

Mesoporous aluminoborates

S. Ayyappan and C. N. R. Rao*

CSIR Centre of Excellence in Chemistry and Materials Research Centre, Indian Institute of Science, Bangalore 560 012, India and Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore 560 064, India

Hexagonal, cubic and lamellar aluminoborate mesophases containing octahedral aluminium and tetrahedral boron are prepared and characterized for the first time.

Since the first synthesis of mesoporous silica,¹ there has been intense activity in the design and synthesis of a variety of mesoporous solids.^{2–4} These studies have also unravelled the mechanism of formation of these materials by means of supramolecular templating involving an unusual combination of surfactant aggregates and anionic silicate species.^{4,5} By varying the pH or the surfactant to silica ratio, hexagonal, cubic and lamellar forms of silica mesophases have been prepared.⁶ Besides ionic surfactants, neutral amines⁷ and polyalkene oxides⁸ have been employed to synthesise the mesophases. The strategy to prepare silica-based mesophases has been extended to prepare a variety of mesoporous metal oxides such as Al_2O_3 ,⁸ TiO_2 ,^{9,10} and ZrO_2 ¹¹ and Nb_2O_5 .¹² AlPO_4 which is isoelectronic with SiO_2 has provided the basis for a distinct family of microporous materials.¹³ However, efforts to make hexagonal mesoporous AlPO_4 have not been successful; instead, only lamellar AlPO_4 has been obtained.¹⁴ We considered it most worthwhile to explore the synthesis of the mesoporous phases of the analogous aluminoborates containing the AlBO_4^{2-} species. There has been some effort¹⁵ to make microporous aluminoborates with different B/Al ratios, but the products do not seem to have been adequately characterized. Here, we report the first successful synthesis and characterization of mesoporous aluminoborate phases in hexagonal, cubic and lamellar forms. It has been possible to remove the surfactant from the hexagonal phase and expand the pore size of the hexagonal phase by using aliphatic hydrocarbons as solubilizing agents.

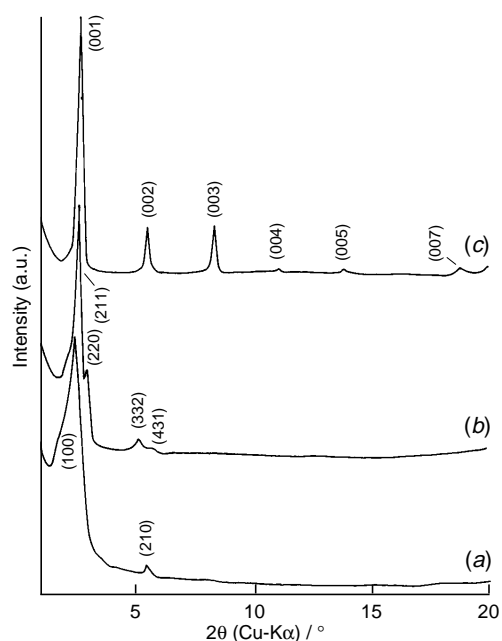


Fig. 1 X-Ray diffraction patterns of the aluminoborate mesophases: (a) hexagonal, (b) cubic and (c) lamellar

