Preparation of lamellar and hexagonal forms of mesoporous silica and zirconia by the neutral amine route: lamellar–hexagonal transformation in the solid state

N. Ulagappan, Neeraj, Battaram V. N. Raju and C. N. R. Rao*

Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore 560012, India and
CSIR Centre of Excellence in Chemistry, Indian Institute of Science, Bangalore 560012, India

The chain length of the surfactant and the solvent composition are two of the factors that determine whether the lamellar or the hexagonal form of mesoporous SiO_2 (or ZrO_2) is formed by the neutral amine route; a lamellar–hexagonal transformation occurs on removal of the amine from the former.

By varying the pH or cationic surfactant : tetraethylorthosilicate (TEOS) ratio, it is possible to obtain hexagonal or lamellar forms of mesoporous silica.[1,2] The hexagonal form of silica has also been prepared by Tanev and Pinnavaia by a neutral templating route based on hydrogen-bonding interactions and self-assembly between primary aliphatic amine micelles and TEOS. These workers employed a neutral diamine to obtain lamellar silica of vesicular morphology.[4] We have investigated the formation of the lamellar phase of mesoporous silica in preference to the hexagonal phase by the neutral amine route and find that the chain length of the amine and the composition of the solvent, in particular the water content, play a crucial role. Investigations of mesoporous zirconia prepared by the neutral amine route also show the importance of these factors in determining the structure of the mesophase. More interestingly, the lamellar forms of silica and zirconia transform into the hexagonal form in the solid state, upon removal of the amine by calcination or by solvent extraction.

The procedure employed by us to prepare mesoporous silica by the neutral amine route was as follows. A known quantity of the amine (0.022 mol) was added to x mol (1.33–4.44) of water and the mixture agitated to obtain a homogeneous phase. To this was added 0.022 mol of TEOS under stirring and the product aged for 18 h at room temperature, before drying it at 383 K overnight. With hexadecylamine as the surfactant, this procedure gave a lamellar phase when x = 4.44 mol, as can be seen from the X-ray diffraction (XRD) pattern in Fig. 1(*a*), with *d*-spacings of 5.38, 2.73 and 1.84 nm due to the 001, 002 and 003 reflections. When the water content was reduced (x = 1.33 mol), however, a hexagonal phase with d_{100} = 5.13 nm was obtained [Fig. 1(*b*)]. The formation of the lamellar and

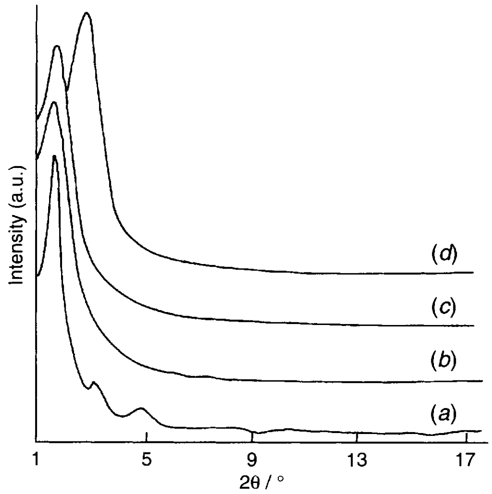

Fig. 1 XRD patterns of the mesophases of silica: (*a*) obtained with hexadecylamine (water content, x = 4.4 mol); (*b*) with hexadecylamine (water content, x = 1.33 mol); (*c*) hexagonal phase obtained by the calcination of (*a*), and (*d*) hexagonal phase obtained with octylamine

