Sol-gel synthesis of ordered mesoporous alumina

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Well-ordered mesoporous alumina materials with high surface area and a narrow pore size distribution were synthesized using a sol-gel based self assembly technique.

Since the first successful synthesis of well-ordered, periodically organized mesoporous silica materials, such as the members of the M41S family[1] and SBA-15,[2] efforts have been directed toward extending the group of mesoporous materials to non-silica systems.[3] In this contribution, we report the synthesis of ordered mesoporous Al_2O_3 which is an interesting and attractive material because of its applications as absorber or catalyst support in heterogeneous catalytic reactions.[4] Although several papers were published in this direction using anionic, cationic or non-ionic templates as structure directing agents, none of the reported procedures resulted in ordered mesoporous alumina structures.[5–10] The present paper describes a highly reproducible process for the synthesis of mesoporous alumina with an SBA-15-like arrangement of ordered channels, with high surface area and a narrow pore size distribution.

During the synthesis, in solution A 1 g of Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, EO = ethylene oxide, PO = propylene oxide) was dissolved in 12 ml of absolute ethyl alcohol and stirred for 15 min at 40 °C. Meantime solution B was prepared from various amounts of 37 wt% hydrochloric acid and 6 ml of absolute ethyl alcohol. Water was not added to the synthesis mixture in addition to the HCl solution. Aluminium tri-*tert*-butoxide (2.46 g) was portioned slowly to solution B under vigorous stirring. After 15 min stirring, the two solutions were mixed together and further stirred at 40 °C. The molar ratio of Al^{3+} : Pluronic P123 : EtOH in the final solution was fixed at 1 : 0.017 : 30, and the hydrolysis rate was varied by changing the $[H_2O]$: $[Al^{3+}]$ ratio between the values of 2 and 12 and the [HCl] : $[Al^{3+}]$ ratio from 0.6 to 3.6. The homogeneous sol was poured into a teflon container for aging for three days at 40 °C under N_2 flow. Eventually the white sticky material that was produced was calcined at 400 °C in a flow of oxygen (flow rate = 100 cm^3 min^{-1}) for 4 h (1.5 °C min^{-1} ramping rate) in a tube furnace to remove the polymers from the pores.

The formation of the hybrid mesophase between the inorganic precursor (aluminium tri-*tert*-butoxide) and the structure directing agent (Pluronc P123) occurred during the slow evaporation of the solvent from the diluted ethanol solution. The precisely controlled conditions we used allowed us to slow down the hydrolysis/condensation reactions and prevent the uncontrolled phase separation between the inorganic and organic components so that a higher degree of cross linking between the precursor molecules occurs during the formation of the mesoscopic assemblies. The water concentration of the final solution turned out to have a strong influence on the nature of the final product. Only using Al^{3+} : Pluronic P123 : EtOH : H_2O : HCl = 1 : 0.017 : 30 : 6 : 1.8 resulted in the formation of mesoporous alumina with a hexagonally ordered channel system as Fig. 1 shows. As the TEM images indicate†, the mesoporous structure is highly ordered with a pore size of 68 Å which is in a good agreement with the data obtained from the physisorption and the small-angle X-ray measurements. The SAXS pattern of the well-ordered mesoporous alumina (Fig. 2A) shows three peaks, the (100), (110) and (200) reflections, which represent a 2D hexagonal mesostructure with space group *P6mm*. The d_{100} distance of 83 Å was calculated using the Bragg equation. The physisorption measurements reveal a high BET surface area (~410 m^2 g^{-1}) and a narrow pore size distribution with a center of 67 Å pore diameter (Fig. 2B), while in the other two cases (when lower or higher water and acid concentrations were used) the BET specific surface area together with the pore volume decreases significantly and a disordered pore system with a wide pore size distribution was obtained (Table 1 and Fig. 3A–B). Furthermore from the physisorption and the SAXS measurements the wall thickness of the final material was calculated to be equal to 28.8 Å, which is consistent with the TEM measurements. At low water concentrations the proper organization of the Pluronic P123 polymer molecules to micelles is most likely hindered leading to the wormhole-like structures.[11] Furthermore using small amounts of water and acid slows down the hydrolysis rate of the aluminium tri-*tert*-butoxide significantly, which makes the dissolution and the dispersion of the precursor molecules difficult in the ethanol solution. Higher water concentration results in fast hydrolysis and condensation reactions of the aluminium alkoxide molecules, leading to uncontrolled phase separation of the polymer and inorganic phases and the massive precipitation of the latter.

