Alkanes-assisted low temperature formation of highly ordered SBA-15 with large cylindrical mesopores†

Junming Sun,[a] He Zhang,[a] Ding Ma,[a] Yangying Chen,[a] Xinhe Bao,*[a] Achim Klein-Hoffmann,[b] Norbert Pfänder[b] and Dang Sheng Su[b]

Received (in Cambridge, UK) 8th July 2005, Accepted 31st August 2005
First published as an Advance Article on the web 27th September 2005
DOI: 10.1039/b509713d

Highly ordered SBA-15 silicas with large cylindrical mesopores (~15 nm) are successfully obtained with the help of NH_4F by controlling the initial reaction temperatures in the presence of excess amounts of alkanes.

With the discovery of M41s,[1] great efforts have been made on the construction of texture controllable mesoporous materials. Among them, tailoring the pore size of the mesoporous materials has been one of the hot issues for the purpose of providing a good performance for specific applications, such as the adsorption/separation of bulky molecules, the immobilization of enzymes as well as the catalytic transformation reactions of macromolecules, *etc*. Methods to modify the pore size of the mesoporous materials include the post synthesis treatment,[2] using different surfactant molecules (template) with different chain lengths[3] and employing organic solvents as swelling agents.[4] The addition of swelling agents, such as TMB, alkanes,[5,6] has been proved to be the most effective way in expanding the pore size of MCM-41 silicas (2–10 nm). Recently, the nonionic triblock copolymers templated SBA-15 silicas have attracted great interests due to their larger pores, thicker pore walls and therefore higher hydrothermal stabilities.[7] Meanwhile, the pore size of SBA-15 could be tuned in the range of 7–30 nm by using TMB as expander. However, extensive studies show that a phase transition from highly ordered SBA-15 (7–12 nm) to mesoporous cellular foams (MCF) with large nodded pore structures (~22–42 nm) occurred with increasing amounts of TMB.[8] Therefore, it is still essential to find other methods of tuning the pore size of highly ordered mesoporous materials. In other works, organic auxiliary chemicals (*e.g.*, DMF,[9] alkanes[10,11]) have also been investigated. Unfortunately, the maximum pore size of the highly ordered SBA-15 is only *ca.* 12 nm (with decane). Furthermore, when alkanes with shorter chain length (such as nonane, octane, *etc.*) were employed, disordered MCF silicas were produced under the temporal reaction conditions.[10] Up to now, to our knowledge, the synthesis of highly ordered SBA-15 silicas with cylindrical pore sizes larger than 12 nm has rarely been reported. Herein, it is demonstrated for the first time that the pore size of highly ordered SBA-15 could be continuously expanded to ~15 nm by carefully controlling the initial reaction temperatures with excess amounts of alkanes (from nonane to hexane). To our knowledge, it is the largest cylindrical mesopore diameter with regard to highly ordered SBA-15 silicas.

As a typical synthesis procedure, 2.4 g of $EO_{20}PO_{70}EO_{20}$ (P123) was dissolved in 84 ml HCl solution (1.30 M), followed by the addition of 0.027 g of NH_4F. The mixture was then stirred at 288 K to yield a clear solution. Different alkanes (with a constant alkane/P123 molar ratio of ~240) and 5.5 ml TEOS were premixed and then introduced into the solution under stirring. The above mixture was stirred at a given temperature for 20 h, and then transferred into an autoclave for further reaction at 373 K for 48 h. The products were collected by filtration, dried in air, and calcined at 813 K for 5 h to remove the templates. The highly ordered SBA-15 silicas with large cylindrical pores were thus obtained.

Various alkanes from nonane to hexane have been investigated at different initial reaction temperatures. It is found that when proper reaction temperatures are employed (Table 1), all the obtained materials have highly ordered mesoporous structures. Fig. 1 (top) gives the SAXD (Small Angle X-ray diffractions) patterns of the calcined samples prepared with different alkanes. All samples show four well-resolved peaks that can be indexed as (100), (110), (200), (210) diffractions, indicating a well-ordered hexagonal mesostructure of the obtained materials. Furthermore, the interplanar spacing d_{100} increases continuously with the decrease of the alkane chain length, indicating a continuous expansion of the pore size of the obtained SBA-15. When excess amounts of hexane are used, the obtained sample exhibits a d_{100} spacing of 14.2 nm (*vs.* 12.3 nm with nonane), and the calculated hexagonal unit cell value ($a_0 = 2d_{100}/3^{1/2}$) of the sample from (100) diffraction peak reaches *ca.* 16.4 nm. Data concerning the physical properties of the samples are shown in Table 1.

