Synthesis of Anionic-Surfactant-Templated Mesoporous Silica Using Organoalkoxysilane-Containing Amino Groups

Toshiyuki Yokoi,[†] Hideaki Yoshitake,[‡] and
Takashi Tatsumi*,[†]

Division of Materials Science and Chemical Engineering, Graduate School of Engineering, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan, and Graduate School of Environment and Information Sciences, Yokohama National University, 79-7 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

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The discovery of a new family of mesoporous molecular sieves, M41S,[1] has stimulated great interest in the surfactant-directed assembly of mesostructures of silica and various metal oxides. Thus far, the assembly for the formation of a mesostructured silica has been promoted by electrostatic charge-matching pathways including S^+I^- [1,2] and $S^+X^-I^+$ [3] (S^+, cationic surfactants; I^- or I^+, anionic or cationic silicates; and X^-, counteranions) and by electrically neutral pathways, which depend on hydrogen bonding, including N^0I^0 [4,5] and S^0I^0 [6] (N^0 or S^0, nonionic or neutral amine surfactants; and I^0, neutral silica species). Although the use of anionic surfactants[7−9] and anionic block copolymers[10] for the synthesis of the mesostructured materials has been reported, the S^-I^+ or $S^-M^+I^-$ (M^-, countercation) pathway for the synthesis of mesoporous silica using an anionic surfactant has not yet been opened. It is considered that negatively charged silicates under basic conditions are difficult to interact with the headgroup of an anionic surfactant due to the electrostatic repulsion. Anionic surfactants are mass-produced and consumed in a wide range of applications because of their highly potent detergency and relatively low cost. Therefore, the utilization of commercial and well-known anionic surfactants for the synthesis of the mesoporous silica has been strongly desired since the discovery of M41S. Our novel strategy for the promotion of the S^-I^+ pathway is utilization of an organoalkoxysilane containing a cationic functional group that can interact with the anionic headgroup (Figure 1). We now report the first synthesis of the anionic-surfactant-templated mesoporous silica (AMS).

Sodium dodecyl sulfate (SDS) was dissolved in water/ethanol (molar ratio 9:1) with vigorous stirring at 333 K followed by addition of a mixture of 3-aminopropyltriethoxysilane (APTES) and tetraethyl orthosilicate (TEOS). The resulting mixture was stirred for 1 h at ambient temperature and kept statically at 373 K for 2 days. The mother gel composition was APTES/TEOS/SDS/H_2O/EtOH (x:1−x:0.1:180:20). The pH of the mother gel was 10.4 at $x = 0.5$. Considering the pK_a of propylamine (around 10.6), the amino group would be substantially protonated, enhancing the S^-I^+ electrostatic interactions. The resulting white precipitate was filtered, washed with deionized water, and dried in air at 373 K. The silica−micelle composite (as-AMS-*x*) (1.0 g) was stirred in HCl/MeCN solution (100 mL of MeCN containing 10.42 g of HCl aq. concentrated ~35 wt %) at 298 K for 2 h to remove the surfactant as dodecylsulfuric acid (−OSO_3H) with aminopropyl moieties intact (ex-AMS-*x*). The CHNS elemental analysis of ex-AMS-0.5 revealed that 89% of SDS was removed by the extraction and the content of residual aminopropyl moieties was 3.6 mmol·g^{-1}. The as-AMS-*x* was calcined at 823 K in air to remove both the surfactant and aminopropyl moieties, resulting in cal-AMS-*x* having the open mesopore.

The XRD patterns of as-, ex-, and cal-AMS-0.5 (Figure 2) exhibited a predominantly single broad peak with the *d* spacings of 5.2, 5.5, and 4.3 nm, respectively, being suggestive of mesostructured silicas. The nitrogen adsorption−desorption isotherms of both ex- and cal-AMS-0.5, exhibited the type IV pattern (Figure S-1 in the Supporting Information), indicating the presence of mesopores. The BET surface areas were found to be 274 and 501 m^2·g^{-1} and the average pore sizes calculated by the D−H method using the adsorption branch were 3.3 and 3.2 nm, respectively. The calcination process should promote the siloxane cross-linking, leading to the shrinkage of the pore size. On the other hand, the extraction process does not promote the siloxane cross-linking to reduce the pore size but will lead to the expansion of the pore due to the release of the electrostatic interaction with the surfactant. The retention of aminopropyl groups on the surface of the extracted sample leads to reduction in the pore size; the expansion of the pore by the removal of the surfactant would be offset by the pore size reduction due to the aminopropyl groups. Thus, incidentally, the extracted sample has almost the same pore size as the calcined one. As shown in the transmission electron microscope (TEM) image (Figure 3), cal-MSA-0.5 has a wormhole-like structure[11]

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* Corresponding author. Tel.: 81-45-339-3943. Fax: 81-45-339-3941. E-mail: ttatsumi@ynu.ac.jp.
[†] Division of Materials Science and Chemical Engineering.
[‡] Graduate School of Environment and Information Sciences.

