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Phase transformations of mesoporous zirconia

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The kinetics of the lamellar→hexagonal→cubic transformations of mesoporous zirconia prepared by using a neutral organic amine as the amphiphile have been studied in phosphoric acid medium. The lamellar→hexagonal transformation is preceded by a loss of the template molecules and the hexagonal→cubic transformation proceeds only when the lamellar form has entirely transformed to the hexagonal phase. The kinetics of the thermal transformation of lamellar zirconia to the hexagonal form have also been examined; this transformation also occurs and is accompanied by a loss of template molecules. Accordingly, the activation energy of the transformation is comparable to the hydrogen bond energy between the amine and the oxo–zirconium species. The phase transformations of mesoporous zirconia can be understood in terms of minimum energy surfaces.

Mesoporous solids are generally prepared by making use of self-assembled ordered aggregates of surfactants as templates, thus rendering the structures exhibited by the mesoporous solids to be similar to those of the self-assembled[1–3] surfactants. Accordingly, mesoporous solids occur in lamellar, hexagonal and cubic forms, just as the surfactant aggregates. Phase transitions among these forms occur in mesoporous materials in the solution phase. For example, changing the pH of the medium or ageing, leads to transformation of the lamellar phase of silica to the hexagonal phase.[4] Lamellar, hexagonal and cubic forms of aluminoborates have been prepared by changing the pH.[5] Other factors such as temperature, presence of counter ions and concentration of the surfactant also affect the phase transitions.[4–10] The phase transitions in mesoporous solids bear some similarity to those in surfactant assemblies.

In surfactant systems, decreasing the concentration of the surfactant instantaneously transforms the lamellar phase to the hexagonal phase.[11,12] The transitions in the surfactant self-assemblies are commonly understood in terms of the surface/interface energies of the ordered aggregates.[13] The effect of ageing on the lamellar to hexagonal phase transformation in mesoporous silica has been related to the extent of polymerization of the silica framework and the balancing of charges.[4] High pH and a low degree of polymerization favour the lamellar phase whereas low pH and highly condensed silica favour the hexagonal phase of silica.[4] The transformation from the hexagonal to the cubic phase in silica has been explained in terms of the formation of a periodic minimal surface governed by a competition between the curvature and packing and the transformation is associated with kinetic barriers.[14] Since there is limited quantitative information on the nature of the phase transitions in mesoporous solids in the literature, we considered it important to investigate the transitions in some detail. For this purpose, we have chosen to investigate mesoporous zirconia which exhibits interesting phase transitions both in solution and in the solid state. Here, we report the results of a kinetic study of the lamellar→hexagonal→cubic transitions of mesoporous zirconia in the presence of phosphoric acid and of the thermal lamellar → hexagonal transition of zirconia in the solid state.

Experimental

The lamellar form of mesoporous zirconium oxide was prepared using dodecylamine (DA) as the surfactant. In a typical synthesis zirconium isopropoxide (0.01 mol) was added to a solution of the dodecylamine (DA) (0.03 mol) in propan-l-ol (0.1 mol) to which ammonium sulfate (0.12 mol) was added under stirring. The pH of the gel was adjusted to 1.5–2.0 by using dilute hydrochloric acid (HCl). The gel was subjected to hydrothermal treatment at 373 K for 20 h, filtered, washed with acetone and dried at 373 K for 2 h. The lamellar nature of the product was verified by X-ray diffraction (XRD) and transmission electron microscopy (TEM). To study the transformation of lamellar ZrO_2 in solution phase, *ca.* 100 mg of the as-synthesized sample was added to 50 ml of 0.87 M phosphoric acid and stirred for different times, filtered, washed with water, acetone and dried at ambient temperature. XRD patterns and TEM images of the samples were recorded for each time.