N_2 adsorption–desorption isotherms of the obtained samples yield type IV isotherms with H1-type hysteresis at the relative pressure of 0.8–0.9, which is characteristic for mesoporous materials with cylindrical channels in hexagonal arrangement (ESI†, Fig. S1). From the N_2 adsorption isotherms, one can observe that the capillary condensation step shifts to the higher relative pressure with the decrease of the alkane chain length. Fig. 1 (bottom) shows the pore size distributions of the obtained samples calculated from the adsortion branches. It is clear that the pore size increases with the decrease of the alkane chain length, which is consistent with the XRD results. The pore size of SBA-15 prepared with hexane can reach *ca.* 15 nm. At the same time, the BET surface area and pore volume of the sample are 614 m^2 g^{-1} and

---

[a] *State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, P. R. China. E-mail: xhbao@dicp.ac.cn; Fax: +86-411-84694447*
[b] *Department of Inorganic Chemistry, Fritz-Haber Institute of the Max Planck Society, Berlin D-14195, Germany*

† Electronic supplementary information (ESI) available: Fig. S1 N_2 adsorption–desorption isotherms of the samples prepared with (a) C_6; (b) C_7; (c) C_9. See http://dx.doi.org/10.1039/b509713d

Table 1 Physical data concerning the samples prepared with different alkanes

Alkanes	Initial reaction temperature/K	d_{100} spacing/nm	Unit cell $(a_0)^a$/nm	Pore diameter^b/nm	Surface areas/$m^2\ g^{-1}$
Nonane	300	12.3	14.2	13.4	637
Heptane	295	13.4	15.5	15.0	620
Hexane	290	14.2	16.4	15.7	614

[a] Calculated from (100) diffraction peak of the corresponding SAXD pattern. [b] Calculated from the adsorption branch of the N_2 adsorption–desorption isotherms of the corresponding sample.

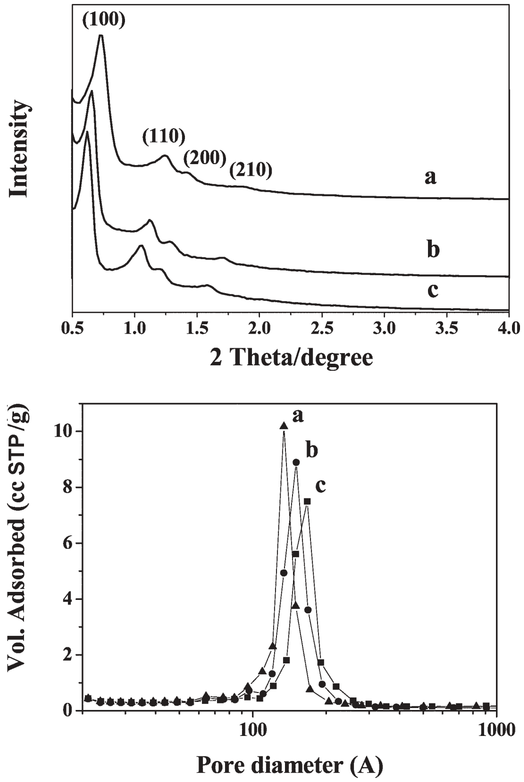

Fig. 1 SAXD patterns (top) and pore size distributions (bottom) of the samples prepared with (a) nonane, (b) heptane, (c) hexane. The pore size distributions were calculated from the adsorption branches.

1.40 cc g^{-1}, respectively. To our knowledge, this is the largest cylindrical pore diameter of all the reported highly ordered mesoporous SBA-15.

Fig. 2 gives the TEM images of the obtained materials prepared with hexane. The TEM image in Fig. 2a clearly shows the highly ordered parallel cylindrical pore channels. The width of a unit cell judged from the cross-sectioned TEM image (Fig. 2b) is *ca.* 16 nm, which is in agreement with the results of the SAXD. It is also concluded by TEM/SAXD that the products obtained before hydrothermal treatments are also highly ordered mesoporous materials, however, the crystallinity is lower than it is after hydrothermal treatment.

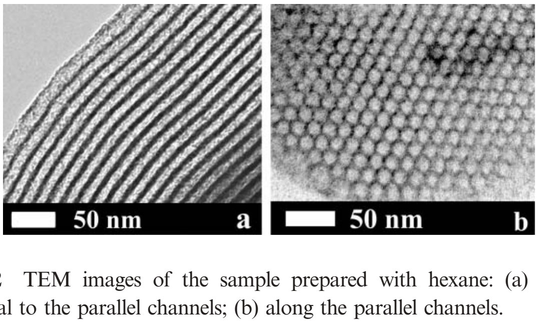

Fig. 2 TEM images of the sample prepared with hexane: (a) taken vertical to the parallel channels; (b) along the parallel channels.