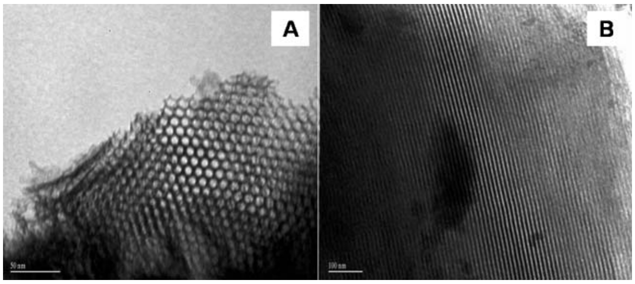

Fig. 1 TEM images of well-ordered mesoporous alumina material after calcinations imaged along the channels (A) and perpendicular to the channels (B). $[H_2O]$: $[Al^{3+}]$ = 6 : 1 was applied in the synthesis.

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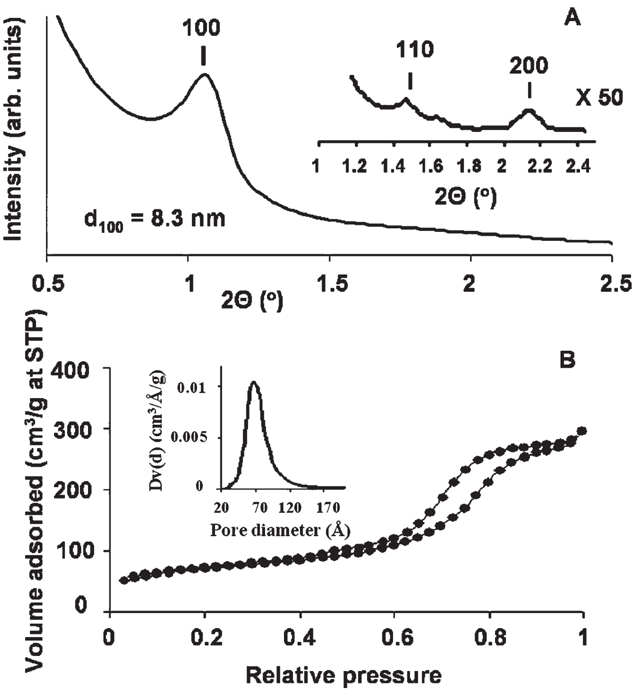

Fig. 2 Small-angle X-ray scattering pattern (A) and the nitrogen adsorption/desorption isotherms with the corresponding pore size distribution curve (B) of the well-ordered mesoporous alumina material after calcination. $[H_2O] : [Al^{3+}] = 6 : 1$ was applied in the synthesis.

Table 1 Characteristics of the mesoporous alumina samples

Sample name[a]	BET/$m^2\ g^{-1}$[b]	V_p/$cm^3\ g^{-1}$[c]	D_p/Å[c]
MP-Al_2O_3_2	206	0.44	39–150
MP-Al_2O_3_6	410	0.80	67
MP-Al_2O_3_12	349	0.62	39–90

[a] The numbers in the sample names denote the different $[H_2O] : [Al^{3+}]$ ratios applied during the reactions. [b] BET surface area. [c] Pore volume (V_p) and the typical pore diameter (D_p) of the mesoporous alumina samples derived from physisorption measurements.

Ordered mesoporous alumina with SBA-15-like structure was synthesized with high reproducibility by the sol-gel based self assembly method. Amphiphilic triblock copolymer (Pluronic P123) as the structure directing agent was used to organize the aluminium precursor molecules into a well-ordered mesoporous structure during the solvent evaporation from an ethanol solution containing a controlled amount of water and acid at elevated temperature.