The kinetics of the lamellar→hexagonal→cubic transition of zirconia in phosphoric acid solution was studied as follows. The (100) reflection of the lamellar and hexagonal phases differ both in intensity and position. Thus, as the lamellar phase ($d_{100} = 3.34$ nm) transforms to the hexagonal phase the intensity of the (100) reflection decreases until it attains a much smaller value, characteristic of that of a disordered hexagonal mesophase (Fig. 1). In addition, the *d*-spacing of the (100) reflection decreases until it reaches a minimum value after the transformation to the hexagonal phase is complete. The intensities of the (200) and (300) reflections of the lamellar phase also decrease continuously with time, as the lamellar→hexagonal transformation proceeds. We have employed both the intensity and position of the (100) reflection to follow the kinetics of the lamellar–hexagonal transformation. These two measurements give slightly different estimates of the phase compositions and we have taken the average value in the kinetic study. The hexagonal to cubic transformation of mesoporous zirconia was followed by the increase in the intensity of the (220) reflection of the cubic phase with time (Fig. 1).

The lamellar→hexagonal thermal transformation of mesoporous zirconia in the solid state was studied by heating the lamellar form at a fixed temperature for different periods of time. The phase composition of the sample subjected to heat treatment was estimated on the basis of the intensity of the (100) reflection, the *d*-spacing showing only small changes in the thermal transformation (Fig. 2). The kinetics of the transformation was studied as a function of time at 373, 403 and 413 K. The transformation was also studied by heating the lamellar sample for a fixed period of 2 h at different temperatures in the range 360–430 K.

Results and Discussion

The lamellar form of mesoporous zirconia, on contact with 0.87 M phosphoric acid, first transforms to the hexagonal form.

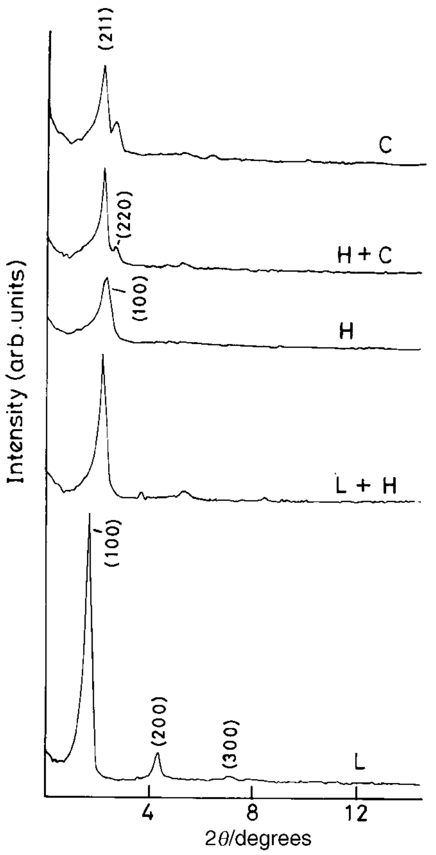

Fig. 1 XRD patterns showing the transformation of lamellar (L) zirconia to hexagonal (H) and then cubic (C) phases in phosphoric acid solution. Intermediate stages during the L–H and H–C transformations are shown.

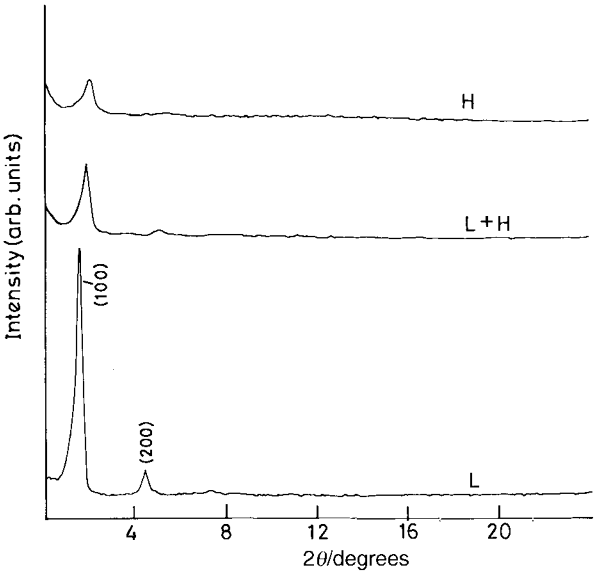

Fig. 2 XRD patterns showing the thermal transformation of lamellar (L) zirconia to the hexagonal (H) form. An intermediate stage during the transformation is shown.

