doi:10.1246/cl.2010.236

Tri(quaternary ammonium) Surfactant with a Benzene Core as a Novel Template for Synthesis of Ordered Porous Silica

Yuki Fukasawa, Ayae Sugawara, Hirotomo Hirahara, Atsushi Shimojima, and Tatsuya Okubo*
Department of Chemical System Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656

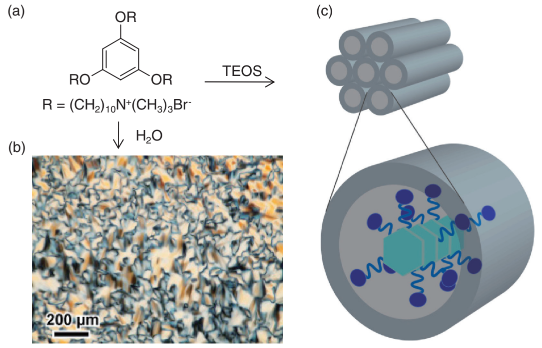
(Received December 8, 2009; CL-091084; E-mail: okubo@chemsys.t.u-tokyo.ac.jp)

A novel rigid-core surfactant where three trimethylammonium heads are attached to a benzene core via flexible hydrocarbon chains was examined as a template for synthesizing ordered porous silica. A well-ordered 2D hexagonal silica structure with relatively small pores was generated owing to the formation of the stable mesophase where the surfactants were stacked to form cylindrical assemblies.

Porous silica with regularly arranged and uniform pores has a wide range of potential applications such as catalysts and adsorbents.[1,2] Mesoporous silica materials are generally synthesized through a surfactant-templating route, in which the size and geometry of the pores can be widely tuned by varying the type of surfactant as well as synthesis conditions. In addition to conventional surfactants consisting of a hydrophobic tail and a terminal hydrophilic head, other surfactant configurations, such as gemini,[3–5] bolaform,[6,7] and disk-like,[8–10] with two or more head groups, have been investigated to expand the variety of mesophases and to control the pore architecture precisely.

Surfactants with rigid hydrophobic segments have attracted particular attention because they usually show more specific self-assembly behavior than those with only flexible chains. For example, bolaform surfactants where two ω-(trimethylammonium)alkyl groups are connected by a biphenyl unit form unusual two-dimensional mesostructures.[6] Disk-like molecules with rigid cores are also of interest because the mobility of side chains are restricted so that structure and pore size of the resulting mesoporous silica should be more unambiguously determined. Phthalocyanine-,[8] triphenylene-,[9] and bipyridine derivatives[10] having amphiphilic side chains have been used to produce 2D hexagonal silica–surfactant mesophases; however, no unique structural feature of the mesoporous silica, as compared to conventional ones, has been demonstrated.

In this letter, we report the synthesis of an ordered porous silica using a novel tri(quaternary ammonium) surfactant consisting of a simple benzene core and three ω-(trimethylammonium)alkyl side chains [$C_6H_3(O(CH_2)_{10}N^+(CH_3)_3Br^-)_3$, hereafter denoted as B-C10TMA] (Scheme 1a). B-C10TMA is a new type of cationic and rigid-core surfactant that is quite different from the aforementioned surfactants having multiple aromatic rings as a core and nonionic alkyl polyoxyethylene ether as side chains in common.[8–10] A well-ordered 2D hexagonal structure with relatively small pores compared to those generated with typical alkyltrimethylammonium-type surfactants was formed here, which was attributable to the specific interactions between B-C10TMA molecules to form stacked cylindrical assemblies.



Scheme 1. (a) Molecular structure of B-C10TMA, (b) polarizing microscopic image showing a lyotropic liquid crystal of B-C10TMA, and (c) structural model of the silica–surfactant composite mesophase.

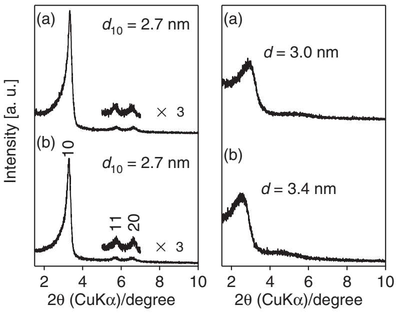


Figure 1. XRD patterns of the products prepared using B-C10TMA (left) and C10TMA (right): (a) without and (b) with the addition of TMB.