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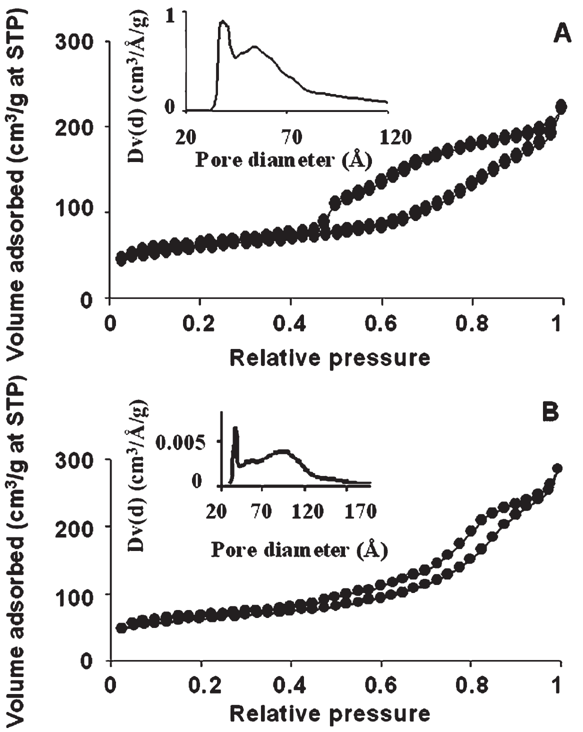

Fig. 3 Nitrogen adsorption/desorption isotherms with the corresponding pore size distribution curves of mesoporous alumina samples after calcination. $[H_2O] : [Al^{3+}] = 12 : 1$ (A), $[H_2O] : [Al^{3+}] = 2 : 1$ (B).

Notes and references

† Characterization of the samples: Transmission electron microscopy (TEM) studies were carried out using a FEI Tecnai 12 microscope operated at 100 kV. Mesoporous alumina samples were dispersed in acetone using sonication and placed onto formvar carbon covered copper grids and dried under air. BET surface areas of the samples were calculated from nitrogen physisorption data collected on a Quantachrome Autosorb-1 analyzer at 77 K. The pore size distributions were calculated using the BJH method from the desorption branch of the isotherms. Small-angle X-ray scattering measurements were performed using a Bruker Nanostar U diffractometer using Cu Kα radiation (1.54 Å) and 107 cm sample to detector distance.

1 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710.
2 D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka and G. D. Stucky, *Science*, 1998, **279**, 548.
3 G. J. de A. A. Soler-Illia, C. Sanchez, B. Lebeau and J. Patarin, *Chem. Rev.*, 2002, **102**, 4093.
4 J. Cejka, *Appl. Catal., A*, 2003, **254**, 327.
5 F. Vaudry, S. Khodabandeh and M. E. Davis, *Chem. Mater.*, 1996, **8**, 1451.
6 (*a*) M. Yada, H. Kitamura, M. Machida and T. Kijima, *Langmuir*, 1997, **13**, 5252; (*b*) M. Yada, H. Hiyoshi, K. Ohe, M. Machida and T. Kijima, *Inorg. Chem.*, 1997, **36**, 5565.
7 S. Cabrera, E. Haskouri, J. Alamo, A. Beltran, D. Beltran, S. Mendioroz, M. Dolores Marcos and P. Amoros, *Adv. Mater.*, 1999, **11**, 379.
8 (*a*) S. A. Bagshaw, E. Prouzet and T. J. Pinnavaia, *Science*, 1995, **269**, 1242; (*b*) S. A. Bagshaw and T. J. Pinnavaia, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1102.
9 W. Zhang and T. J. Pinnavaia, *Chem. Commun.*, 1998, **35**, 1185.
10 (*a*) P. Yang, D. Zhao, D. I. Margolese, B. F. Chmelka and G. D. Stucky, *Nature*, 1998, **396**, 152; (*b*) P. Yang, D. Zhao, D. I. Margolese, B. F. Chmelka and G. D. Stucky, *Chem. Mater.*, 1999, **11**, 2813.
11 G. J. de A. A. Soler-Illia, G. J. E. Scolan, A. Louis, P. A. Albouy and C. Sanchez, *New J. Chem.*, 2001, **25**, 156.