Initial reaction temperature plays a key role in the synthesis of highly ordered SBA-15 in the presence of alkanes. It was reported that those SBA-15 materials prepared with short chain alkanes such as nonane or octane were always disordered large-pore mesoporous cellular foams (MCF) under the temporal synthesis conditions.[10] In the present study, highly ordered SBA-15 with large cylindrical mesopores is successfully prepared with such short chain alkanes by finely controlling the initial reaction temperature. For each alkane, there is a temperature when there is a phase transition from highly ordered mesoporous structure to disordered one (*e.g.* MCF). For example, in the case of hexane, the reaction temperature should be strictly lower than 290 K. Otherwise, other structures (such as, MCF materials) would form. In the case of heptane and nonane, the initial temperature should be lower than 295 K and 300 K, respectively. This indicates that the reaction temperature used in the current study depends strongly on the chain length of the alkanes (Table 1) in order to obtain highly-ordered SBA-15 silicas, *i.e.*, the shorter the chain length of alkanes, the lower the reaction temperature should be chosen. However, when the initial reaction temperature is lower than 283 K, only amorphous silica gels are obtained for all alkanes. Therefore, the preparation of highly ordered materials is carried out in a specific temperature range for each alkane. Within this range, a higher temperature on the initial reaction stage will lead to a slight shift of the (100) diffraction peaks to lower angles, indicating a slight increase of the pore size of the obtained SBA-15.[7] The synthesis reaction temperatures we chose (see Table 1) are close to but below the corresponding phase transition temperatures.

From Table 1, it shows that the shorter the alkane chain, the larger the pore diameter would be. The pore size expansion tendency is obviously different from that of MCM-41. In the case of MCM-41, where the traditional cationic surfactant was used, the pore size would enlarge with the increase of alkane chain length.[5,6] This is possibly related to the nature of the interactions between different surfactants and alkanes. It is well known that the nonionc copolymer surfactants (*e.g.* P123 in the current case) have a large number of monomers blocks and therefore can have many configurations. The solubilization behavior of different alkanes in the hydrophobic microdomains, which can lead to the dilution of PPO blocks and swelling of nonionic copolymer micelles, has been studied extensively.[12] It has been found that, with the decrease of alkane chain length, the solubilization capacity of alkanes in hydrophobic core of P123 surfactant increases, *i.e.*, the shorter the alkane chain length is, and the more the alkanes would be accommodated in the micelles cores, which results in larger swollen micelles dimension. Therefore, it can be concluded that, in the present situation, the higher solubilization capacity of shorter chain length alkanes (such as hexane) determines the ultimate larger pore diameter of SBA-15 silicas. In addition, at relatively higher initial reaction temperatures (such as in the case of hexane, higher than 290 K), disordered mesostructures (*e.g.*, MCF) are obtained, which may also be related to the solubilization behavior of alkanes.

On the other hand, the effect of inorganic salts (ion strength) on the organization behavior of nonionic surfactants has been widely studied,[13] and the synthesis temperature of SBA-15 has been decreased considerably with the addition of a proper amount of inorganic salts.[14] In the current P123 templated system, it is found that, without alkanes, the products prepared at 290 K are just amorphous silica gels even in the presence of NH_4F, indicating that it is the existence of alkanes other than inorganic salts that plays the key role in the organization of the hybrid composites at low temperature. Meanwhile, with alkanes, disordered mesoporous materials would be formed in the absence of fluoride at 290 K, confirming that the addition of fluoride can improve the ordering of obtained mesoporous materials.[11] Moreover, it is reported that the PPO moieties of the P123 show increasing hydrophilic tendency with the decrease of temperatures, which results in no aggregation of surfactants at lower temperatures.[15] Therefore, the condensation of the inorganic–organic hybrid surfactant monomers at relatively lower temperatures, *i.e.* room temperature, often leads to amorphous silica gel.[7] The hydrophobic PPO blocks have been reported to be mainly responsible for the micellization.[16] At the low temperature, the PPO blocks are easily hydrated and exhibit a certain degree of hydrophilic property and lead to the increase of critical micelle concentration (c.m.c.) of the P123 surfactants, and thus fail to serve as the template for mesoporous SBA-15.[15] In the current case, we propose that the doping of PPO blocks with alkanes may suppress the hydration of the hydrophobic PPO blocks, and therefore the corresponding c.m.c. of the surfactant is lower at low temperatures. At the same time, the solubilization of alkanes in the PPO blocks swells hydrophobic cores of the hybrid micelles. Highly ordered SBA-15 silicas with large cylindrical pore size are thus produced in the presence of a small amount of fluoride at the relatively low temperatures.

