

# Synthesis of double-mesopore silica using aqueous ammonia as catalyst

Xiaozhong Wang,\*† Tao Dou and Yongzhuang Xiao

Institute of Special Chemicals, Taiyuan University of Technology, Taiyuan, 030024, China

**Double-mesopore silica with a characteristic N<sub>2</sub> adsorption isotherm and narrow bimodal mesopore distribution is synthesized rapidly at room temperature by using aqueous ammonia as the catalyst.**

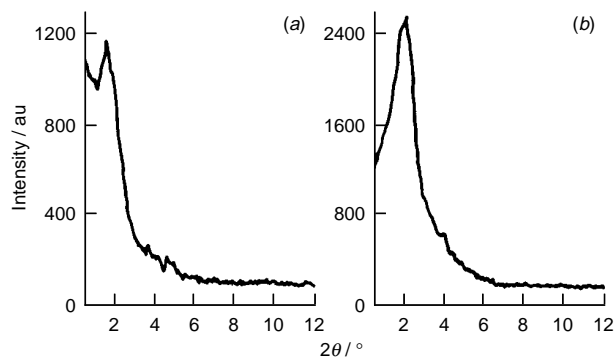
The synthesis of inorganic frameworks with specific and organized pore networks is of potential importance in catalysis,<sup>1,2</sup> separation technology<sup>3</sup> and biomaterials engineering.<sup>4,5</sup> Since the first synthesis of mesoporous MCM-41 materials,<sup>6,7</sup> there has been intense activity in the design and synthesis of a variety of mesoporous solids. Generally, the typical N<sub>2</sub> adsorption isotherm, which plays a significant role in characterization of the new mesoporous materials, of MCM-41 materials shows type IV behavior with a sharp inflection characteristic of capillary condensation within uniform mesopores at  $P/P_0$  ca. 0.3–0.4<sup>8</sup> and with an additional hysteresis loop following in the  $P/P_0$  region of 0.8–1.0.<sup>1,7</sup> The hysteresis loop at  $P/P_0 > 0.8$  is now acknowledged to arise from interparticle capillary condensation<sup>1,9</sup> or from the structure collapse of portions of the MCM-41 structure during the hydrothermal treatment or calcination.<sup>10,11</sup> However, if this hysteresis loop lifts up sharply, this may imply that a change in the texture has occurred on the mesoporous frameworks of the product. Pang and coworkers<sup>12</sup> recently presented a report on the synthesis of bimodal mesopore distribution silica with a sharp lefting-up hysteresis loop at  $P/P_0 > 0.8$  on its N<sub>2</sub> adsorption isotherm by calcining a wet surfactant-containing silicate gel. However, there is no discernible inflection in the vicinity of  $P/P_0 = 0.35$  on the N<sub>2</sub> adsorption–desorption isotherms to indicate the existence of smaller mesopores. Kloetstra *et al.*<sup>13</sup> also succeeded in synthesizing a bimodal pore size distribution molecular sieve by overgrowing mesoporous MCM-41 on a faujasite. Unfortunately, they have not provided any information on the detailed analysis of the N<sub>2</sub> adsorption isotherm and the corresponding pore size distribution curve. Double-mesopore molecular sieves of narrow pore distribution may find broad potential applications in electronic, optical or sensing devices.<sup>14,15</sup> Here, we present a synthesis of a double-mesopore silica mesostructure which has a typical mesopore X-ray diffraction pattern but narrow bimodal mesopore distribution. In the synthesis the process was completed in a relatively short time at room temperature by using aqueous ammonia as the catalyst.

The preparation procedure is as follows: stoichiometric surfactant cetyltrimethylammonium bromide (CTAB) was added to deionized water with stirring at room temperature until the solution became clear. The silica source tetraethylorthosilicate (TEOS) was then added to the solution with stirring. Finally, aqueous ammonia was slowly added until the pH of the solution was ca. 9.5. The molar composition of final gel mixtures was 2.0TEOS : 0.68–2.0NH<sub>3</sub>·H<sub>2</sub>O : 0.4CTAB : 230H<sub>2</sub>O. The mixtures were stirred continuously for ca. 7 min. During this short time the fluid mixture became progressively more viscous, and eventually set into jelly-like monoliths that assumed the shape of the container. Then the jelly-like solid product was washed repeatedly with distilled water in a centrifuge, dried in air at 353 K and finally calcined in air at 2 K min<sup>-1</sup> to 823 K for 6 h to remove the template.

