In-situ small angle X-ray scattering (SAXS) studies on the formation of mesostructured aluminophosphate / surfactant composite materials

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Mesostructured aluminophosphate / surfactant composite materials were prepared from aqueous and alcoholic systems. Syntheses in ethanol or methanol, respectively, lead to mixtures of two nanostructured phases. One of these consists of hexagonally arranged rod-like assemblies of the surfactant molecules with the head groups located in the centres, encapsulating the inorganic aluminophosphate; the other is lamellar. The syntheses were monitored by *in-situ* temperature- and time-resolved small angle X-ray scattering (SAXS).

1. INTRODUCTION

Over the last years the utilisation of supramolecular arrays of surfactant molecules as structure-directing templates [1] has been applied to the synthesis of numerous mesostructured aluminophosphates [2-11]. In most cases the preparations were carried out in aqueous systems under hydrothermal conditions, but tetraethylene glycol and/or unbranched primary alcohols were also used [2,4]. Several discussions have been made on the reaction mechanisms that are involved in the syntheses of mesostructured materials [1,12-15] and recently a number of *in-situ* investigations on the formation processes of mesostructured silica phases in aqueous media have been reported; these studies employed small angle X-ray diffraction [16-19] as well as ^2H, ^{13}C, ^{29}Si, and ^{81}Br NMR spectroscopy and polarised light optical microscopy [17].

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2. EXPERIMENTAL SECTION

For the synthesis of aluminophosphate / surfactant composite materials a mixture of mono-dodecyl phosphate surfactant ($C_{12}PO_4$) and the respective solvent was homogenised by stirring at room temperature (ethanol, methanol) or 50°C (water), respectively. Equal amounts of aluminium triisopropoxide ($Al[O^iPr]_3$) and phosphoric acid (H_3PO_4) were then added at room temperature followed by 10 minutes stirring. (In a typical synthesis the molar composition of the reaction mixture was $C_{12}PO_4$ / $Al(O^iPr)_3$ / H_3PO_4 / solvent = 1 / 1 / 1 / 50.) The mixture was kept for 24 hours at the desired reaction temperature in closed glass tubes or teflon-lined autoclaves, respectively. The solid products were filtered off, washed with ethanol, and dried under vacuum. Powder X-ray diffraction was performed on a Philips PW 1050/25 diffractometer (Cu-Kα radiation).

Temperature- and time-resolved small angle X-ray scattering (SAXS) investigations were carried out at the European Molecular Biology Laboratory (EMBL), Outstation at Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany, beamline X 13. The samples were placed in the X-ray beam in flame sealed glass capillaries of 1 mm diameter. The temperature was controlled by a circulating water bath at a heating rate of 5 °C per minute; the samples were kept at the desired temperature for 3 minutes before the data were taken. Diffraction patterns were recorded with a 1024 channel linear detector (4 minutes data collection for each pattern). Data processing was carried out with OTOKO software [20]; diffraction peak positions were calibrated against silver behenate (d_{001} = 5.8380(3) nm) [21]. Investigations on samples with the inorganic species present were carried out within 5 - 10 minutes after the addition of $Al[O^iPr]_3$ and H_3PO_4 to the surfactant / solvent mixture.

3. RESULTS AND DISCUSSION

The utilisation of dodecyl phosphate as a structure-directing template in the synthesis of mesostructured aluminophosphate materials in aqueous systems yields lamellar products over a large surfactant concentration region [9]. Varying the synthesis time and/or temperature does not affect this structure, although the degree of order in the products increases with longer synthesis times (within the region from 12 to 72 hours) or when the temperature is raised (between 20 and 120 °C). The powder XRD diagram of an example product synthesised in water (30 % w/w surfactant) at 120 °C (24 hours) is shown in Figure 1a; the d_{001} value is 3.47 nm.

