COMMUNICATION

ChemComm
www.rsc.org/chemcomm

A novel and template-free method for the spontaneous formation of aluminosilicate macro-channels with mesoporous walls

Alexandre Léonard and Bao-Lian Su*

Laboratoire de Chimie des Matériaux Inorganiques, The University of Namur (FUNDP), 61, rue de Bruxelles, B-5000 Namur, Belgium. E-mail: bao-lian.su@fundp.ac.be; Fax: +32 81 725414; Tel: +32 81 724531

Received (in Cambridge, UK) 16th April 2004, Accepted 19th May 2004
First published as an Advance Article on the web 21st June 2004

A simple and template-free synthesis pathway was developed leading to hierarchical meso-macroporous aluminosilicates made of an assembly of macro-channels with openings between 0.5 and 2.0 µm and mesoporous walls.

Recent interest has been devoted to the development of synthesis and processing procedures for preparing porous materials with a hierarchy of different length scales (*e.g.* meso-macroporous or micro-mesoporous) in the same material. Challenges arise in the preparation of meso/macroporous structures including eliminating a significant proportion of closed pores, controlling independently the sizes of the mesopores and macropores, regulating the compositions as desired and improving the thermal stability to avoid structure collapse upon calcination.[1] Hierarchical materials with different pore sizes integrated in one body can be expected to combine reduced resistance to diffusion and high surface areas for yielding improved overall reaction and adsorption/separation performances and can be extended to biological applications.[2] In the past 6 years, there has been considerable work accomplished on the preparation of SiO_2, Al_2O_3, Nb_2O_5, TiO_2, ZrO_2…structures with multiscale porosity.[3] Recently, we extended the research to hierarchical aluminosilicate compounds with well-defined mesopores and tubular macrochannels with openings at the micrometer level.[4] Analogues were also prepared with quite low aluminium content by a combined surfactant-PMMA spheres templating approach.[5] Very stable hierarchical aluminosilicates made of mesopores with microporous zeolitic walls have been reported.[6] These compounds are of considerable interest in the aim of treating bulky vacuum gas–oil molecules.[7] Actual FCC catalysts are composites of USY zeolites mixed with an amorphous silica, silica/alumina, alumina matrix and clay. It has been shown that mesoporous aluminosilicates could be used as matrices for supporting the zeolite as they are more active than their amorphous analogues in precracking heavy feedstocks.[8] The overall catalytic performance is known to be dictated by acidity and mass transport. Promoting the catalytic activity thus involves an increase in inter-channel accessibility.[9] Hierarchical meso-macroporous aluminosilicates recently prepared by us therefore show important potential as catalyst and catalyst supports.[4] The originality of the proposed syntheses relied on a simple surfactant templating pathway and on the absence of latex spheres, cosolvents or other additives commonly employed to generate the macropores. Further investigations have since been carried out in order to understand the formation of these materials. Here we provide a novel and facile method for the preparation of hierarchical meso-macroporous aluminosilicates without need of either surfactant or latex spheres or emulsion states, by just controlling the hydrolysis and polycondensation rates of the inorganic sources.† Indeed, the reported preparation pathways of regular arrays of macropores nearly always require a templating approach. Present results suggest that the presence of the surfactant induces the good regularity within the mesoporous part of the compound whereas the templating molecules are not indispensable for the macropore creation.

The preparations were carried out at different starting pH values (2, 7 and 10). The results reported hereafter apply to materials obtained after hydrothermal treatment. In all cases, the macropores are clearly visualized by scanning electron microscopy (Fig. 1). The micrographs show non-interconnected tubular macro-channels, which are quite parallel to each other and perpendicular to the monolithic (larger than 50 µm) particle's surface. Similarly to the surfactant assisted pathway,[4] the present preparation method leads to tubular macropores rather than to holes and these channels extend throughout the whole particle as can be seen from SEM micrographs. Higher starting pH values can favor the creation of macropores, although no striking change in the morphology can be noticed with regard to the influence of pH values.

Fig. 2A shows the wide angle XRD patterns of the samples prepared at different starting pH values. At pH = 2, no reflections can be detected, indicative of a totally amorphous framework. Some weak reflections at higher angles can be detected at higher starting pH values, suggesting the appearance of crystalline phases within the material. These can be assigned to a boehmite AlOOH phase according to the literature.[10] Higher starting pH values thus favor the formation of crystalline domains inside the compound. The X-ray diffractogram of a material prepared at pH = 2 and