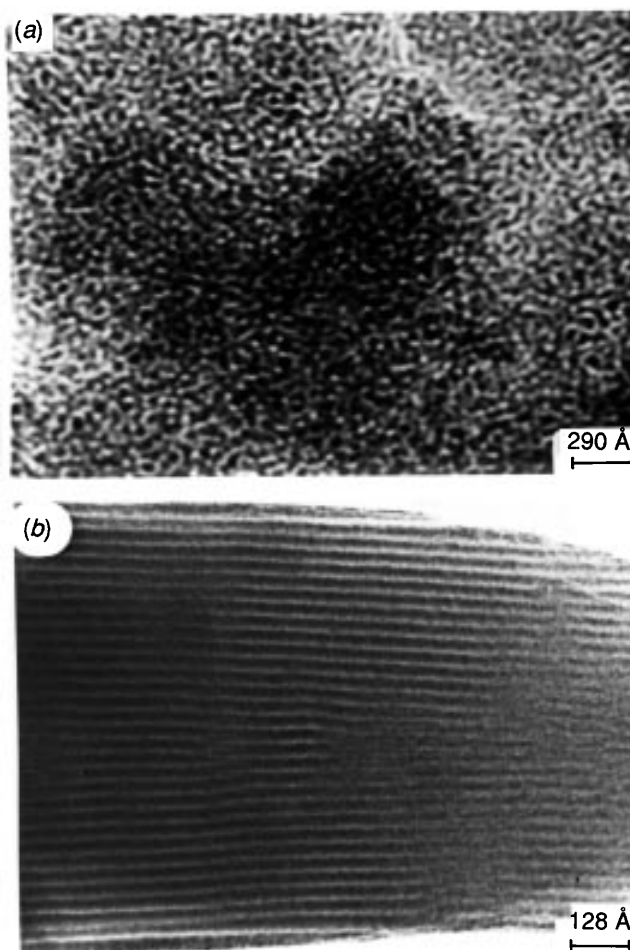


Fig. 2 TEM images of (a) hexagonal and (b) lamellar aluminoborate mesophases

Mesoporous aluminoborate phases could not be obtained when cationic surfactants or long-chain amines were employed for the synthesis. They could however be prepared by employing sodium dodecyl sulfate (SDS) as the surfactant. In a typical preparation, to a solution containing Ca, Al and B in 1 : 1 : 1 molar ratio, prepared by dissolving appropriate quantities of CaO and $\text{Al}(\text{NO}_3)_3$ and boric acid in aqueous nitric acid, sodium dodecyl sulfate (1.0 mol with respect to Ca or Al) was added under stirring. Ammonia was added to the resulting turbid solution under constant stirring to reach the desired value of pH. The resultant gel was maintained at room temperature for 48 h. The product so obtained was washed several times with distilled water and dried at 100 °C in a hot air oven. X-Ray diffraction (XRD) patterns of the dried solids were recorded with a Rich–Seifert (model XRD 3000TT) instrument. Fig. 1 shows the XRD patterns of the products obtained at different pH values. The XRD pattern of the product obtained at pH 2 [Fig. 1(a)] is characteristic of a hexagonal phase with a d_{100} value of 36.1 Å ($a_0 = 41.7$ Å). The XRD pattern of the product

obtained at a pH of 3.5 [Fig. 1(b)] corresponds to that of a cubic phase. This pattern could be indexed with $a = 83.5 \text{ \AA}$. The XRD pattern of the product obtained at pH *ca.* 5.5 [Fig. 1(c)] is characteristic of a lamellar phase and accordingly exhibits the various $00l$ reflections ($d_{001} = 32.5 \text{ \AA}$). The scanning electron micrographs of the hexagonal and lamellar phases exhibit characteristic differences in morphology, the lamellar form showing the flaky structure. The transmission electron microscope (TEM) image (recorded with a JEOL JEM 3010 microscope) reveals the presence of disordered hexagonal pores with an opening of *ca.* 32 \AA with a wall thickness of *ca.* 11 \AA [Fig. 2(a)]. The TEM image of the lamellar phase shows an interlayer separation of *ca.* 32 \AA [Fig. 2(b)].

EDAX analysis of the aluminoborate mesophases showed the Ca : Al molar ratio to be 1 : 1, while an ICP analysis gave a Al : B molar ratio of 1 : 1. Thermogravimetry showed the loss of water by $150 \text{ }^\circ\text{C}$ and of the surfactant by $600 \text{ }^\circ\text{C}$. Based on the mass loss data and assuming the Ca : Al : B molar ratio to be 1 : 1 : 1, the composition of the aluminoborate-surfactant adduct works out to be $\text{CaO} \cdot 0.5\text{Al}_2\text{O}_3 \cdot 0.5\text{B}_2\text{O}_3 \cdot 0.6\text{SDS} \cdot 1.5\text{H}_2\text{O}$. The %mass of boron from the ICP analysis ($3.15 \pm 0.25\%$) is also consistent with the theoretical value of 3.2% based on the empirical formula. The IR spectrum of this adduct showed a boron-oxygen stretching band in the region $900\text{--}1100 \text{ cm}^{-1}$ due to BO_4 tetrahedra. The IR band characteristic of BO_3 units in the region $1200\text{--}1400 \text{ cm}^{-1}$ was absent. Significant structural information was obtained by means of ^{27}Al and ^{11}B MAS NMR spectra (recorded with a Bruker MSL-300 spectrometer) of the hexagonal aluminoborate mesophase. The ^{27}Al NMR signal is centred around $\delta 0.0$ [Fig. 3(a)], characteristic of an octahedral environment of Al.¹⁶ The ^{11}B NMR signal is also centred around $\delta 0.0$ [Fig. 3(b)] suggesting a tetrahedral environment for boron.¹⁷

By heating the as-prepared hexagonal mesophase to $300 \text{ }^\circ\text{C}$, we could remove some of the surfactant without destroying the structure. Thus, the XRD pattern of the resulting product shows the mesoporous structure with a d_{100} value of 35.2 \AA . We could

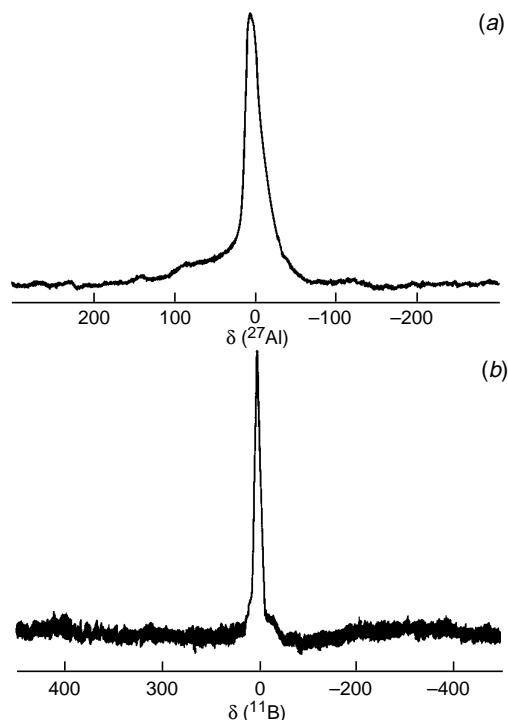


Fig. 3 MAS NMR spectra of mesoporous aluminoborate: (a) ^{27}Al spectrum and (b) ^{11}B spectrum