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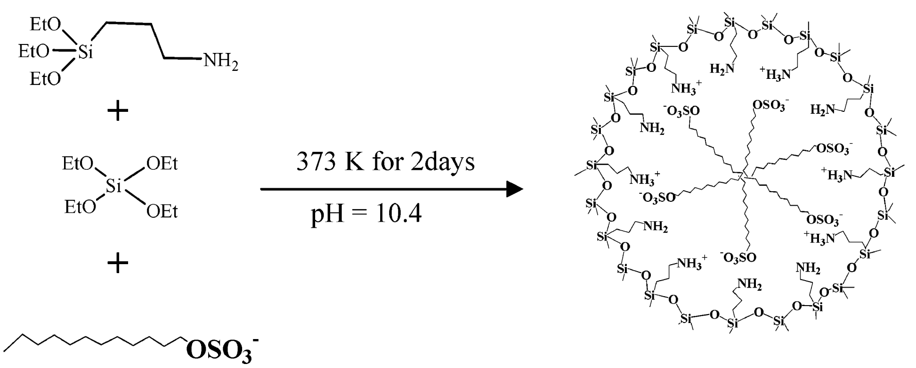

Figure 1. Formation of the mesostructured silica−micelle composite via the anionic templating route. The electrostatic interaction between the positively charged amino groups in 3-aminopropyltriethoxysilane and the negatively charged sulfate headgroups in sodium dodecyl sulfate is a driving force for the self-assembly of silica−micelle composite.

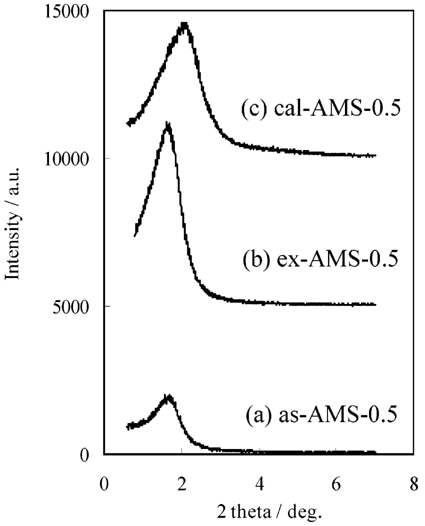

Figure 2. XRD patterns of (a) silica−micelle composite, as-AMS-0.5; (b) extracted silica by acid treatment, ex-AMS-0.5; and (c) calcined silica at 823 K for 10 h, cal-AMS-0.5.

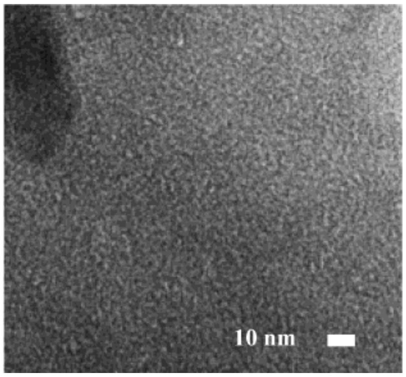

Figure 3. Transmission electron microscope (TEM) image of calcined mesoporous silica, cal-AMS-0.5.

with uniform mesopores. Scanning electron micrograph (SEM) images of as-, ex-, and cal-AMS-0.5 samples showed spherical particles with a uniform diameter of ca. 1 μm.

The argentometric titration with 0.1 N $AgNO_3$ following neutralization with HCl showed that the amount of the exposed aminopropyl moieties on the surface of ex-AMS-0.5 was found to be 3.4 mmol·g^{-1}, which is unprecedentedly high and basically agrees with the result of the CHNS elemental analysis, indicating that almost all aminopropyl moieties were on the internal and external surfaces. Aminopropyl-functionalized mesoporous silicas via cationic or nonionic templating routes have been synthesized with APTES by postsynthesis grafting,[12] direct co-condensation,[13] and displacement of the surfactant[14,15] methods. To the best of our knowledge, the maximum loading of aminopropyl moieties was 2.5 mmol·g^{-1}.[14] For the aminopropyl-functionalized MCM-41 synthesized by direct co-condensation of APTES/TEOS with a molar ratio of 0.4:0.6, the content of the aminopropyl moieties estimated by the elemental analysis and the argentometric titration were 2.03 and 1.66 mmol·g^{-1}, respectively, suggesting that 18.6% of the aminopropyl moieties were unexposed to the surface. In AMS, however, almost all aminopropyl moieties were present on the surface, probably due to the direct electrostatic interaction between cationic amino groups in APTES and anionic headgroups in SDS.