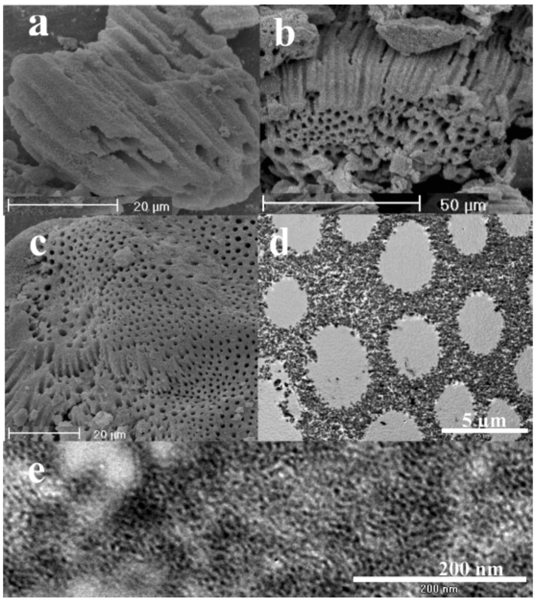

Fig. 1 (a), (b) and (c): SEM images of the meso-macroporous aluminosilicate material prepared at pH 2, 7 and 10 respectively; (d) and (e): TEM images of (a) at different scales.

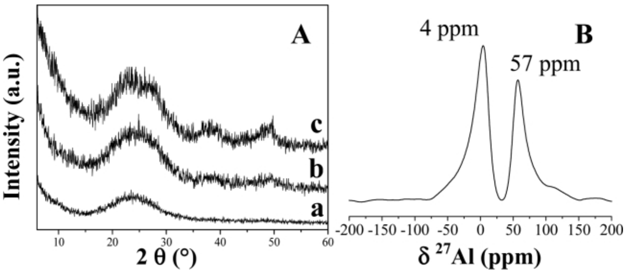

Fig. 2 A: X-Ray diffraction patterns of the samples prepared at different starting pH values: (a) 2, (b) 7 and (c) 10; B: ^{27}Al MAS NMR spectrum of the sample prepared at pH 2.

DOI: 10.1039/b405663a

calcined at 823 K still shows an amorphous framework and intact meso- and macroporosity, indicative of the thermal stability of such materials.

^{27}Al MAS NMR spectra give evidence that aluminium atoms exist in both tetrahedral and octahedral positions (Fig. 2B). A larger peak at 4 ppm however suggests that sixfold-coordinated aluminium atoms prevail over the tetrahedral incorporated species. In the surfactant-assisted preparations made by the present authors, almost all the Al atoms are in the tetrahedral position,[4] suggesting that the surfactant helps the incorporation of the Al atoms into the framework. The higher starting pH values also lead to materials with octahedral aluminium atoms in large majority.

The isotherm corresponding to a sample prepared with a starting pH value of 2 is given in Fig. 3. Its shape is located between types IV and II, corresponding respectively to mesoporous and macroporous materials. A poorly defined plateau followed by strong nitrogen uptake at high relative pressure values can be noticed, suggesting a material made of both mesopores and larger sized openings. The corresponding pore size distribution (PSD), calculated by the BJH method and given as an insert, is broad with a maximum centered at 4.5 nm. If the preparation pH increases to 7, the isotherm becomes more or less type II and the PSD becomes broader with a maximum at about 5 nm. Finally, at pH = 10, the isotherm is fully type II, characteristic of macroporous structures, meaning the complete loss of mesoporosity. Nitrogen adsorption measurements thus show that hierarchical structures with well-defined meso- and macropores, can only be prepared when the starting aqueous solution has a pH value of 2. A macroporous structure of mixed SiO_2–Al_2O_3 will be obtained by elevating the pH value of the synthesis gel. This differs from the surfactant-assisted preparations, where meso-macroporous aluminosilicate compounds can even be synthesized at pH = 7 and 10. This suggests that surfactant molecules help not only the incorporation of Al atoms into the framework but also the creation of mesopores, whereas it is not indispensable in the obtention of the tubular macropores.

The pore volumes are comprised between 1.1 and 1.5 $cm^3 g^{-1}$ and the specific surface areas are very high; 661, 556 and 598 $m^2 g^{-1}$ for starting pH values of 2, 7 and 10 respectively. The specific surface area of a calcined sample prepared at pH = 2 rises to 698 $m^2 g^{-1}$, proving the thermal resistance of the materials.

Similar results have been observed for samples prepared without hydrothermal treatment. The specific surface areas exceed 500 $m^2 g^{-1}$ and the PSD is even better defined at pH = 7.

Very recently, Mann *et al.* reported an ammonia induced template-free and non-stirring method for the preparation of macroporous titania.[11] They claimed that the rapid dropwise injection of the inorganic source into aqueous NH_3, the rates of hydrolysis/condensation and the nature of the alcohol by-product are important factors for the spontaneous formation of these materials. In our case, the preparations were performed under acidic, neutral and basic conditions, without surfactant molecules but with stirring. Meso-macroporous aluminosilicates can be formed with high yield only at pH = 2 while pure macroporous mixed oxides were obtained at pH = 10. Hierarchical meso-macrostructured aluminosilicates can thus be obtained by adjusting the pH value of the synthesis gel in the absence of surfactant molecules and without ammonia as inductor.

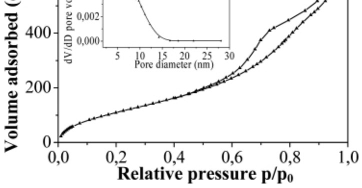

Fig. 3 Nitrogen adsorption–desorption isotherm of a meso-macroporous hierarchical structure. The corresponding PSD is given as an insert.