B-C10TMA was synthesized by the reaction of 1,3,5-trihydroxybenzene with an excess amount of 1,10-dibromodecane to form 1,3,5-tri(10-bromodecyloxy)benzene,[11] followed by reaction with trimethylamine (see Supporting Information for details).[12] A polarizing microscopic image of B-C10TMA in water shows a fan-like texture characteristic of a columnar lyotropic liquid crystal (Scheme 1b).

Ordered porous silica was synthesized using tetraethoxysilane (TEOS) as a silica source under standard basic conditions.[5] TEOS was added to the mixture of B-C10TMA, sodium hydroxide, and water in the molar ratios of 1TEOS:0.4NaOH:140H_2O:0.02B-C10TMA. After 24 h of stirring at room temperature, the mixture was aged at 60 °C for 24 h. Precipitates were recovered by filtration, air-dried at 60 °C, and finally calcined at 450 °C for 3 h to remove surfactant.

Powder X-ray diffraction (XRD) pattern of the calcined sample (Figure 1, left, a) shows well-defined peaks indexed to the (10), (11), and (20) reflections of a 2D hexagonal structure. Periodic hexagonal and stripe patterns are clearly observed by TEM (Supporting Information, Figure S2).[12] The nitrogen adsorption/desorption isotherm (Figure S3)[12] of this sample is close to IUPAC type I classification[13] but has a slight shoulder below the relative pressure of 0.15, suggesting that the pore size is in an intermediate range between micropore and mesopore regions. The average pore sizes calculated based on Barrett–Joyner–Halenda (BJH) theory[13] and nonlinear density functional theory (NLDFT)[14] are 1.5 and 2.2 nm, respectively (Table S1).[12] Note that BJH theory tends to underestimate the pore size in the miropore region.[15] The BET surface area and pore volume are calculated to be 870 $m^2\,g^{-1}$ and 0.5 $cm^3\,g^{-1}$, respectively.

To clarify the specific properties of B-C10TMA, decyltrimethylammonium bromide (C10TMA) was also examined as template. A control experiment was performed at the molar ratios of 1TEOS:0.4NaOH:140H_2O:0.06C10TMA under otherwise identical conditions. In contrast to the highly ordered pore structure achieved with B-C10TMA, the sample prepared with C10TMA is less ordered, exhibiting broader peaks in the XRD pattern (Figure 1, right, a). A lower BET surface area (360 $m^2\,g^{-1}$) is also confirmed. These results are consistent with the fact that it is generally difficult to obtain highly ordered porous silica using alkyltrimethylammonium surfactants with short alkyl chains containing less than 12 carbons, due to hydrophobic interaction poorer than the electric repulsion between cationic head groups.[16,17] Thus, the rigid benzene core of B-C10TMA should play a crucial role in the formation of highly ordered structure.

UV–vis spectroscopy indicates π–π stacking of benzene cores in the silica–B-C10TMA composites[18] (Figure S4). The absorption bands of the composites are red-shifted compared to those of the simple mixture of silica powder and B-C10TMA. Such π–π stacking in addition to the hydrophobic interactions of B-C10TMA should stabilize the silica–surfactant composite mesophase. It is plausible that B-C10TMA molecules are stacked to form cylindrical micelles where the side chains radiate outward from the central benzene cores (Scheme 1c). This model is supported by the experimental result that the expansion of the micelle diameter hardly occurred even by adding TMB, a typical swelling agent. In general, the d_{10} spacing is increased by the addition of hydrophobic swelling agents[5] when conventional surfactants like C10TMA are used as template; however, such a behavior was not observed for B-C10TMA (Figure 1b).

In the silica–B-C10TMA mesophase, a trisubstituted benzene core should be rotated to some degree from the adjacent core to minimize the steric repulsion between alkylene spacers. It appears that the alkylene spacers are not in a fully extended state, because the pore size of the calcined sample is much smaller than the molecular size of B-C10TMA with all-trans alkylene spacers (ca. 3.8 nm). Note that cationic head groups do not thrust into silica walls, unlike nonionic surfactants which penetrate silica walls and produce micropores. It is also interesting that despite the presence of the benzene core (ca. 0.7 nm in diameter, including ether oxygen atoms), the pore size is slightly smaller than that templated with C10TMA (1.6 nm).[12] This can be explained by the low number density of trimethylammonium(alkyl) groups in the silica–B-C10TMA composite. In fact, the N/Si ratio calculated by combination of CHN analysis and thermogravimetry was 0.18, which is lower than for the sample prepared with C10TMA (0.20).

