important branched channels. The wormhole or tube channel motif is a potentially important structural feature for favorable catalytic reactivity, because channel branching within the framework can facilitate access to reactive sites on framework walls. The synthesis of tube silicates requires electrically neutral amine surfactants and water–alcohol cosolvents; thus, the textural porosity of these silicates is determined by the balance of complex factors, mainly because alcohol molecules generally deteriorate surfactant assemblies.

To develop a rational design for tube silicates, it is desirable that the synthesis of such silicates is carried out in pure water, namely, under much simpler and more environmentally friendly conditions.

Furthermore, the use of supramolecular amphiphiles formed from commercially available materials is important for the wide industrial application of tube structures. In this study, we report that rodlike aggregates are formed from the mixture of CTAB and 2,3-DHN in pure water, and they act as templates to direct the sol–gel synthesis of tube structures.

Powdery samples of 2,3-DHN (8×10^{-4} g, 5×10^{-6} mol) or catechol (5.5×10^{-4} g, 5×10^{-6} mol) was added an aqueous solution of CTAB (1×10^{-3} M, 5 mL) at an equimolar ratio and the mixtures were stirred overnight at 30 °C.

In Figure 1, transmission electron micrographs of aqueous 2,3-DHN/CTAB and catechol/CTAB systems are shown, respectively (HITACHI H-7100, acceleration voltage, 75 kV). These aqueous mixtures are aged at 30 °C for 2 h before dropping the solution on the carbon-coated copper grid, and are post-stained with uranyl acetate (2 wt %). The transmission electron microscopy of the aqueous mixture 2,3-DHN/CTAB indicates the presence of rodlike aggregates (Figure 1a, diameter, ca. 31 nm), consistent with the observed higher kinematic viscosity. On the other hand, only globular aggregates (diameter, ca. 250–300 nm) are observed for aqueous catechol/CTAB systems (Figure 1b).

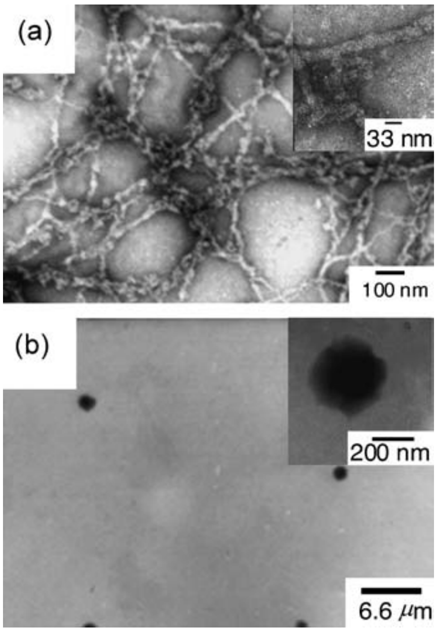

Figure 1. TEM images of (a) 2,3-DHN/CTAB aggregate and (b) catechol/CTAB aggregate.

The schematical formation of rodlike aggregates for 2,3-DHN/CTAB and globular aggregates for catechol is shown in Figure 2. These hydrophobic aromatic molecular aggregates efficiently bind to CTAB micelles and may adopt an anisotropic orientation with their hydrophobic moiety directed inside and their hydrophilic hydroxy groups oriented to the outer surface of the aggregates. As the fibers developed are formed only from 2,3-DHN/CTAB mixtures and not from the other combinations, the interaction between alkyl chains and aromatic moiety are apparently affected by the chemical structure and size of diols. The formation of flexible tubular liposomes has also been reported for an aqueous mixture of CTAB and 4-hydroxybiphenyl,[13] and it seems that the hydrophobic nature is important when a neutral phenol derivative is employed.[14–16]

The rodlike aggregate formed from 2,3-DHN/CTAB was then employed as a template for the sol–gel silicate synthesis. Silica gel (5.4 g, Wakogel Q63), sodium hydroxide (6 g) and

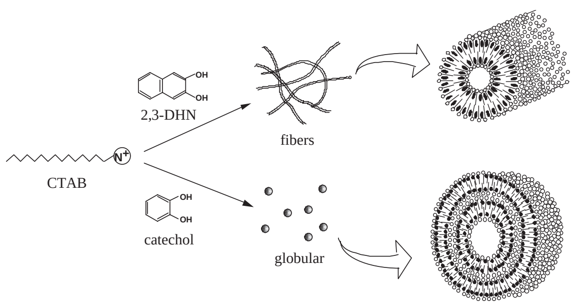

Figure 2. Schematical formation of rodlike aggregates for 2,3-DHN/CTAB and globular aggregates for catechol/CTAB.