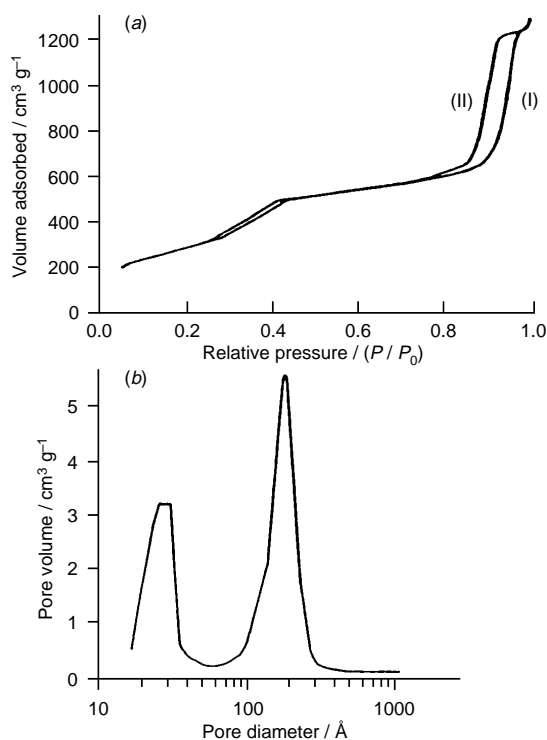
Powder X-ray diffraction (XRD) patterns (recorded on a D/max-rA diffractometer with Cu-K $\alpha$  radiation, 40 kV, 20 mA)

of the as-synthesized and calcined silica products are shown in Fig. 1. Different from the results of Pang and coworkers<sup>12</sup> that the gel precursor dried at room temperature is amorphous according to XRD, the pattern for the as-synthesized silica product exhibits a broad, yet clear, diffraction peak with a  $d$ -spacing of 5.2 nm. The appearance of a diffraction peak at this low angle suggests that after a short time of stirring mesostructure has been formed in the jelly-like solid product with a pore system lacking long-range order. Upon removal of the template by calcination, the basal spacing decreases to 4.4 nm and the scattering intensity increases substantially, suggesting that the calcination process may promote siloxane cross-linking and thereby improve the ordering of the oxide framework. The XRD patterns are reminiscent of HMS<sup>11</sup> and MSU<sup>9</sup> mesoporous materials.

Important trends are revealed in Fig. 2 by the N<sub>2</sub> adsorption–desorption isotherms and the corresponding BJH<sup>16</sup> pore size distribution based on the desorption branch (obtained on an ASAP 2000 analyser) for the calcined product. This is a typical irreversible type IV adsorption isotherm with two separate, well expressed H1 hysteresis loops as defined by IUPAC<sup>17</sup> at relative pressures  $P/P_0$  of 0.24–0.45 and 0.8–1.0. Nevertheless, the pore size distribution reveals that there are two mesopore sizes in the material, *i.e.* a bimodal distribution. The first condensation step on the isotherm at  $P/P_0 = 0.24$ –0.45 is similar to that for usual MCM-41 materials with markedly higher saturation sorption capacity, though not very steep. This was attributed to a slight pore size heterogeneity of the sample with a pore size of ca. 2.6–3.0 nm as seen in Fig. 2(b), but an exceptionally high mesopore surface area of 1064.6 m<sup>2</sup> g<sup>-1</sup>, corresponding to a total pore volume of 0.66 cm<sup>3</sup> g<sup>-1</sup>. This is in agreement with the XRD results, *i.e.* broad lines are observed. However, the second condensation step on the isotherm at  $P/P_0 > 0.8$  is much steeper than the first. This indicates the presence of a significant amount of secondary mesopores with a remarkably narrow pore size distribution centred at ca. 19 nm. The total pore volume for the larger mesopores is 1.18 cm<sup>3</sup> g<sup>-1</sup> with a total surface area of 243.1 m<sup>2</sup> g<sup>-1</sup>. This inflection at higher relative pressures differs completely from that of previously-synthesized mesoporous materials. In addition, the broad hysteresis loops in the isotherms reflect its long mesopores with no pore-blocking effects, which limit the emptying and filling of the accessible



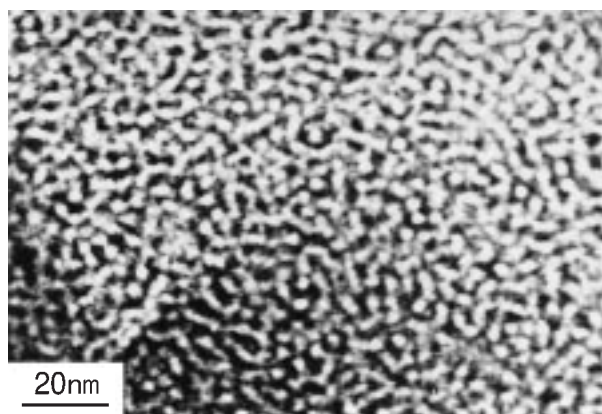
**Fig. 1** Powder X-ray diffraction patterns of (a) as-synthesized sample and (b) calcined sample