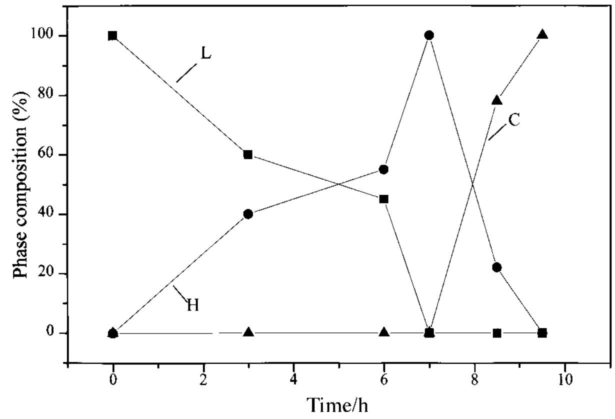

Fig. 3 Time variation in the phase composition of zirconia in phosphoric acid solution; L, lamellar; H, hexagonal; C, cubic

This transformation is complete in 7 h. We have followed the lamellar→hexagonal transformation as a function of time. Fig. 3 shows the progress of the lamellar→hexagonal transformation by plotting the percentages of the lamellar and hexagonal phases *vs.* time. We see that the proportion of the lamellar form decreases while that of the hexagonal form increases. It is noteworthy that the transformation of the hexagonal form to the cubic form starts only after the lamellar phase has completely transformed to the hexagonal phase. The hexagonal to cubic transformation occurs over a short time (<3 h).

The lamellar→hexagonal transformation of ZrO_2 is likely to be initiated first by the removal of some of the surfactant species, followed by the curling of the surfactant bilayer in order to minimize the surface/interface energy as shown in Fig. 4(a) and (b).[13,15] The curled bilayers transform to cylindrical rods to further minimize the surface energy as shown in Fig. 4(c) and the cylindrical rods assemble to give the ordered hexagonal structure shown in Fig. 4(d). In order to examine

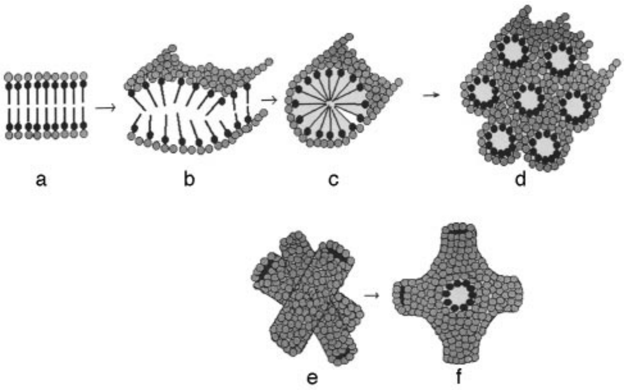

Fig. 4 Schematic representation of lamellar→hexagonal phase transformation (a through d) and the hexagonal→cubic transformation (e and f). The shaded circles around the surfactant aggregates represent the inorganic species (generally metal alkoxides or other metal–oxo species).

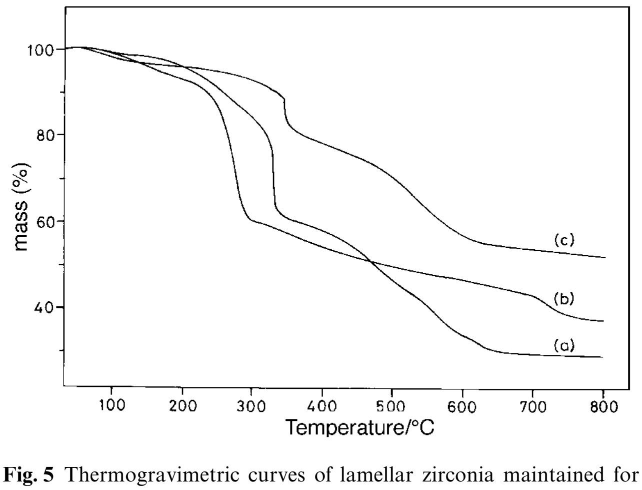

Fig. 5 Thermogravimetric curves of lamellar zirconia maintained for different periods in phosphoric acid solution: (a) as-prepared lamellar zirconia, (b) after 3 h and (c) after 7 h

