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A Condensable Amphiphile with a Cleavable Tail as a "Lizard" Template for the Sol–Gel Synthesis of Functionalized Mesoporous Silica

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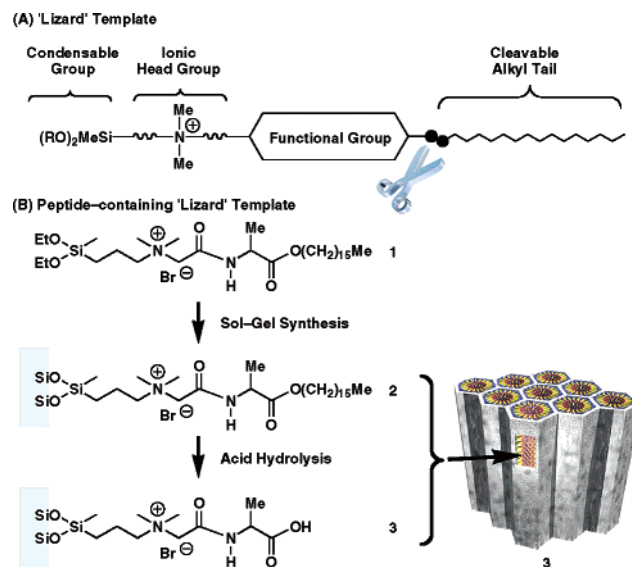
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Sol–gel synthesis of mesoporous silica with functional templates¹ has attracted attention for the fabrication of, for example, optoelectronic nanocomposite materials, because this method, in contrast with statistical postloading approaches, guarantees dense filling of organic functional groups in the silicate channels. However, for other applications such as sensing, separation, and catalysis,² additional tricks must be exploited for a limited accessibility of external guests to those interior functional groups. We now report a new synthetic method that copes with both dense functionalization and guest accessibility of the silica channels, by using a condensable amphiphile with a cleavable alkyl tail (Chart 1A).³ The dialkoxysilane functionality, attached to its onium ion headgroup, is co-condensed under sol–gel conditions with tetraethyl orthosilicate (TEOS), to form mesoporous silica whose channels are filled with an organic group of the template. Thus, subsequent cleavage and removal of the alkyl tail leave nanopores with a covalently functionalized surface. Condensable amphiphiles have been first utilized for the synthesis of 2D nanostructures⁴ such as LB films^{4a,b} and vesicles,^{4c,e} and more recently for sol–gel synthesis of mesoporous silica.⁵ In the present Communication, we highlight alanine-containing **1** as the condensable amphiphilic template (Chart 1B). Acid hydrolysis of the template ester in the resulting composite (**2**) leaves alanine-functionalized mesoscopic channels **3**. Here, the template behaves like a "lizard", whose tail can be cleaved off after anchoring.

Typically, **3** can be synthesized as follows. A mixture of TEOS, H₂O, HCl, and EtOH at a molar ratio of 1/4/3/0.01, respectively, was heated for 2 h at 70 °C for partial condensation. To an aliquot of the reaction mixture (0.20 g) were successively added **1** (0.041 g), H₂O (0.82 g), and concentrated aqueous HCl (0.43 g), and the mixture was stirred at room temperature for 4 h. Filtration of the reaction mixture allowed isolation of **2** as white powder. **2** (0.05 g) was then suspended in THF (50 mL) containing 0.5 mL of concentrated aqueous HCl. After being refluxed for 8 h, the reaction mixture was filtered to give a white solid, which was washed with THF and air-dried to give **3**.

X-ray diffraction (XRD) analysis of **2** (Figure 1A) showed a set of peaks characteristic of a hexagonal silicate structure with a *d*-spacing for the (100) diffraction peak of 4.2 nm. The hexagonal structure was preserved not only on calcination of **2** at 550 °C but also after hydrolytic removal of the hexadecyl tail to give **3**. Although the calcination resulted in a considerable decrease in *d*-spacing to 3.3 nm, the hydrolytic treatment did not cause any substantial shrinkage of the silica channel (*d*-spacing = 4.5 nm). ²⁹Si MAS NMR spectroscopy of **3** showed two intense signals at δ –111 and –101 ppm due to Si(OSi–)₄ (Q⁴) and Si(OH)(OSi–)₃ (Q³), respectively,⁶ where the integral ratio of the signals Q⁴/Q³ was evaluated to be 1.7, which is typical of mesoporous silica such as MCM-41.⁷ The spectrum also showed a signal at δ –17 ppm due to (–C)₂Si(OSi–)₂ (D²),⁶ suggesting that organic functionalities

Chart 1. Schematic Representations of (A) "Lizard" Template and (B) Its Alanine-Containing Version (**1**) for the Synthesis of a Functional Porous Silica Hybrid (**3**)



are covalently attached to the silica surface. The D² content was evaluated as 13 mol %. Selective hydrolysis of the template ester in **2** was clearly demonstrated by IR spectroscopy of **3** (Figure 1B), where a vibrational band due to the ester carbonyl at 1742 cm^{–1}

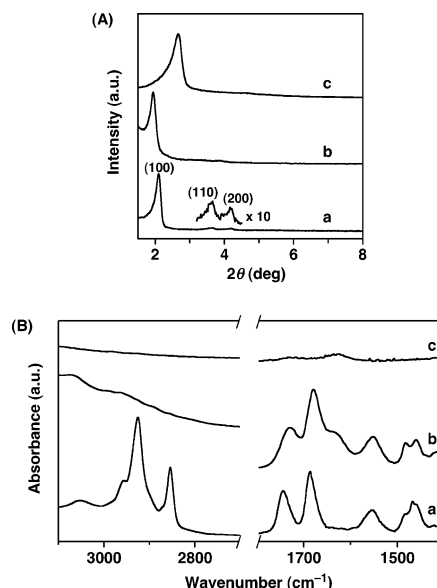


Figure 1. (A) XRD patterns and (B) IR spectra of (a) as-synthesized **2**, (b) hydrolyzed **3**, and (c) mesoporous silica obtained from **2** by calcination.