A similar though considerably less well-ordered lamellar product is obtained when ethanol or methanol are used instead of water under solvothermal conditions; Figure 1b shows the powder XRD diagram of a sample prepared in ethanol at 90 °C (d_{001} = 3.50 nm). Considerably different products, however, are obtained when alcohols are used at lower temperatures, i.e. under non-solvothermal conditions. Figures 1c and 1d show the diffraction patterns of two example products from syntheses in methanol at 25 °C and in ethanol at 10 °C, respectively. In both cases the XRD reflections can be attributed to two distinct phases. One of these has a hexagonal symmetry with a d_{100} value of 1.88 nm; this mesophase will be discussed in detail below. An additional broad reflection is found at a Bragg angle comparable to that of the 001

reflection of the lamellar product from the solvothermal synthesis ($d = 3.35$ nm for the methanol synthesis and 3.65 nm for ethanol, respectively). In these two diffraction patterns no further reflections of this second mesophase can be identified. Taking into account, however, that the second and third order reflections of the lamellar product from the solvothermal synthesis in ethanol are relatively weak, it may be assumed that this phase is also lamellar and that the higher order reflections are too weak to be detected, especially as the 002 reflection is then hidden by the 100 reflection of the hexagonal phase. The lamellar structure of this mesophase is also suggested by transmission electron microscopic investigations; further indications will result from the SAXS investigations (see below).

The relative amounts in which these two phases are formed are highly dependent on the synthesis conditions, particularly on the temperature. The phase with the single broad reflection becomes increasingly dominant when the temperature is raised; Figure 2 shows the powder XRD diagrams of four products synthesised in ethanol at different non-solvothermal temperatures (16 hours reaction time). A similar effect is found when the synthesis time is varied; longer reactions favour the formation of the (supposedly) lamellar phase in the final product.
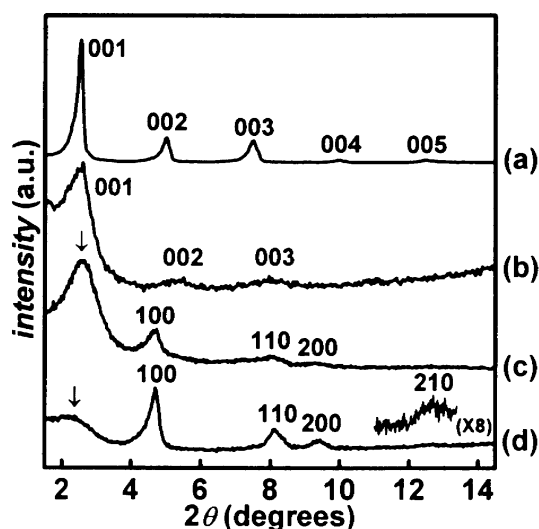

Figure 1. Powder XRD diagrams of mesostructured aluminophosphate / surfactant composite materials prepared in: (a) water (120°C), (b) ethanol (90°C), (c) methanol (25°C), (d) ethanol (10°C). Lamellar and hexagonal phases are indexed; "↓" corresponds to a phase with presumably lamellar structure.
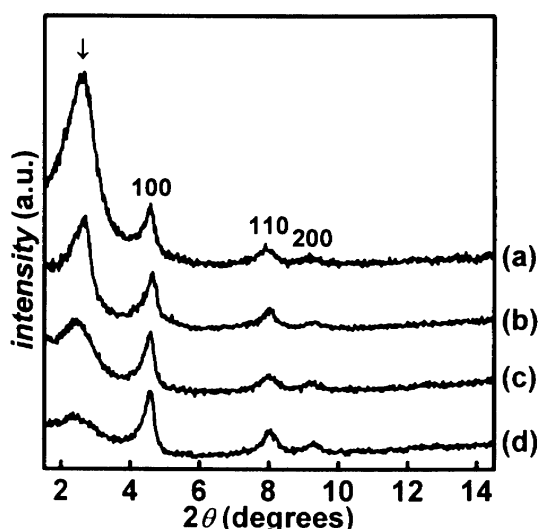
Figure 2. Powder XRD diagrams of mesostructured aluminophosphate / surfactant composite materials prepared in ethanol at various temperatures: (a) 60°C, (b) 40°C, (c) 25°C, (d) 10°C. A hexagonal phase is indexed; "↓" corresponds to a phase with presumably lamellar structure.