**Fig. 2** (a)  $N_2$  adsorption (I)–desorption (II) isotherms on the calcined sample and (b) the pore size distribution of the material

volume. Fig. 3 is a TEM image of the calcined sample (recorded on a JEOL 200CX microscope). It is evident that, different from most crystalline mesoporous sieves such as MCM-41 which has a well organized hexagonal pore structure, the present material contains a large number of randomly distributed channels with both smaller cylindrical- to hexagonal-shaped channels and larger stripe-like channels lacking long-range packing order. As can be seen from the TEM image, both sets of mesopores are present as a 'homogeneous' mixture throughout the entire sample. The formation of larger stripe-like mesopores may be due to the incomplete condensation of  $SiO_2$  species between adjacent surfactant micelles.

In summary, we have discovered a simple and novel synthesis of a double-mesopore silica with a characteristic  $N_2$



**Fig. 3** Transmission electron micrograph of the calcined sample

adsorption isotherm and narrow bimodal mesopore distribution. The synthesis process is completed in a relatively short time at room temperature by using aqueous ammonia as the catalyst. This may imply that surfactant micelles in the initial reaction mixtures are of different size or shape, and the hydrolysis of  $SiO_2$  species with surfactant micelles was incomplete over the short time of reaction. Further experimental results show that the similar double-mesopore silicas can also be synthesized by substituting tetraethylammonium hydroxide or NaOH for aqueous ammonia as the catalyst and that pH adjustment of the reaction mixtures plays a critical role in the synthesis. However, if the pH in the reaction mixtures increases beyond a certain degree, the double-mesopore silica will change into considerably ordered single-peaked mesoporous silica. These results provide us with a new angle for a further understanding of the formation mechanism of mesoporous silica materials. More detailed synthetic investigations and studies of the mechanism of formation of double-mesopore silica are in progress.

We would like to thank Dr Guoyi T. and Xihua C. at the Tsinghua University for the TEM data, Dong W. and Yanzheng F. at the Institute of Coal Chemistry, the Chinese Academy of Sciences for the XRD data and  $N_2$  adsorption measurements respectively, and we are also grateful to the National Natural Science Foundation of China, the Oversea-Returned Personnel Foundation of Shanxi Province and the Natural Science Foundation of Shanxi Youth for financial support.

## Notes and References

† E-mail: mailbox@tyut.edu.cn

- P. T. Tanev, M. Chibev and T. J. Pinnavaia, *Nature*, 1994, **368**, 321.
- R. Burch, N. Cruise, D. Gleeson and S. C. Tsang, *Chem. Commun.*, 1996, 951.
- R. M. Barrer, *Hydrothermal Chemistry of Zeolites*, Academic Press, London, 1982.
- G. Guillemin, J. L. Patat, S. Fournie and M. Chetail, *J. Biomed. Mater. Res.*, 1989, **21**, 557.
- J. L. Casci, *Stud. Surf. Sci. Catal.*, 1994, **85**, 329.
- J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schnitt, C.-T. W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins and J. L. Schlenkere, *J. Am. Chem. Soc.*, 1992, **114**, 10834.
- C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710.
- P. J. Branton, P. G. Hall and K. S. W. Sing, *J. Chem. Soc., Chem. Commun.*, 1993, 1257.
- S. A. Bagshaw, E. Prouzet and T. J. Pinnavaia, *Science*, 1995, **269**, 1242.
- Z. Luan, H. He, W. Zhou, C. Cheng and J. Klinowski, *J. Chem. Soc., Faraday Trans.*, 1995, **91**, 2955.
- P. T. Tanev and T. J. Pinnavaia, *Science*, 1995, **267**, 865.
- W. Lin, J. Chen, Y. Sun and W. Pang, *J. Chem. Soc., Chem. Commun.*, 1995, 2367.
- K. R. Kloetstra, H. W. Zandbergen, J. C. Jansen and H. Van Bekkum, *Microporous Mater.*, 1996, **6**, 287.
- G. D. Stucky, *Mater. Res. Soc. Symp. Proc.*, 1991, **206**, 507.
- A. Stein, G. A. Ozin and G. D. Stucky, *J. Soc. Photogr. Sci. Technol. Jpn.*, 1990, **53**, 322.
- E. P. Barrett, L. G. Joyner and P. P. Halenda, *J. Am. Chem. Soc.*, 1951, **73**, 373.
- K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscow, R. A. Pieroff, J. Rouquerol and T. Siemieni-ewska, *Pure Appl. Chem.*, 1985, **57**, 603.

Received in Cambridge, UK, 5th January 1998; 8/00113H