Structural Control of Mesoporous Silica by a Bicontinuous Microemulsion-aided Process

Isamu Moriguchi,*[†,††] Yuki Shono,[†] Hiromi Tachikawa,[†] Hirotoshi Yamada,[†] Tetsuichi Kudo,[†]
Yasutake Teraoka,[†††] and Taisei Nishimi[††††]
[†]*Department of Applied Chemistry, Faculty of Engineering, Nagasaki University, 1-14, Bunkyo-machi, Nagasaki, 852-8521*
[††]*PRESTO JST*
[†††]*Department of Molecular and Material Sciences, Graduate School of Engineering Sciences,*
Kyushu University, Fukuoka 816-8580
[††††]*Fuji Photo Film Co. Ltd., 210 Nakanuma, Minami-Ashigara 250-0193*

(Received February 8, 2005; CL-050184)

Mesoporous silica was successfully synthesized via a sol–gel process in a bicontinuous microemulsion of tetradecane/didodecyldimethylammonium bromide/aq HCl ternary system. The surface area, pore size and pore volume of silica varied dependent on the composition of bicontinuous microemulsion.

Synthesis and application of porous materials are currently the subjects of intensive research in materials science. A lot of self-assembly systems of surfactants,[1] amphiphilic block copolymers,[2] and colloidal particles[3] were employed as templates for directing porous structures of silica, metal oxides, and carbons. From the viewpoint of controlling porous structure, the use of bicontinuous microemulsion, which forms in a water/surfactant/oil ternary system with a balanced hydrophilicity and lipophilicity, as a reaction medium for inorganic synthesis has a potential to be a unique process for porous material synthesis. The bicontinuous microemulsions are structured as compartmentalized liquid phases, in which the oil and water phases are separated by surfactant layers into highly branched and three-dimensionally interconnected nanometer-wide channel networks.[4] The volume and average width of each channel can be easily controlled with components and composition of water/surfactant/oil. Therefore, three-dimensional bicontinuous porous structures of inorganic materials, the dimensions of pore and wall thickness of which are tunable in wide range, are expected to be constructed if a mineralization reaction takes place dominantly in the one compartmentalized phase. However, there are only a few studies concerning the bicontinuous microemulsion-aided synthesis, and the reported studies are limited to a preparation of macroporous frameworks of silica and calcium phosphate.[5,6] Although we have reported very recently a synthesis of mesoporous TiO_2 by the bicontinuous microemulsion-aided process,[7] a wide range control of porous structure expected above is not yet accomplished due to a fast gelation of titanium alkoxide. The present work succeeded for the first time a control of pore size and pore volume of mesoporous silica dependent on the composition of bicontinuous microemulsion. This would be contrast to the micelle-templating process, in which the pore size reflects the micelle size dependent on surfactant molecular length and the amount of auxiliary additives such as mesitylene if incorporated.[8]

Bicontinuous microemulsions were prepared by mixing didodecyldimethyammonium bromide (DDAB), tetradecane (TD) and aq HCl (4×10^{-3} mol dm^{-3}) with the composition [A]–[D] indicated in Table 1. All of the composition of TD/DDAB/aq HCl used here are in the bicontinuous microemulsion region of phase diagram reported by Ninham et al.,[9] and it was confirmed that the dilute HCl little affects on the phase diagram by a preliminary experiment. The mixture solution of TD/DDAB/aq HCl was stirred for 30 min at room temperature until a transparent solution of bicontinuous microemulsion was obtained (Figure 1a). Tetramethoxy silane (TMOS) was added dropwise to the stirred bicontinuous microemulsion solution with a constant weight ratio of DDAB:TMOS = 3.4:1.4. After further stirring for 30 s, the solution was stored under static condition at 25 °C with a thermocontrolled bath for 1 day. The solution became turbid with passing time (Figure 1b), and a conservative and semitransparent gel was obtained after 1 day (Figure 1c). The gel was washed thoroughly with hexane, dried in an oven at 110 °C for 12 h and finally calcined in air at 550 °C for 6 h, to yield porous silica. It was confirmed by thermogravimetric measurements that all of organics were removed out from the silica by heating in air upto 400 °C (Seiko Instruments Inc.