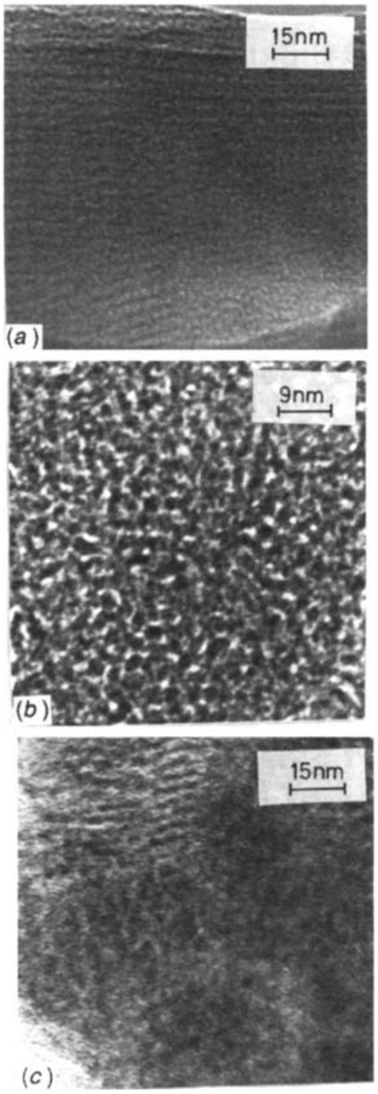

Fig. 2 TEM images of the mesophases of silica: (*a*) lamellar silica obtained with hexadecylamine (x = 4.4 mol); (*b*) hexagonal phase obtained with hexadecylamine (x = 1.33 mol) and (*c*) a mixture of the two phases during the lamellar–hexagonal transformation

hexagonal mesophases depending on the water content in the reaction mixture was verified by recording transmission electron microscope (TEM) images [see Fig. 2(*a*), (*b*)]. When octylamine was used as the surfactant, we obtained the hexagonal phase independent of the water content [see the XRD pattern in Fig. 1(*d*)]. The hexagonal structure was also confirmed by TEM images. The chain length of the amine, which determines the magnitude of the hydrophobic interaction, appears to be a crucial factor in determining the structure of the mesophase, the longer chain amines favouring the lamellar phase.

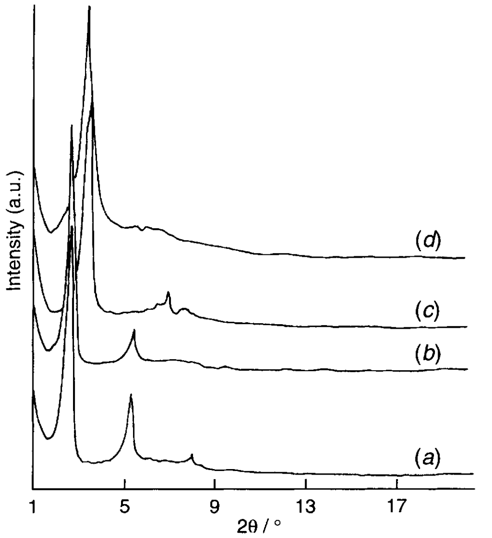

Fig. 3 XRD patterns of the mesophases of zirconia: (*a*) lamellar phase obtained with hexadecylamine; (*b*) lamellar phase obtained with dodecylamine; (*c*) lamellar phase obtained with octylamine (x = 1.5 mol) and (*d*) hexagonal phase obtained with octylamine (x = 0.6 mol)

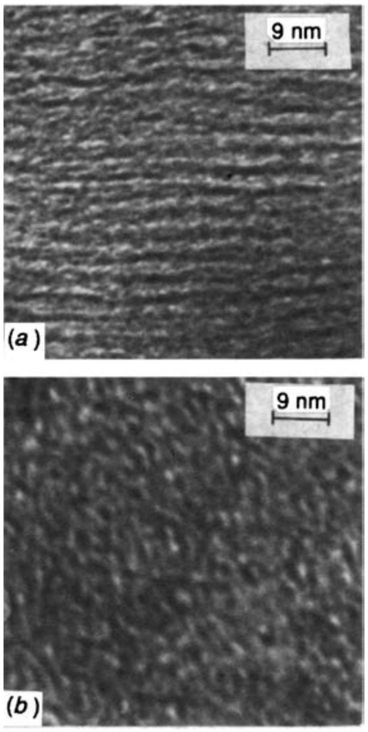

Fig. 4 TEM images of the mesophases of zirconia: (*a*) lamellar phase obtained with octylamine (x = 1.5 mol) and (*b*) hexagonal phase obtained with octylamine (x = 0.6 mol)