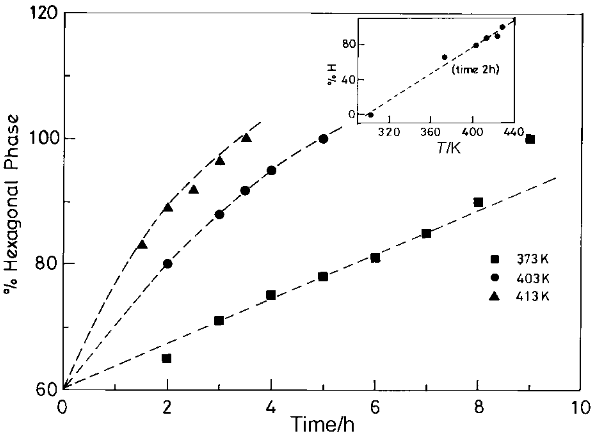

Fig. 6 Kinetics of the lamellar to hexagonal transformation of zirconia at different temperatures. Inset shows the temperature variation of the percentage of the hexagonal (H) phase in a fixed period of 2 h.

whether the loss of the surfactant species precedes the lamellar→hexagonal transformation, we have carried out thermogravimetric analysis (TGA) studies. We find that there is a significant loss of the surfactant in the lamellar→hexagonal→cubic transformation in phosphoric acid solution.

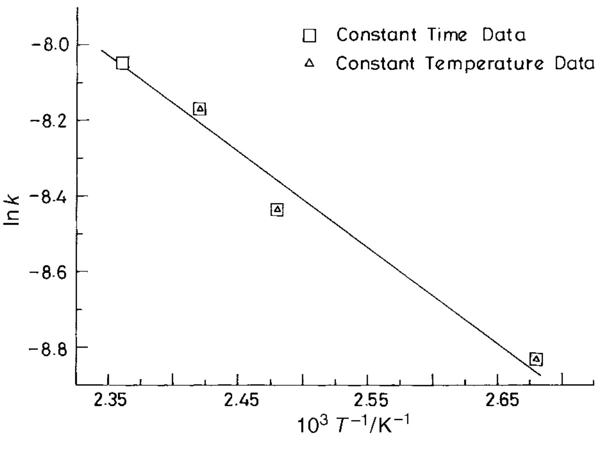

Fig. 7 Arrhenius plots of the kinetic data of the lamellar→hexagonal transformation of zirconia in the solid state

TGA of the lamellar zirconia [Fig. 5(a)] shows a marked mass loss at around 593 K and gradual loss of mass from 593 to 973 K. There is negligible loss of mass below 430 K due to water and other species. The mass loss at 593 K and above appears to be entirely due to the loss of the surfactant. The lamellar ZrO$_2$ sample treated for 3 h in phosphoric acid [Fig. 5(b)] showed a sharp mass loss around 543 K, followed by a gradual loss up to 973 K. Since the entire mass loss is only due to the surfactant, we can take the difference in the mass loss, say at 973 K, between the curves Fig. 5(a) and (b) as equal to the amount of the surfactant lost by phosphoric acid treatment. We see that around 8% of the surfactant is lost after 3 h of treatment. The ZrO$_2$ sample treated in phosphoric acid for 7 h was entirely hexagonal and showed a sharp mass loss around 613 K and a gradual loss thereafter, up to 973 K [Fig. 5(c)]. The difference between curves Fig. 5(a) and (c) shows that 23% of the surfactant has been removed after 7 h of treatment. Phosphoric acid treatment for 9.5 h gave the cubic phase, and *ca.* 30% of the template had been removed at this stage. The TGA studies suggest that the loss of the surfactant is a necessary initial step in the lamellar→hexagonal transformation.

The transformation from the hexagonal to the cubic phase is driven by the tendency of the cylindrical rods of the hexagonal phase to minimize their energy by forming a three-dimensional network of rods, forming bicontinuous cubic phases as shown in Fig. 4(e) and (f). The cubic phase can be described using the concept of periodic minimal surface,[15,16] with the space groups $Pn3m$, $Pm3n$, $P4_332$, $Im3m$, $Ia3d$ or $Fd3m$.[16] The XRD pattern of the cubic phase obtained after the complete transformation of the hexagonal ZrO$_2$ phase in phosphoric acid, appears to be consistent with the space group $Ia3d$.