The CHNS elemental analysis of as-AMS-0.5 revealed that the molar ratios of N/S and S/Si are about 4.0 and 0.1, respectively, which are almost the same as the starting molar gel compositions, APTES/SDS (5.0) and SDS/(APTES + TEOS) (0.1). A more important point is that, considering the charge balance, amino groups not interacting with SDS were present in the silica−micelle composite, suggesting that positively charged aminopropyl moieties ($-NH_3^+$) electrostatically interacted with $-OSO_3^-$ and also with anionic siloxanes species ($\equiv Si-O^-$) under the synthesizing condition (pH 10.4). Neutral aminopropyl groups ($-NH_2$) also would be present in the composite. In ex-AMS-0.5, the molar ratio of C/N attributed to aminopropyl moieties was estimated at 3.0, indicating that the aminopropyl group remained intact through the synthesis and extraction processes. The ^{13}C CP-MAS NMR spectrum of ex-AMS-0.5 indicated the presence of three types of C atoms at 10$^{\alpha}$, 21$^{\beta}$, and 43$^{\gamma}$ ppm corresponding to $\equiv Si-{}^{\alpha}CH_2{}^{\beta}CH_2{}^{\gamma}CH_2NH_3Cl^-$, respectively (Figure S-2), supporting the

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presence of aminopropyl moieties in the extracted silica.

The peaks at −52, −58, and −61 ppm attributed to T^1, T^2, and T^3 silicons ($T^n = R{-}Si(OSi)_n(OH)_{3-n}$), respectively, and the peaks at −92, −101, and −109 ppm attributed to Q^2, Q^3, and Q^4 silicons ($Q^n = Si(OSi)_n(OH)_{4-n}$), respectively, were observed in the ^{29}Si MAS NMR spectra of as-AMS-0.5 (Figure S-3a) and ex-AMS-0.5 (Figure S-3b), indicating the presence of Si−C bonds. The proportion of silicon bound to the organic group to total silicon, $\Sigma T^n/\Sigma(T^n + Q^n)$, were found to be 42 and 41% for as- and ex-AMS-0.5 respectively, supporting that the aminopropyl moieties were retained after the extraction process. After calcination, all T^n peaks disappeared completely while Q^3 and Q^4 peaks remained, as shown in the spectrum of cal-AMS-0.5 (Figure S-3c).

To reveal the importance of the electrostatic interaction between the positively charged aminopropyl ($-NH_3^+$) in APTES and negatively charged headgroup ($-OSO_3^-$) in SDS, the influence of pH on the formation of as-AMS-0.5 was investigated by changing the pH of the mother gel in the range from 2 to 13 by means of adding an aqueous solution containing NaOH, NH_3, CH_3COOH, or HCl. When the pH of the mother gel was increased to 11.0, the obtained silica was lamellar, and when the pH was further increased to 13.0, no precipitate was formed. Because the pK_a of an aminopropyl group is around 10.6 at ambient temperature, high pH (over 11.0) makes the amino groups neutral, resulting in the weakened interaction with $-OSO_3^-$. Actually, the CHNS elemental analyses revealed that the N/S molar ratio was 0.1 at pH 12.0. On the other hand, when pH of the mother gel was decreased to 9.0, the XRD peak decreased in intensity, and when the pH was further decreased to 8.0, no precipitate was formed because of difficulty in the hydrolysis of alkoxysilanes.

When only TEOS was used as the Si source, and the pH in the mother gel was raised to 11 by the addition of propylamine to enhance the hydrolysis of TEOS, no precipitate was obtained after 2 days, suggesting that the interaction between the cationic amino group attached to Si in APTES and the anionic headgroup in SDS was indispensable for the formation of a silica−micelle composite. The peak intensity of the XRD pattern was gradually decreased as x was decreased from 0.5. This would be likely because the interaction of $-NH_3^+$ and $-OSO_3^-$ is decreased. When x was between 0.6 and 0.8, the obtained silica-micelle composites were a mixture of the wormhole-like structure and the lamellar one. When x was above 0.8, the resulting structure was completely lamellar with the d spacing 4.6 nm.

Various anionic surfactants such as fatty cid salts and alkylbenzenesulfonates can be used for the synthesis of the mesostructured silica−micelle composite. For example, when AMS was synthesized by using lauric acid sodium salt at $x = 0.5$, the BET surface areas of extracted and calcined samples were found to be 610 and 760 $m^2 \cdot g^{-1}$, respectively.

The results given in this study provide the first example of synthesis of mesoporous silica via the anionic templating route, which will open up ample opportunities in the synthesis of mesoporous silica because of the availability of a much wider variety of anionic surfactants than cationic surfactants. Our findings are strongly suggestive of a structural control effect of functional groups in inorganic precursors for the formation of mesoporous metal oxides.

Supporting Information Available: Nitrogen adsorption−desorption isotherms of (a) ex- and (b) cal-AMS-0.5; ^{13}C CP-MAS NMR spectra of ex-AMS-0.5; ^{29}Si MAS NMR spectra of (a) as-, (b) ex-, and (c) cal-AMS-0.5. These materials are available free of charge via the Internet at http://pubs.acs.org.

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