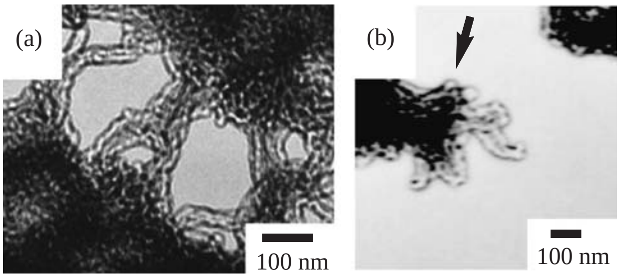

Figure 3. TEM views of calcined product prepared from 2,3-DHN/CTAB system.

water (50 mL) were placed in a polypropylene vessel and the mixture was stirred at 40 °C for 48 h. This aqueous silicate solution was diluted with water 10 times, and pH of the solution was adjusted to approximately 7 by adding 1 M HBr. Then 3 mL of the solution was mixed with an aqueous solution of 2,3-DHN/CTAB (1 mL, 1×10^{-3} M). After stirring the mixture at room temperature for 30 min, the solution was gradually suspended. The resulting product was filtered and repeatedly washed with pure water. The powder was lyophilized for 48 h. The presence of silicate in the powder was confirmed by IR spectroscopy (*n*Si–O–Si, 1000 cm^{-1}). The obtained product was calcined from room temperature to 300 °C in flowing nitrogen (flow rate, 20 mL min^{-1}, the temperature was changed at a rate of 1 °C min^{-1}.) and from 300 to 600 °C in flowing air (under the same condition).

Figures 3a and 3b show a TEM photograph of the calcined silicate. It is composed of irregular flakes and the expanded view indicates the presence of tube structures with diameters of approximately 31 nm and wall thickness of approximately 2 nm, which are similar to the tubular assemblies of aqueous 2,3-DHN/CTAB (Figure 1a). Therefore, it is reasonable to assume that the observed tube nanostructures are templated by 2,3-DHN/CTAB. The N_2 adsorption property of the product was then investigated.

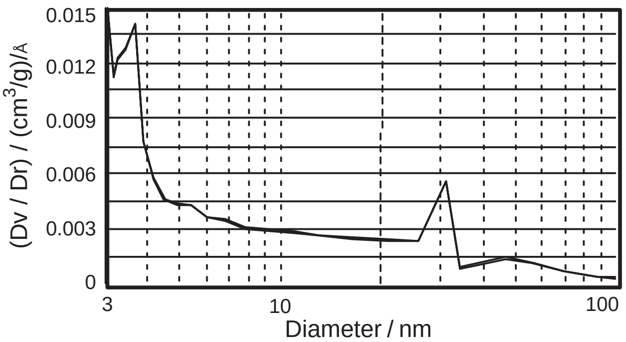

Figure 4. Pore size distributions for calcined silicate obtained from 2,3-DHN/CTAB (calculated by BJH method).

Figure 4 shows the pore size distribution plot for the calcined sample which was calculated by the BJH method. Bimodal peaks are observed at 3.8 and 31 nm. The 3.8-nm peak corresponds to pores on silica tubes, because it is observed for the almost equal position silica powder which did other how to make.[17,18] On the other hand, the 31-nm peak, which corresponds to a pore diameter of a silica tube, possess narrow pore size distribution (width at half height 5 nm). The latter pore size is significantly larger than those reported for MCM-41 (2–10 nm) and wormhole framework structures (ca. 2–4 nm). The average BET surface area measured for two independent samples was 700 m^2 g^{-1}, which is smaller than that reported for wormhole structures (ca. 1000 m^2 g^{-1}).

In conclusion, we succeeded in preparing tube silicates using the aqueous supramolecular template 2,3-DHN/CTAB. Silicates prepared by this method are larger than the pore size of MCM-41, which is almost equal to that of the silicate structure prepared using the bilayer membrane. It is possible to induce variation in the size and structure molecular aggregate by adding a compound. This compound does not need to be a new synthesized compound.

References and Notes

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