We have examined the lamellar phases obtained with the longer chain amines in some detail. The amines can be removed from the interlamellar space by calcination or by extraction with ethanol. To our surprise, the product after the removal of the amine had the hexagonal structure as found from the XRD pattern [Fig. 1(*c*)] and the TEM image. In Fig. 2(*c*), we show a TEM image recorded during the course of the thermal transformation of the lamellar phase to the hexagonal phase. The image shows features of both phases. The lamellar–hexagonal transformation of mesoporous silica in the solid state found here is indeed unique and should not be confused with the structural evolution found to accompany changes in pH or the surfactant : silica ratio.[1,2]

We have carried out similar experiments on the synthesis of mesoporous zirconia by the amine route. In a typical synthesis, $Zr(OPr^i)_4$ (0.01 mol) was added to a solution of the amine (0.01 mol) in propan-1-ol (0.1 mol) to which $(NH_4)_2SO_4$ (0.12 mol) and water (x mol) were added under stirring. The pH of the gel was adjusted to 1.5–2.0 by using dilute HCl. The gel was subjected to hydrothermal treatment at 373 K for 20 h, filtered and washed with acetone. With hexadecylamine, we obtained the lamellar phase of ZrO_2 independent of the water content (x = 1–2 mol). We show a typical XRD pattern in Fig. 3(*a*) with d values of 3.44, 1.71 and 1.13 nm due to the 001, 002 and 003 reflections. A lamellar phase was obtained with dodecylamine as well [Fig. 3(*b*)] with d values of 3.3 and 1.66 nm due to the 001 and 002 reflections. When octylamine was used as the surfactant with x = 1.5 mol, we obtained a lamellar phase (probably in a mixture with a small proportion of the hexagonal phase), as can be seen from the XRD pattern [Fig. 3(*c*)] with d values of 2.55 and 1.28 nm for the 001 and 002 reflections. The TEM image shows essentially the lamellar phase with a layer separation of 2.6 nm [Fig. 4(*a*)]. By reducing the water content in the reaction mixture (x = 0.6 mol), we obtained the hexagonal phase of ZrO_2 with d_{100} = 2.65 nm in the XRD pattern [Fig. 3(*d*)]. The TEM image also bears evidence for the hexagonal structure [Fig. 4(*b*]. This preparation of the hexagonal mesophase of ZrO_2 is an alternative to the methods reported recently in the literature.[6,7] More importantly, we have found that the lamellar phase obtained with octylamine transforms into the hexagonal phase on removal of the amine.

References

1 A. Monnier, F. Schuth, Q. Huo, D. Kumar, D. Margolese, R. S. Maxwell, G. D. Stucky, M. Krishnamurthy, P. Petroff, A. Firouzi, M. Janicke and B. F. Chmelka, *Science*, 1993, **261**, 1299.
2 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. L. Schlenker, D. H. Olson and E. W. Sheppard, *Chem. Mater.*, 1994, **6**, 2317.
3 P. T. Tanev and T. J. Pinnavaia, *Science*, 1995, **267**, 365.
4 P. T. Tanev and T. J. Pinnavaia, *Science*, 1996, **271**, 1267.
5 A. Matijasic, A.-C. Voegtlin, J. Patarin, J. L. Guth and L. Huve, *Chem. Commun.*, 1996, 1123.
6 J. A. Knowles and M. J. Hudson, *J. Chem. Soc., Chem. Commun.*, 1995, 2083.
7 U. Ciesla, S. Schacht, G. D. Stucky, K. K. Unger and F. Schuth, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 541.

Received, 9th July 1996; Com. 6/04814E