Pore size control of surfactant-templated and ordered porous silica is important from a practical viewpoint. Although the increase of pore size is relatively facile, e.g., by using swelling agent or block copolymers, the generation of well-regulated small pores is still difficult.[16,17] In this context, the tricationic surfactant used in this study provides a promising method. Further decrease of the pore size can be achieved by reducing the length of the alkylene spacers. When B-C6TMA having C6 spacers was used as template, only a broad peak was observed by XRD (data not shown); however, the pore size was greatly decreased to 1.1 nm, as evaluated by NLDFT (BJH theory is no more applicable for such a small pore).

In conclusion, a novel rigid-core surfactant consisting of three trimethylammonium heads attached to a benzene core via flexible hydrocarbon chains was examined as a template for synthesizing ordered porous silica. This surfactant was effective for generating small and regularly arranged pores, which is attributed to its strong tendency to form cylindrical assemblies. The synthesis of such ordered porous silica with small mesopores is of both scientific and practical importance.

This work was supported in part by a Grant-in-Aid for Scientific Research (B) from the Japan Society for the Promotion of Science. This work was partly conducted in the Center for Nano Lithography & Analysis, The University of Tokyo, supported by the Ministry of Education, Culture, Sports, Science and Technology, Japan. We thank Prof. Kazunari Domen at the University of Tokyo for UV–vis measurements.

References and Notes

1 T. Kimura, K. Kuroda, *Adv. Funct. Mater.* **2009**, *19*, 511.
2 Y. Wan, D. Y. Zhao, *Chem. Rev.* **2007**, *107*, 2821.
3 S. Manne, T. E. Schäffer, Q. Huo, P. K. Hansma, D. E. Morse, G. D. Stucky, I. A. Aksay, *Langmuir* **1997**, *13*, 6382.
4 A. E. Garcia-Bennett, S. Williamson, P. A. Wright, I. J. Shannon, *J. Mater. Chem.* **2002**, *12*, 3533.
5 Q. Huo, D. I. Margolese, G. D. Stucky, *Chem. Mater.* **1996**, *8*, 1147.
6 D. Y. Zhao, Q. Huo, J. Feng, J. Kim, Y. Han, G. D. Stucky, *Chem. Mater.* **1999**, *11*, 2668.
7 S. Shen, A. E. Garcia-Bennett, Z. Liu, Q. Lu, Y. Shi, Y. Yan, C. Yu, W. Liu, Y. Cai, O. Terasaki, D. Y. Zhao, *J. Am. Chem. Soc.* **2005**, *127*, 6780.
8 M. Kimura, K. Wada, K. Ohta, K. Hanabusa, H. Shirai, N. Kobayashi, *J. Am. Chem. Soc.* **2001**, *123*, 2438.
9 A. Okabe, T. Fukushima, K. Ariga, T. Aida, *Angew. Chem., Int. Ed.* **2002**, *41*, 3414.
10 W. Otani, K. Kinbara, T. Aida, *Faraday Discuss.* **2009**, *143*, 335.
11 T. L. Tyler, J. E. Hanson, *Chem. Mater.* **1999**, *11*, 3452.
12 Supporting Information is available electronically on the CSJ Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.
13 S. Brunauer, L. S. Deming, W. E. Deming, E. Teller, *J. Am. Chem. Soc.* **1940**, *62*, 1723.
14 P. I. Ravikovitch, D. Wei, W. T. Chueh, G. L. Haller, A. V. Neimark, *J. Phys. Chem. B* **1997**, *101*, 3671.
15 L. D. Gelb, K. E. Gubbins, *Langmuir* **1999**, *15*, 305.
16 R. Ryoo, I.-S. Park, S. Jun, C. W. Lee, M. Kruk, M. Jaroniec, *J. Am. Chem. Soc.* **2001**, *123*, 1650.
17 J. S. Beck, J. C. Vartuli, G. J. Kennedy, C. T. Kresge, W. J. Roth, S. E. Schramm, *Chem. Mater.* **1994**, *6*, 1816.
18 A. R. A. Palmans, J. A. J. M. Vekemans, E. E. Havinga, E. W. Meijer, *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2648.