Amorphous Carbon-promoted Low-temperature Crystallization of Silica

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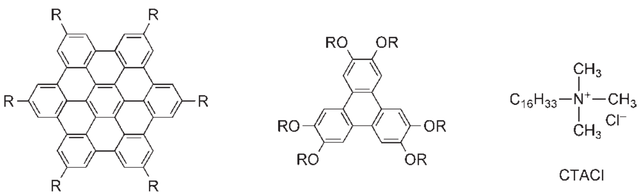
Heating of mesoporous silica hybridized with self-assembled disc-like molecules such as hexabenzocoronene and triphenylene derivatives at ≥900 °C under N_2 resulted in low-temperature crystallization of its amorphous silicate framework into cristobalite, a form of crystalline silica that appears in a much higher temperature range in the phase diagram.

Mesoporous silicates with a regular array of hexagonal nanoscopic channels have attracted much attention, because they are capable of unidirectional alignment of guest substances along the channels.[1] By using aromatic amphiphiles derived from triphenylene (TP) and hexabenzocoronene (HBC) as templates (Figure 1), we have recently succeeded in the fabrication of novel mesoporous silica composites whose channels are completely filled with one-dimensional columnar assemblies of disc-like molecules.[2,3] Mesoporous silicates containing organic guests are interesting as they are potential precursors for low-dimensional carbon materials. For instance, pyrolysis of organic substances such as sucrose[4] and acetylene[5] in the mesoporous silicate channels has been reported to give mesoporous carbon and multiwalled carbon nanotubes, respectively. Being motivated by these examples, we investigated pyrolysis of the π-stacked TP and HBC amphiphiles in the silicate channels. To our surprise, the amorphous silicate framework was converted at 900 °C into cristobalite, a form of crystalline silica that appears at 1470–1713 °C in the phase diagram under an atmospheric pressure. Here, we report an unprecedented catalytic activity of amorphous carbon for crystallization of amorphous silica.

A mesoporous silica film templated by HBC **1** was prepared by a method similar to that reported previously.[3] The formation of a honeycomb architecture was confirmed by X-ray diffraction analysis (XRD) and transmission electron microscopy (TEM).[6] Upon heating at 1000 °C under N_2 for 10 h, the yellow-colored silica composite turned black. Optical microscopy revealed the presence of black dots due to a carbonized organic template (Figure 2A). Interestingly, this pyrolyzed sample showed an XRD profile with sharp diffraction peaks at $2\theta > 20°$, which are typical of α-cristobalite[7] (Figure 3A(a)). Electron diffraction analysis displayed spots with a d spacing of 0.41 nm, which can be indexed as the (101) diffraction of α-cristobalite (Figure 2B inset). On the other hand, as observed by TEM (Figure 2B) and XRD (Figure 3A(a)), the honeycomb architecture of the mesoporous silica was completely disrupted.



HBC (**1**)
R = $(CH_2)_8CO_2(CH_2CH_2O)_3CH_3$

TP (**2**)
R = $(CH_2)_{10}(OCH_2CH_2)_3OCH_3$

CTACl

Figure 1. Structural formulae of template molecules for silica composites.

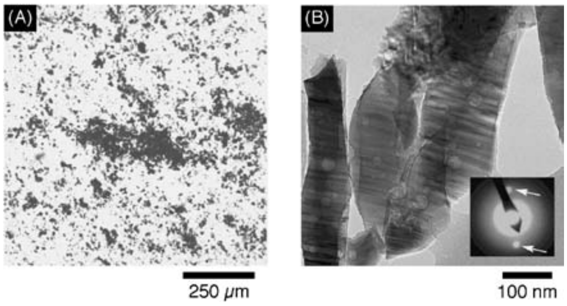


Figure 2. Optical (A) and TEM (B) micrographs of a black substance formed by heating of a mesoporous silica composite of **1** at 1000 °C under N_2 for 10 h. Inset in (B): electron diffraction pattern. Arrows indicate diffraction spots with a d spacing of 0.41 nm.

The transformation of amorphous silica into cristobalite occurred even at 900 °C under otherwise identical conditions to the above (Figure 3A(b)), whereas no crystallization took place below 800 °C (Figures 3A(c) and 3A(d)) even upon prolonged heating. We also found that a mesoporous silicate filled with amphiphilic TP (**2**)[6] undergoes a similar low-temperature crystallization of the silicate framework. When this composite was heated at ≥900 °C under N_2, a black-colored substance again resulted, whose XRD profiles (Figures 3B(a) and 3B(b)) were identical to that observed for the pyrolyzed product of the silica composite of **1** (Figures 3A(a) and 3A(b)). In sharp contrast, neither template-free mesoporous silica[6] nor mesoporous silica filled with aliphatic surfactants underwent crystallization. For example, thermal treatment at 1000 °C under N_2 of as-prepared mesostructured silica using cetyltrimethylammonium chloride (CTACl) as a template[6] gave a colorless substance. The XRD profile (Figure 3C) of this product was featureless and did not show any sign of the formation of cristobalite. These contrasting results indicate that carbonized species, left after the pyrolysis of the organic templates, play a role in the low-temperature crystallization of the silicate framework.