The characterisation of the hexagonal mesophase (i.e. of the samples with low amounts of the other phase) reveals a number of significant properties: (i) The d_{100} value is remarkably low (1.88 nm), which is not consistent with the usual hexagonal arrangement of rod-like

surfactant assemblies within an inorganic network, in which the hydrocarbon chains are inside the rods and the polar head groups are facing outwards (see Figure 3a). The d spacing of such an arrangement is expected to be considerably larger (between 3 and 4 nm, as typical of mesostructured hexagonal phases prepared with C_{12} surfactants), corresponding approximately to the double length of the surfactant molecules plus the aluminophosphate layer between two adjacent surfactant rods. (ii) The samples are extremely unstable towards heat; at temperatures around $ca.$ 40 °C the solid products will transform into single lamellar phases, as was confirmed by calorimetric investigations (not discussed here). (iii) The organic fraction in the composites is remarkably high; according to thermal investigations and elemental analysis (C, H, Al, P) the samples consist of up to 80 % (weight) carbon. (iv) Any attempts to remove the surfactant without collapse of the structure (e.g. by solvent extraction) in order to obtain a porous aluminophosphate network have failed. For these reasons it is suggested that the hexagonal mesophase has a structure as schematically displayed in Figure 3b: The surfactant chains are arranged around individual aluminophosphate domains, that are not connected with each other; the hydrophobic surfactant chains are turned outside. In these rod-like assemblies, i.e. inverse surfactant micelles with the inorganic part encapsulated in the cores, there is more space available to each individual hydrophobic surfactant chain than in the non-inverse structure, leading to a reduced radial extension. Also, the micelles may be interpenetrating each other. These two aspects are possible explanations for the low d_{100} value. This structure model also accounts for the poor thermal stability and the high relative amounts of the organic component. Nanostructured materials with this type of inverse arrangement have been reported for metal chalcogenides [22], but so far no aluminophosphates with a similar structure have been observed.
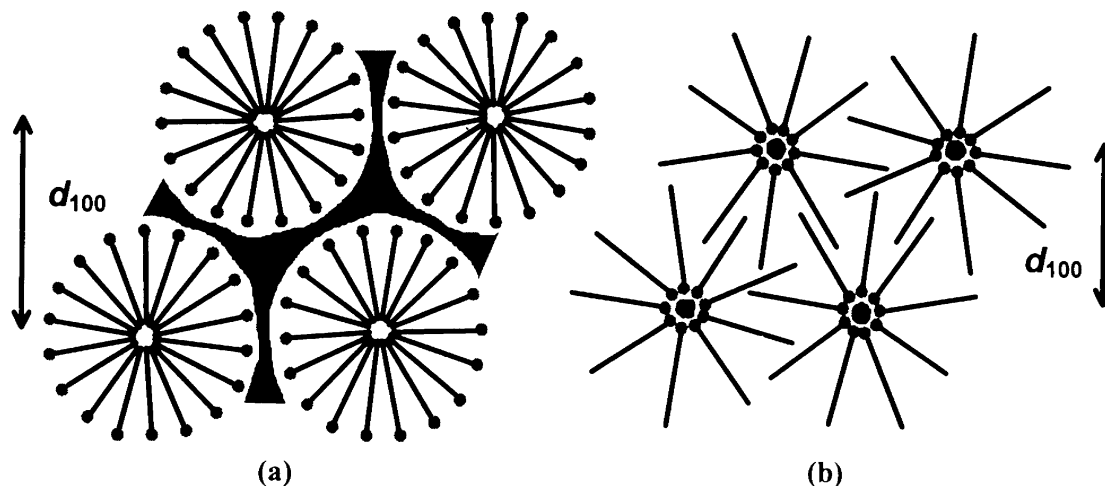

(a)   (b)

Figure 3. Schematic representation of two different hexagonal arrangements in mesostructured inorganic / surfactant composites; the hydrophobic chains are drawn as straight lines for simplicity. (a) The normal structure with a fully-connected inorganic network (dark area). (b) Inverse surfactant assemblies with single domains of the inorganic material enclosed in the centres. In the latter case the hydrophobic surfactant chains are allowed more space for their distribution, leading to a smaller d spacing. In this picture they are also interpenetrating each other.