Our results indicate that alkanes with shorter chain length (from nonane to hexane) could be used as expanders to synthesize highly-ordered large-pore SBA-15 silicas with the help of NH_4F. It is observed that in a certain range, the shorter the alkane chain length, the larger the pore size of the obtained SBA-15 silicas. By using this method, the largest pore size of the obtained SBA-15 with highly ordered cylindrical porous structure is about 15 nm. Up to now, it is the largest cylindrical pore size among all the highly ordered SBA-15 samples reported. The obtained materials have potential applications in bulky macromolecular catalysis, separation of biomolecules as well as enzymes immobilization. Detailed investigation on the temperature induced structure transition by different alkanes is being processed.‡§

We are grateful for the support of the National Natural Science Foundation of China (No. 90206036) and the Ministry of Science and Technology of China (G1999022406). Junming Sun thanks Gang Hu (University of Oxford) for reading through the paper.

Notes and references

‡ XRD patterns were collected on a Rigaku D/MAX 2400 diffractometer equipped with a CuKα X-ray source operating at 40 kV and 50 mA. The N_2 adsorption–desorption isotherms were recorded on an ASAP 2000 instrument.

§ The TEM images were obtained with a Philips CM 200 Transmission Electron Microscope equipped with a CCD camera.

1 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710.
2 A. Sayari and Y. Yang, *J. Phys. Chem. B*, 1999, **103**, 3651.
3 Q. Huo, D. I. Margolese and G. D. Stucky, *Chem. Mater.*, 1996, **8**, 1147; S. S. Namba, A. Mochizuki and M. Kito, *Stud. Surf. Sci. Catal.*, 1998, **117**, 257; M. Kruk, M. Jaroniec and A. Sayari, *Microporous Mesoporous Mater.*, 2000, **35–36**, 545.
4 P. Y. Feng, X. H. Xu and D. J. Pine, *Langmuir*, 2000, **16**, 5304; J. Fan, C. Z. Yu, L. M. Wang, B. Tu, D. Y. Zhao, Y. Sakamoto and O. Terasaki, *J. Am. Chem. Soc.*, 2001, **123**, 12113.
5 Q. Huo, D. I. Margolese, U. Giesla, G. D. Demuth, P. Feng, T. E. Gier, P. Sieger, A. Firouzi, B. F. Chmelka, F. Schuth and G. D. Stucky, *Chem. Mater.*, 1994, **6**, 1176.
6 J. Blin and B. Su, *Langmuir*, 2002, **18**, 5303.
7 D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka and G. D. Stucky, *Science*, 1998, **279**, 548; D. Zhao, Q. Huo, J. Feng, B. F. Chmelka and G. D. Stucky, *J. Am. Chem. Soc.*, 1998, **120**, 6024.
8 P. Schmidt-Winkel, W. W. Lukens, D. Zhao, P. Yang, B. F. Chmelka and G. D. Stucky, *J. Am. Chem. Soc.*, 1999, **121**, 254; J. S. Lettow, Y. J. Han, P. Schmidt-Winkel, P. Yang, D. Zhao, G. D. Stucky and J. Y. Ying, *Langmuir*, 2000, **16**, 8291.
9 D. Y. Zhao, J. Y. Sun, Q. Z. Li and G. D. Stucky, *Chem. Mater.*, 2000, **12**, 275.
10 K. J. Suman, N. Reiichi, S. Kazuya, K. Tsuyoshi and N. Seitaro, *Microporous Mesoporous Mater.*, 2004, **68**, 133.
11 H. Zhang, J. M. Sun, D. Ma, X. H. Bao, A. Klein-Hoffmann, G. Weinberg, D. S. Su and R. Schlögl, *J. Am. Chem. Soc.*, 2004, **126**, 7440.
12 R. Nagarajan, M. Barry and E. Ruckenstein, *Langmuir*, 1986, **2**, 210; R. Nagarajan, *Colloids Surf., B*, 1999, **16**, 55.
13 G. Wanka, H. Hoffmann and W. Ulbricht, *Macromolecules*, 1994, **27**, 4145; M. Almgren, W. Brown and S. Hvidt, *Colloid Polym. Sci.*, 1995, **273**, 2; M. Antonietti and S. Forster, *Adv. Mater.*, 2003, **15**, 1323 and references therein.
14 C. Z. Yu, B. Z. Tian, B. Fan, G. D. Stucky and D. Y. Zhao, *Chem. Commun.*, 2001, **24**, 2726.
15 P. R. Desai, N. J. Jain, R. K. Sharma and P. Bahadur, *Colloids Surf., A*, 2001, **178**, 57; P. Alexandridis and T. A. Hatton, *Colloids Surf., A*, 1995, **96**, 1.
16 P. Alexandridis, J. F. Holzwarth and T. A. Hatton, *Macromolecules*, 1994, **27**, 2414.