Pyrolysis experiments at varying temperatures for 10 h under N_2 showed that carbonization of HBC amphiphile **1** takes place at 600 °C, a much lower temperature than that observed for the crystallization of the mesoporous silica host. The Raman spectrum of the pyrolyzed product was typical of amorphous carbon, displaying D and G bands at 1330 and 1590 cm^{-1}, respectively (Figure 4).[8] Thermogravimetric analysis (TGA) under

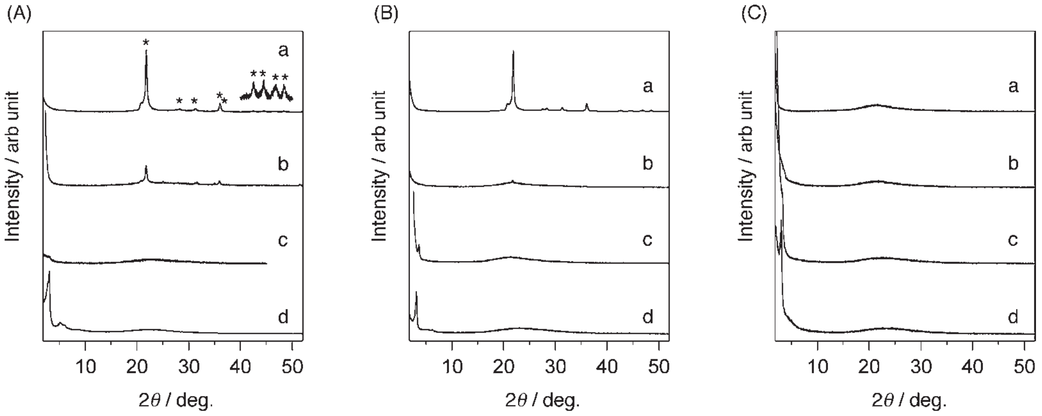


Figure 3. XRD patterns of pyrolyzed products, at 1000 (a), 900 (b), 800 (c), and 600 °C (d) under N_2 for 10 h, of mesoporous silicates hybridized with **1** (A), **2** (B), and CTACl (C). Insets in (A)(a): magnified (×10) diffraction peaks. Asterisked peaks in (A)(a) are the diffractions of α-cristobalite.

N_2 showed an initial weight loss of 1% at 25–175 °C due to dehydration, followed by a major weight loss of 33% at 175–600 °C due to a pyrolytic decomposition of the organic template. On the other hand, calcination at a constant temperature of 600 °C under air allowed complete removal of the organic template with a weight loss of 44%. This weight loss is comparable to those observed for mesoporous silica/organic composites reported previously.[2,9] From these results, the quantity of the amorphous carbon, left after the pyrolysis, was evaluated as 25 wt % of the initial amount of **1**. Upon subsequent heating at 1000 °C to allow crystallization of the silicate framework, the quantity of the carbon residue dropped to 4 wt % of the initial amount of **1**. A comparable quantity (2 wt %) of the carbon residue was observed for the pyrolyzed product of the silica composite of **2** at 1000 °C under N_2. It is worthy of note that such a small amount of amorphous carbon is effective for the formation of cristobalite. In contrast, upon heating under air, where no carbon residues remained in the silicate framework (vide ante), the low-temperature crystallization of silica did not occur irrespective of whether the template was HBC or TP.

Cristobalite has attracted attention both in mineralogy and geophysics, as it occurs upon volcanic eruptions.[10] So far, similar promotion effects on crystallization of amorphous silica have been reported for alkali metal ions,[11] noble metals,[12] and high-pressure hot water,[13] and different mechanistic proposals have been made. While the formation of high-quality fibers of cristobalite have been observed in the presence of activated carbons,[14] low-temperature formation of cristobalite promoted by amorphous carbon has never been reported. We consider that the radical character of the in situ generated amorphous carbon is likely responsible for this interesting phenomenon. We confirmed by electron spin resonance spectroscopy[6] that the pyrolyzed silica contains carbon radical species (g-value $= 2.0029$) with a spin concentration of 1.6×10^{20} spins/g of carbon.[15] Cleavage of Si–O–Si bridges by carbon radicals could allow easier reorganization of the silica framework, leading to the reduction of a kinetic barrier to the crystallization.

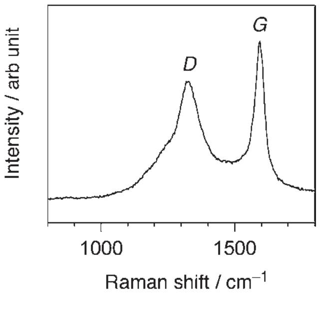


Figure 4. Raman spectrum of a black substance obtained by pyrolysis of a mesoporous silica composite of **1** at 600 °C under N_2 for 10 h.

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6 See Electronic Supporting Information.
7 Although α and β forms of cristobalite are known, α-cristobalite is the only observable form at room temperature because of a rapid phase transition from β- to α-cristobalite at 268 °C upon cooling.
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