In order to further investigate the effects of the synthesis conditions on the structures and compositions of the products small angle X-ray scattering (SAXS) studies were carried out. Figure 4 shows the SAXS diagrams of the pure dodecyl phosphate / water system (30 % w/w surfactant) without the inorganic components at variable temperatures. In all of the following temperature-resolved SAXS investigations the time between two successive measurements was 11 minutes (4 min. heating, 3 min. temperature equilibration, and 4 min. data collection; see experimental section). The surfactant / water system is a lyotropic phase with a lamellar structure over the entire temperature region from 20 to 100 °C; this is also confirmed by polarised light optical microscopy. The d_{001} value is 9.83 nm at 20 °C and becomes slightly smaller upon increase of the temperature (9.02 nm at 100 °C); this is caused by a shrinkage of the surfactant bilayers due to a stronger brownian lateral oscillation of the hydrophobic surfactant chains. In general, the interlamellar distance of such a phase depends on the surfactant concentration, i.e. the relative amount of water between two adjacent bilayers [23].
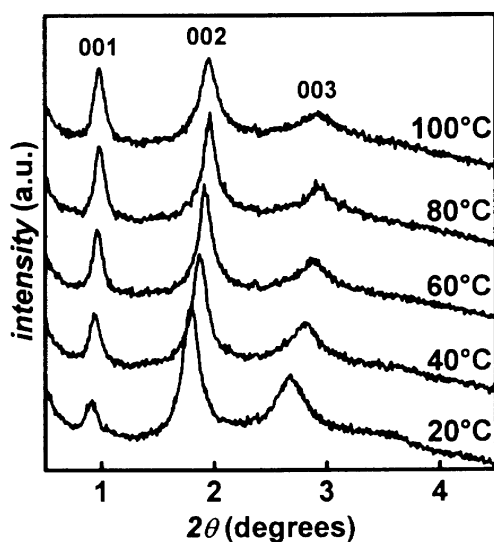

Figure 4. Thermal evolution of the SAXS patterns of the system $C_{12}PO_4$ / water (30/70 w/w). The lamellar lyotropic phase is indexed; d_{001} = 9.83 nm (20°C).
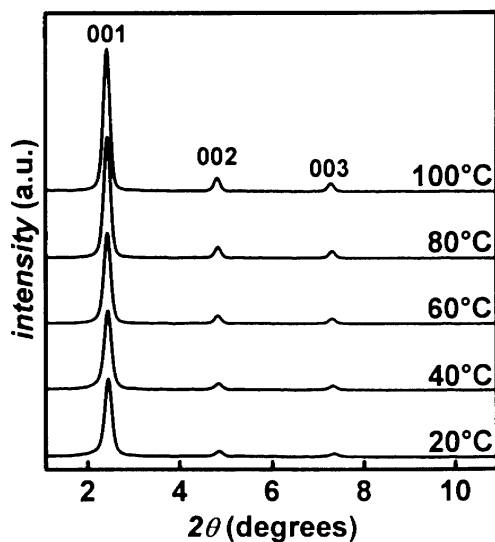
Figure 5. Thermal evolution of the SAXS patterns of the system $C_{12}PO_4$ / water (30/70 w/w) / Al[O'Pr]$_3$ / H$_3$PO$_4$. (Freshly prepared; equal molar amounts of $C_{12}PO_4$, Al[O'Pr]$_3$, and H$_3$PO$_4$). The lamellar mesophase is indexed; d_{001} = 3.61 nm.

Figure 5 shows the respective SAXS patterns of the $C_{12}PO_4$ / water system immediately after the addition of Al[O'Pr]$_3$ and H$_3$PO$_4$; this mesophase is also lamellar. The intensity of the peaks, i.e. the degree of order in the structure, increases with higher temperatures. Note that these SAXS patterns were recorded within a few minutes after the addition of the inorganic components. At this time the condensation of the reactants and thus the formation of a solid network, which usually requires several hours, is by far not completed yet; at this stage of the reaction no structured materials can be isolated. Nevertheless the d_{001} value remains constant over the entire temperature region, which suggests that there is already a weak connection

between the inorganic building units which prevents a shift of the reflections at higher temperatures through increased thermal movement (see next paragraph). It should also be pointed out that as soon as the inorganic reactants are added the d_{001} value is diminished to 3.61 nm, approximately the same as that of the final solid product synthesised from the same system (see Figure 1a), which means that most of the water is immediately removed from the regions between the surfactant bilayers.