In our case, the macrochannels are formed under stirring and without ammonia. According to the mechanism proposed by Mann *et al.*, the micropipette addition of TMOS and TBOA into the aqueous solution would lead to droplets with a thin and dense SiO_2–Al_2O_3 layer at their surface. Hydrolysis and condensation reactions then proceed inwardly leading to a SiO_2–Al_2O_3 solid phase in which water/alcohol channels exist due to the hydrodynamic flow of the solvent. The wormhole-like mesoporous nature of the inorganic regions, which form the walls of the macrochannels, results from a regular packing mechanism of nanometer sized aluminosilicate particles as evidenced by TEM pictures (Fig. 1d). This mechanism was previously applied to explain the formation of mesoporous aluminosilicates in acidic conditions without using surfactants.[12]

In conclusion, a careful control of the hydrolysis and condensation rates of the inorganic sources can lead to hierarchical meso-macrostructured aluminosilicates or to the spontaneous formation of pure macroporous mixed oxides depending on the starting pH value of the solution.

Notes and references

† Three solutions, twice-distilled water, an aqueous solution acidified to pH = 2 with H_2SO_4 and an aqueous solution basified to pH = 10 with NaOH, were used as starting solutions and heated at 70 °C. The inorganic precursors, first aluminium tri-*sec*-butoxide [TBOA, $C_{12}H_{27}AlO_3$, > 95%, Fluka], then tetramethyl orthosilicate [TMOS, $C_4H_{12}O_4Si$, 98%, Aldrich] were added under moderate stirring with a Si/Al molar ratio of 4.0 into these three solutions. The resulting gels were homogenized for 1 hour at 70 °C. To study the influence of hydrothermal treatment, the gels were either directly dried at 50 °C or hydrothermally treated for 24 hours at 80 °C in teflon cartridges sealed in stainless steel autoclaves, followed by drying. The morphologies of the final materials were visualized with SEM (Philips XL-20). The structure was assessed by XRD measurements (Philips PW1820 with Cu Kα radiation). TEM was carried out on a Philips Tecnai 10 and nitrogen adsorption–desorption isotherms were collected with Micromeritics Tristar 3000 or ASAP 2010 porosimeters. ^{27}Al MAS-NMR spectra were recorded in a Bruker MSL400 spectrometer.

1 H. Maekawa, J. Esquena, S. Bishop, C. Solans and B. F. Chmelka, *Adv. Mater.*, 2003, **15**, 591.
2 G. J. A. A. Soler-Illia, C. Sanchez, B. Lebeau and J. Patarin, *Chem. Rev.*, 2002, **102**, 4093.
3 B. T. Holland, C. F. Blanford and A. Stein, *Science*, 1998, **281**, 538; P. Yang, T. Deng, D. Zhao, P. Feng, D. Pine, B. F. Chmelka, G. M. Whitesides and G. D. Stucky, *Science*, 1998, **282**, 2244; D. M. Antonelli, *Microporous Mesoporous Mater.*, 1999, **33**, 209; W. Deng, M. W. Toepke and B. H. Shanks, *Adv. Funct. Mater.*, 2003, **13**, 61; J. L. Blin, A. Léonard, Z. Y. Yuan, L. Gigot, A. Vantomme, A. K. Cheetham and B. L. Su, *Angew. Chem., Int. Ed*, 2003, 1644.
4 A. Léonard, J. L. Blin and B. L. Su, *Chem. Commun.*, 2003, 2568.
5 G. Gundiah, *Bull. Mater. Sci.*, 2001, **24**, 211.
6 Y. Liu, W. Zhang and T. J. Pinnavaia, *J. Am. Chem. Soc.*, 2000, **122**, 8791; D. T. On and S. Kaliaguine, *Angew. Chem., Int. Ed*, 2002, **41**, 1036.
7 G. de la Puente, E. Falabella Sousan-Aguiar, A. Figueiredo Costa and U. Sedran, *Appl. Catal. A: Gen.*, 2003, **242**, 381.
8 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710; A. Corma, *Chem. Rev.*, 1997, **97**, 2373.
9 W. H. Chen, Q. Zhao, H. P. Lin, Y. S. Yang, C. Y. Mou and S. B. Liu, *Microporous Mesoporous Mater.*, 2003, **66**, 209.
10 Z. Zhang, R. W. Hicks, T. R. Pauly and T. J. Pinnavaia, *J. Am. Chem. Soc.*, 2002, **124**, 1592.
11 A. Collins, D. Carriazo, S. A. Davis and S. Mann, *Chem. Commun.*, 2004, 568.
12 N. Yao, G. Xiong, K. L. Yeung, S. Sheng, M. Y. He, W. S. Yang, X. M. Liu and X. H. Bao, *Langmuir*, 2002, **18**, 4111.

Typeset and printed by Black Bear Press Limited, Cambridge, England