The thermal transformation of the lamellar form of mesoporous ZrO$_2$ to the hexagonal form occurs in the solid state. Thus, on heating at 428 K for 2 h, the lamellar phase completely transforms to the hexagonal phase. We have followed the kinetics of the lamellar→hexagonal transformation at three fixed temperatures. Fig. 6 shows the kinetics of the lamellar→hexagonal transformation at different temperatures. We have also examined the kinetics of this transformation by heating lamellar zirconia at different temperatures for a fixed time of 2 h. The inset of Fig. 6 shows how the proportion of the hexagonal form increases with temperature at a given time (2 h). We were able to fit these kinetic data to a first order

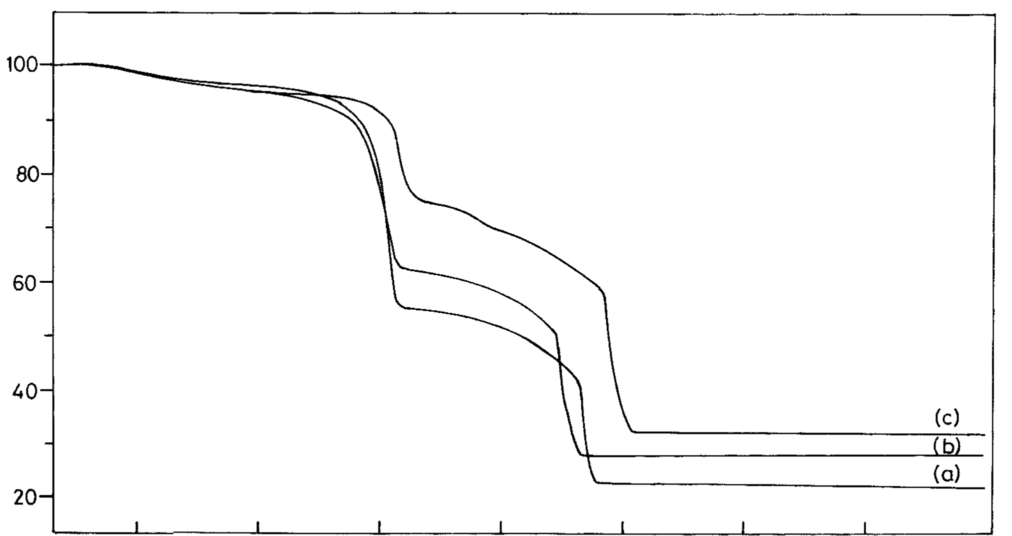

Fig. 8 Thermogravimetric curves of lamellar form heated at different temperatures: (a) as-prepared lamellar zirconia, (b) 403 K, 2 h and (c) 428 K, 2 h.

rate equation. The rate data follow the Arrhenius equation as shown in Fig. 7. The data give an activation energy of *ca.* 22 kJ mol^{-1} for the lamellar→hexagonal transformation in the solid state. This value of the activation energy is comparable to the energy of a medium strength hydrogen bond. This is understandable since the removal of surfactant molecules from the lamellar phase is necessary for the transformation to occur. The surfactants interact with the oxo–zirconium species primarily through hydrogen bonding.

TGA studies show that on heating the lamellar phase to 403 K for 2 h, around 6% of the surfactant is lost (Fig. 8). On heating to 428 K the sample loses 11% of the surfactant. These data demonstrate that during the thermal transformation of the lamellar phase to the hexagonal phase, the amine template is partially removed, leading to the reorganization of the self-assembled surfactant aggregate. The magnitude of the loss of the surfactant in the thermal transformation is somewhat smaller than that accompanying in the transformation in phosphoric acid solution.

In conclusion, the present study of the kinetics of the lamellar to hexagonal transformation of mesoporous zirconia shows that a loss of surfactant molecules accompanies the transformation. Transformation to the cubic form seems to require that all the starting material be in the hexagonal form. The thermally induced lamellar→hexagonal transformation is associated with an activation energy comparable to the hydrogen bond energy.

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