however remove the surfactant by refluxing the hexagonal mesophase with acidified ethanol for 3 h. The removal of the template was confirmed by the absence of mass loss over the temperature range where the template is normally removed as well as by the XRD pattern. The removal of the surfactant from the hexagonal phase was confirmed by the IR spectra, which showed the near-absence of bands arising from CH_2 groups. Accordingly, the surface area of the hexagonal aluminoborate obtained by calcination was *ca.* $100 \text{ m}^2 \text{ g}^{-1}$ and that of the sample obtained by alcohol extraction was $470 \text{ m}^2 \text{ g}^{-1}$; their XRD patterns were not identical.

We have been able to expand the pore size of the hexagonal mesoporous aluminoborate by the use of *n*-alkanes as solubilizing agents. For this purpose, we added the alkane along with the surfactant solution to the acidic solution containing Ca, Al and B, maintaining the molar ratio of the alkane to the surfactant to be 1 : 1. This molar ratio was found to be optimal for expanding the pore size. The XRD patterns gave d_{100} values of 49.0 and 56.6 \AA respectively with *n*-octane and *n*-hexadecane, compared to the value of 36.1 \AA obtained in the absence of the alkanes.

We have also varied the Al : B ratio and obtained hexagonal mesoporous phases with Al : B ratios down to 0.5 : 1.5. By using Na^+ as the cation instead of Ca^{2+} , a hexagonal mesoporous phase with a Na : Al : B ratio of 2 : 1 : 1 was obtained with a d_{100} value of 35.5 \AA .

References

- 1 J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T. W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins and J. L. Schlenker, *J. Am. Chem. Soc.*, 1992, **114**, 10 834.
- 2 P. Behrens and G. D. Stucky, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 696.
- 3 P. Behrens, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 515.
- 4 J. S. Beck and J. C. Vartuli, *Curr. Opinion Solid State Mater. Sci.*, 1996, **1**, 76.
- 5 Q. Huo, D. I. Margolese, U. Ciesla, D. G. Demuth, P. Feng, T. E. Gier, P. Sieger, A. Firouzi, B. F. Chmelka, F. Schüth and G. D. Stucky, *Chem. Mater.*, 1994, **6**, 1176; Q. Huo, D. Margolese and G. D. Stucky, *Chem. Mater.*, 1996, **8**, 1147.
- 6 A. Monnier, F. Schüth, Q. Huo, D. Kumar, D. Margolese, R. S. Maxwell, G. D. Stucky, M. Krishnamurty, P. Petroff, A. Firouzi, M. Janicke and B. F. Chmelka, *Science*, 1993, **261**, 1299; J. C. Vartuli, K. D. Schmitt, C. T. Kresge, W. J. Roth, M. E. Leonowicz, S. B. McCullen, S. D. Helbring, J. S. Beck, J. S. Schlenker, D. H. Olson and E. W. Sheppard, *Chem. Mater.*, 1994, **6**, 2317.
- 7 P. T. Tanev and T. J. Pinnavaia, *Science*, 1995, **267**, 365.
- 8 S. A. Bagshaw and T. J. Pinnavaia, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1102.
- 9 D. M. Antonelli and J. Y. Ying, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2014.
- 10 N. Ulagappan and C. N. R. Rao, *Chem. Commun.*, 1996, 1685.
- 11 U. Ciesla, S. Schacht, G. D. Stucky, K. K. Unger and F. Schüth, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 426; N. Ulagappan, Neeraj, B. V. N. Raju and C. N. R. Rao, *Chem. Commun.*, 1996, 2243.
- 12 D. M. Antonelli and J. Y. Ying, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 426.
- 13 S. T. Wilson, B. M. Lok, C. A. Messina, T. R. Connan and E. M. Flanagan, *J. Am. Chem. Soc.*, 1982, **104**, 1176.
- 14 A. Sayari, V. R. Karra, J. S. Reddy and I. L. Moudrakovski, *Chem. Commun.*, 1996, 411.
- 15 J. Wang, S. Feng and R. Xu, *J. Chem. Soc., Chem. Commun.*, 1989, 265; J. Yu, K. Tu and R. Xu, in *Zeolites and Related Microporous Materials: State of the Art*, ed. J. Weitkamp, H. G. Karge, H. Pfeifer and W. Hölderich, Elsevier, Amsterdam, 1994.
- 16 C. A. Fyfe, G. C. Gobbi, J. Klinowski, J. M. Thomas and S. Ramdas, *Nature*, 1982, **96**, 530.
- 17 C. A. Fyfe, L. Berni, H. G. Clark, J. A. Davies, G. C. Cobbi, J. S. Hartman, P. J. Hayes and R. E. Wasilyshen, *Adv. Chem. Ser.*, 1983, **211**, 405.

Received, 18th November 1996; Com. 6/07782J