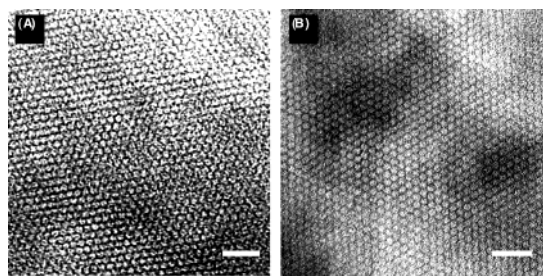


Figure 2. Transmission electron micrographs (TEM) of (A) as-synthesized **2** and (B) hydrolyzed **3**. Scale bars, 25 nm.

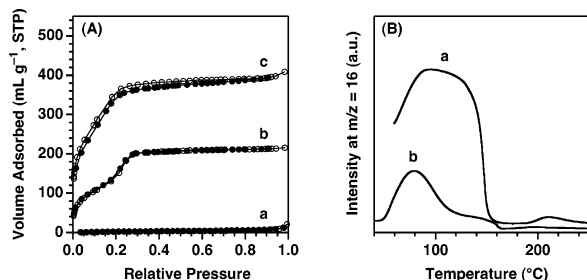


Figure 3. (A) N_2 adsorption (\circ)/desorption (\bullet) isotherms of (a) as-synthesized **2**, (b) hydrolyzed **3**, and (c) mesoporous silica obtained from **2** by calcination. (B) Temperature-programmed NH_3 desorption (TPD) profiles ($10\text{ }^\circ\text{C min}^{-1}$) of (a) hydrolyzed **3** and (b) mesoporous silica obtained from **2** by calcination.

(a) was red shifted to 1733 cm^{-1} (b) characteristic of CO_2H , while the amide bands at 1685 (amide I) and 1555 (amide II) cm^{-1} remained intact. The disappearance of the vibrational bands at 2924 (ν_{as}) and 2854 (ν_s) cm^{-1} indicates a complete removal of the alkyl tail from the silica channel. Thermogravimetric analysis (TGA) of as-synthesized **2** and hydrolyzed **3**, upon decomposition of the organic moiety at $180\text{--}420\text{ }^\circ\text{C}$, showed weight losses of 46% and 27%, respectively.⁶ The former value is typical of those reported for template-containing mesoporous silica, while the latter is close to a theoretical value (24%) calculated from the molecular weight change upon hydrolysis of the ester linkage. From the TGA analysis, the density of the alanine-containing organic functionality in hydrolyzed **3** was estimated to be 1.0 mmol g^{-1} , which is close to that expected from the D^2 content (1.2 mmol g^{-1}).

Transmission electron microscopy (TEM) of as-synthesized **2** clearly showed the presence of hexagonally aligned silicate channels with a diameter of 3.5 nm (Figure 2A). The TEM analysis of hydrolyzed material **3** clearly demonstrated a complete preservation of the hexagonal porous structure with a channel diameter of 3.6 nm (Figure 2B). Of interest, although as-synthesized **2** was inert for N_2 adsorption, **3** displayed a clear N_2 adsorption/desorption isotherm (type IV) with a distinct capillary condensation step and a narrow pore size distribution (Figure 3A). Therefore, the silicate channels in **3**, although densely functionalized with alanine- CO_2H , are open to external environments (Chart 1B). While the BET surface area of the porous material obtained by calcination of **2** ($1301\text{ m}^2\text{ g}^{-1}$) was typical of those of mesoporous silicates,

hydrolyzed material **3**, as expected, showed a smaller BET surface area of $536\text{ m}^2\text{ g}^{-1}$ with a maximum BJH pore size distribution of 2.0 nm. We also conducted temperature-programmed desorption (TPD) analysis with NH_3 as a basic guest, which possibly interacts with the alanine- CO_2H groups in the silicate channel. From the desorption profile shown in Figure 3B, porous **3** was found to adsorb NH_3 up to 0.7 mmol g^{-1} , which is comparable to the alanine- CO_2H content (vide ante), while it is obviously greater than that observed for the porous silica obtained by calcination of **2** (0.1 mmol g^{-1}).

In conclusion, we have reported a novel and general synthetic approach to silicate “nanopores” with a densely functionalized surface (**3**) by using a condensable amphiphile with a cleavable alkyl tail (**1**) as a “lizard” template (Chart 1). The dialkoxysilane functionality, attached to the ammonium ion headgroup of **1**, allows selective and dense functionalization of the channel surface via a covalent linkage, which is tolerant to the posttreatment for the cleavage of the alkyl tail. The results with alanine amphiphile **1** also demonstrate a possible incorporation of “chirality” on the channel surface. Application of the “lizard” templating method to the fabrication of nanopores with a variety of organic functional groups and exploration of their potential applications are the subjects worthy of further investigation.

Acknowledgment. We thank Dr. J. P. Hill for a helpful discussion.

Supporting Information Available: Details of synthesis and characterization of **1**, TGA profiles of **2** and **3**, IR spectrum of **1**, and ^{29}Si MAS NMR spectrum of **3** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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