Table 1. The composition of bicontinuous microemulsion used for the synthesis and parameters associated with porous structure of silica

Samples	Composition of TD/DDAB/aq HCl[a]	Sa /m^2 g^{-1} [b]	V /cm^3 g^{-1} [c]	D /nm[d]
SiO_2 [A]	25/25/50	1290	1.41	2.8
SiO_2 [B]	30/30/40	903	1.66	4.2
SiO_2 [C]	35/35/30	652	2.96	5.5, 20
SiO_2 [D]	15/30/55	1008	0.80	2.0

[a]wt %, [b]BET surface area, [c]mesopore volume, [d]mean pore size.

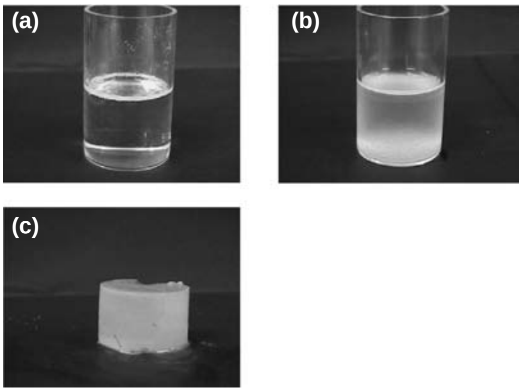

Figure 1. Feature change of a solution of bicontinuous microemulsion during the sol–gel reaction; (a) a bicontinuous microemulsion with composition [B], (b) passing 1 h and (c) passing 1 day after adding TMOS.

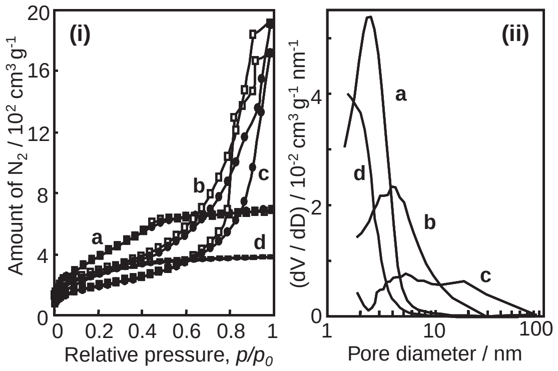

Figure 2. (i) Nitrogen adsorption–desorption isotherms and (ii) BJH pore size distributions of porous silica; (a) SiO_2[A], (b) SiO_2[B], (c) SiO_2[C], (d) SiO_2[D]. The closed and opened symbols indicate adsorption and desorption processes, respectively.

TG/DTA6200). In the following, the SiO_2 samples after the calcinations at 550 °C are denoted as SiO_2[A]–[D], where [A]–[D] indicates the TD/DDAB/aq HCl composition of bicontinuous microemulsion in Table 1.

On X-ray diffraction (XRD) measurements (Rigaku RINT2200), all the samples showed no distinct XRD peak, suggesting that the silica did not have an ordered porous structure like as in micelle-templated mesoporous silica. Figure 2i shows N_2 adsorption and desorption isotherms of the obtained SiO_2 samples, which were measured at 77 K (Micromeritics, Gemini 2370). The pore volume and BJH pore size distribution were calculated using their adsorption branches, and the specific surface area was determined by the multipoint Braunauer–Emmett–Teller (BET) method (Table 1, Figure 2ii). For SiO_2[A], the TD/DDAB/aq HCl composition of which was 25/25/50 by weight, the inflection characteristics of capillary condensation into mesopores is observed in the adsorption isotherm at $0.2 < p/p_0 < 0.5$, confirming the presence of mesopores in SiO_2[A]. The values of BET surface area and mesopore volume of SiO_2[A] were $1290\,m^2\,g^{-1}$ and $1.41\,cm^3\,g^{-1}$, respectively, which are almost comparable to or larger than those of mesoporous silica generally obtained by micelle-template process.[10] With the change of TD/DDAB/aq HCl composition as [A] → [B] → [C], in which the wt % of water decreases while keeping the constant weight ratio of DDAB/TD in the bicontinuous microemulsion, the inflection characteristic of capillary condensation into pores shifted to higher value of the relative pressure. As indicated in Table 1 and Figure 2ii, BET surface area of mesoporous silica decreases, and the pore size and pore volume increase respectively with the composition change [A] → [B] → [C], although the pore size-distribution became broadened. The SiO_2[C] seems to have a bimodal porous structure, which might be due to a formation of lamella phase at a high surfactant concentration. On the other hand, the change of [A] → [D], which is the direction to decreasing oil fraction at almost the same DDAB/aq HCl composition, resulted in the decreasing pore size and pore volume of silica (Table 1, Figure 2ii). These results mean that the ratio of water or oil content in the composition of bicontinuous microemulsion remarkably affects on the porous structure of mesoporous silica, that is, the increase in oil fraction causes increasing silica pore size and pore volume. It can be suggested that the sol–gel reaction of TMOS occurs preferentially in the water phase or at the interface of water/surfactant, and the space of oil phase would mainly contribute to the porous space of mesoporous silica for the bicontinuous microemulsion-aided process. This is supported by the TEM observation of the formation of tube-like precursor gels containing surfactant phase at the inner space for the reported bicontinuous microemulsion-aided synthesis of mesoporous TiO_2.[7] The increase in surface area and the decrease in pore volume with the composition change of [B] → [D], which is the condition of constant surfactant amount in the bicontinuous microemulsion, confirm again that the porous structure of silica can be controlled with the composition ratio of water/oil. Further study concerning an effect of surfactant amount in bicontinuous microemulsion on the porous structure is now in progress.