A different situation is found for the alcoholic systems. Here the pure surfactant / alcohol solutions are optically isotropic, as detected by polarised light optical microscopy; these samples do not show any SAXS reflections. However, after the addition of $Al[O^iPr]_3$ and H_3PO_4 the reflections of two mesostructured phases emerge immediately. Figure 6 displays the SAXS patterns of a sample with 20 % w/w surfactant in ethanol. Similarly as for the aqueous sample, these SAXS patterns resemble the powder XRD diagram of the respective final solid product (see Figure 1d). The 003 reflection of the lamellar phase can clearly be identified whereas the 002 reflection is hidden by the 100 reflection of the hexagonal phase. This sample significantly changes with temperature; the relative intensity of the lamellar reflections grows with respect to that of the reflections of the hexagonal phase. This is consistent with the respective relative compositions of solid samples prepared at different reaction temperatures (see Figure 2).
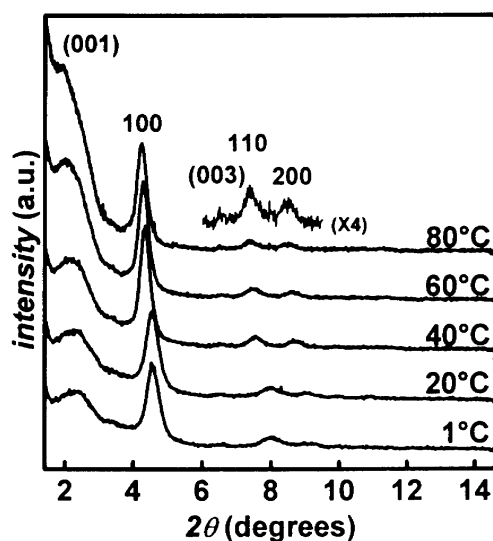

Figure 6. Thermal evolution of the SAXS patterns of the system $C_{12}PO_4$ / ethanol (20/80 w/w) / $Al[O^iPr]_3$ / H_3PO_4. (Freshly prepared; equal molar amounts of $C_{12}PO_4$, $Al[O^iPr]_3$, and H_3PO_4). The hexagonal phase and the lamellar phase (in brackets) are indexed.
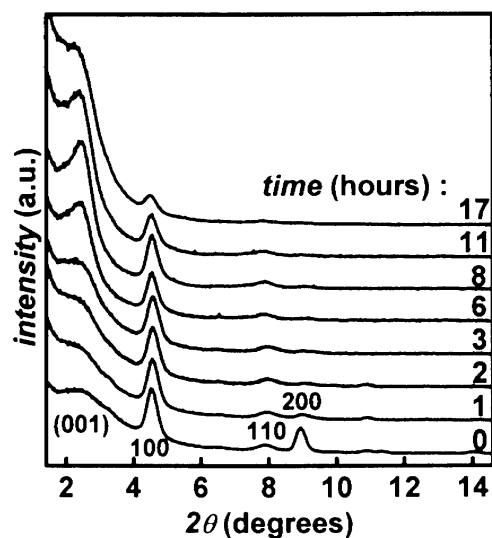
Figure 7. Time evolution of the SAXS patterns of the system $C_{12}PO_4$/ ethanol (20/80 w/w) / $Al[O^iPr]_3$ / H_3PO_4 at 20 °C. (Equal molar amounts of $C_{12}PO_4$, $Al[O^iPr]_3$, and H_3PO_4). The hexagonal phase and the lamellar phase (in brackets) are indexed.

With increasing temperature the reflections of both the hexagonal and the lamellar phase shift towards lower Bragg angles; the d_{100} value of the hexagonal phase changes from

1.94 nm (at 1 °C) to 2.08 nm (at 80 °C) and the d_{001} value of the lamellar phase from 3.84 to 4.30 nm. This is presumably caused by an increased thermal movement of the inorganic species and was not observed in the respective aqueous system (see paragraph above). In ethanol the degree of condensation of the inorganic reactants into a rigid network after these few minutes is obviously much lower than in water, which is to be expected in the light of a much slower hydrolysis of $Al[O^iPr]_3$ in alcohols than in water.

It is also possible to monitor the effect of the reaction time on the final mesostructured samples by *in-situ* SAXS. Figure 7 shows the time-resolved diffraction patterns of a 20 % w/w sample in ethanol at room temperature. The 001 reflection of the lamellar phase becomes more dominant in the course of time. Again, this is consistent with the relative compositions of the final mesostructured samples obtained from syntheses employing different reaction times.

In conclusion, the synthesis of mesostructured aluminophosphate / surfactant materials in alcoholic systems yields a mixture of an inverse hexagonal and a lamellar phase, the latter of which is more stable, as its formation is relatively favoured by higher temperatures and/or longer reaction times. The synthesis is highly cooperative; the surfactant / alcohol systems without the inorganic species do not show any lyotropic behaviour.

4. ACKNOWLEDGEMENTS

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23. Detailed SAXS investigations on the dodecyl phosphate / water system are to be published.