Since the controllable surface area, mean pore size and pore volume of mesoporous silica were in the range of 652–$1290\,m^2g^{-1}$, 2–20 nm and 0.8–$2.96\,cm^3g^{-1}$, respectively, only in the present conditions, the microemulsion-aided process would has a potential of controlling the porous structure in wide range.

This work was in part supported by a Grant-in-Aid for Scientific Research from Ministry of Education, Culture, Science, Sports and Technology of Japan. The study made use of instruments (XRD) in the Center for Instruments Analysis of Nagasaki University.

References

1 For examples, a) C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, and J. S. Beck, *Nature*, **359**, 710 (1992). b) D. M. Antonelli and J. Y. Ying, *Angew. Chem., Int. Ed. Engl.*, **34**, 2014 (1995). c) I. Moriguchi, K. Koga, R. Matsukura, Y. Teraoka, and M. Kodama, *Chem. Commun.*, **2002**, 1844.
2 For example, a) D. Zhao, Q. Huo, F. Feng, B. F. Chmelka, and G. D. Stucky, *J. Am. Chem. Soc.*, **120**, 6024 (1998). b) B. Lee, D. Lu, J. N. Kondo, and K. Domen, *J. Am. Chem. Soc.*, **124**, 11256 (2002). c) R. Ryoo, S. H. Joo, and S. Jun, *J. Phys. Chem. B*, **103**, 1401 (1999).
3 For example, a) B. T. Holland, C. F. Blanford, T. Do, and A. Stein, *Chem. Mater.*, **11**, 795 (1999). b) H. Yamada, N. Yamato, I. Moriguchi, and T. Kudo, *Solid State Ionics*, **175**, 195 (2004). c) M. A. Carreon and V. V. Guliant, *Chem. Commun.*, **2001**, 1438. d) I. Moriguchi, F. Nakahara, H. Furukawa, H. Yamada, and T. Kudo, *Electrochem. Solid-State Lett.*, **7**, A221 (2004).
4 K. Shinoda and B. Lindman, *Langmuir*, **3**, 135 (1978).
5 S. D. Sims, D. Walsh, and S. Mann, *Adv. Mater.*, **10**, 151 (1998).
6 D. Walsh and S. Mann, *Chem. Mater.*, **8**, 1994 (1996).
7 I. Moriguchi, Y. Katsuki, H. Yamada, and T. Kudo, *Chem. Lett.*, **33**, 1102 (2004).
8 J. S. Beck, J. C. Vatuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Scmitt, C. T.-W. Chu, D. H. Olsen, E. W. Sheppard, S. B. McCullen, J. B. Higgins, and J. L. Sclenker, *J. Am. Chem. Soc.*, **114**, 10834 (1992).
9 M. Allen, D. F. Evans, D. J. Mitchell, and B. W. Ninham, *J. Phys. Chem.*, **91**, 2320 (1987).
10 Y. M. Setoguchi, Y. Teraoka, I. Moriguchi, S. Kagwa, N. Tomonaga, A. Yasutake, and J. Izumi, *J. Porous Mater.*, **4**, 129 (1997).