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Novel synthetic pathways to layered iron(hydro)oxyhydroxide–surfactant composites

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Mesostructured lamellar iron(hydro)oxyhydroxide–surfactant composites have been prepared using novel synthetic methods based on the hydrolysis chemistry of Fe^{III}. By carefully adjusting the reaction conditions, composites with inorganic walls from *ca.* 19–26 Å can be synthesised in a controllable manner.

The discovery of mesoporous materials[1,2] with pore openings in the range from 20–100 Å has opened the way to a new class of inorganic oxides with a wide potential for applications in gas separation, sorption and catalysis. Generally, the synthesis involves the cooperative assembly of surfactant molecules with hydrolysable inorganic precursors into a mesostructured precipitate. By varying the surfactant head group, the kind of precursor and other synthesis parameters like temperature, addition of an acid or base *etc*., the preparation of an amazing number of (metal) oxide–surfactant composites has been achieved.[3] Among these, materials with a lamellar structure have not attracted as much interest as their hexagonal or cubic variants. This is due to the fact that upon removal of the surfactant template, either by oxidative calcination or by extraction, the lamellar structure collapses and a dense phase is obtained. However, based on the special two-dimensional structure of the inorganic part, with nanometer-sized dimensions in one direction, layered metal oxide–surfactant composites should exhibit special magnetic and optical properties which differ from those of the corresponding bulk oxides. Therefore, they are attractive from both the theoretical and the application points of view. Recently, Tolbert *et al.*[4] have shown that the magnetic properties of composites based on surfactants carrying a sulfate group ($C_nH_{2n+1}SO_4^-$, $n=10$, 12, 14, 16, 18; in the following designated as C_nS^-) and inorganic walls of hydrated iron(hydro)oxyhydroxide species vary with the thickness of the inorganic part. Their synthetic method involves the oxidation of layered Fe^{II}–surfactant compounds with H_2O_2 resulting in layered Fe^{III}–surfactant compounds with a thickness of the inorganic layer of approximately 16.8 (for $C_{10}S^-$, $C_{12}S^-$, $C_{14}S^-$) or 11 Å ($C_{16}S^-$, $C_{18}S^-$), respectively. We will show that by using different novel synthetic approaches, the thickness of the inorganic part can be increased up to *ca.* 26.4 Å and that it can be controlled and varied nearly continuously in a broad range, from *ca.* 19.2 Å to that value. Unlike the method of Tolbert *et al.*[4] our synthetic procedures start with Fe^{3+}. All our materials are layered composites, their X-ray diffraction patterns showing mainly the d_{001} reflections.

The first two of our novel approaches involve control of the pH and ageing times. The general procedure starts with a 0.1 M solution of $FeCl_3$ which has a pH of 1.65. To 50 ml of this solution, different amounts (5, 8, or 11 ml) of a 2.5% ammonia solution were added. These solutions of the inorganic precursor are then aged under stirring for a certain period t_A. Afterwards, 10 ml of a 0.07 M solution of C_nS^- is added. The experiments with $C_{10}S^-$ and $C_{12}S^-$ were carried out at room temperature. Due to the lower solubilities of $C_{14}S^-$, $C_{16}S^-$ and $C_{18}S^-$ at room temperature, the corresponding experiments were carried out at 45, 52 and 62 °C, respectively. In all cases, a brown precipitate was formed immediately after the combination of the solutions.

To exemplify the influence of the pH we present the results obtained using different amounts of ammonia solution, but with a constant ageing time of 120 min. By the addition of 5, 8 or 11 ml of a 2.5% ammonia solution, the pH of the precursor solution was increased to 1.90, 2.00, or 2.13 Å, respectively, after 120 min of stirring. The solids isolated for the $C_{12}S^-$ composites [X-ray diffraction patterns in Fig. 1(*a*),(*b*)] have d_{001} spacings of 42.0, 45.7 and 45.9 Å, respectively. A comparison of the composites obtained with the different surfactants from $C_{10}S^-$ to $C_{18}S^-$ gives further information: straight line extrapolation of their d_{001} spacings *versus* n to $n=0$ allows a rough estimate of the thickness of the inorganic wall (shown in Fig. 2, for the synthesis carried out at pH 1.90). The results show that this thickness increases from 19.2 to 24.5 Å, when the amount of ammonia solution used is increased from 5 to 8 ml. A further increase to 11 ml results in materials with even thicker inorganic walls of *ca.* 26.4 Å (in agreement with elemental analysis showing an increasing Fe : C_nS^- ratio). The slopes

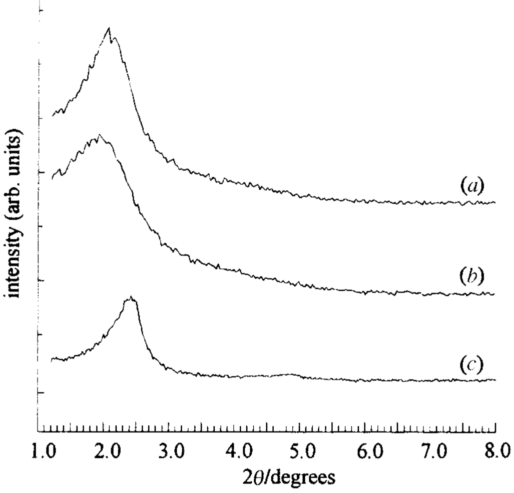

Fig. 1 Typical powder X-ray diffraction patterns (Cu-Kα radiation) of lamellar mesostructured iron(hydro)oxyhydroxide species obtained by (*a*) increasing the pH of a 0.1 M $FeCl_3$ solution with NH_3 to 1.90 and adding 10 ml of 0.07 M $C_{12}S^-$ solution after 120 min, (*b*) using the same method and concentrations as in (*a*) but at a pH of 2.13, and (*c*) by mixing 500 ml of a 0.01 M $FeCl_3$ solution with 100 ml of a 0.007 M $C_{12}S^-$ solution

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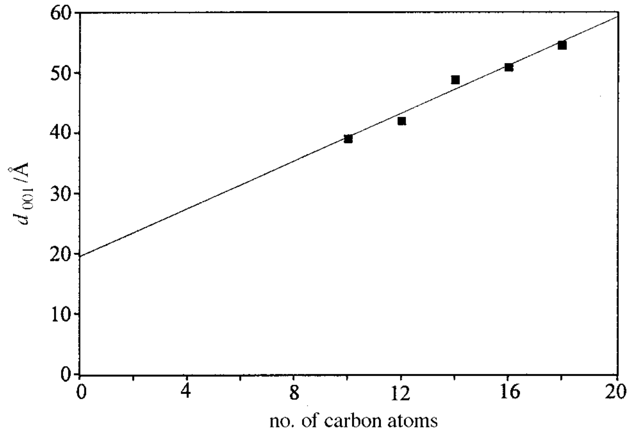

Fig. 2 Extrapolation of d_{001} spacings *versus* number of carbon atoms, showing an intercept of 19.2 Å and a slope of 1.99 Å per carbon atom (starting pH = 1.90)

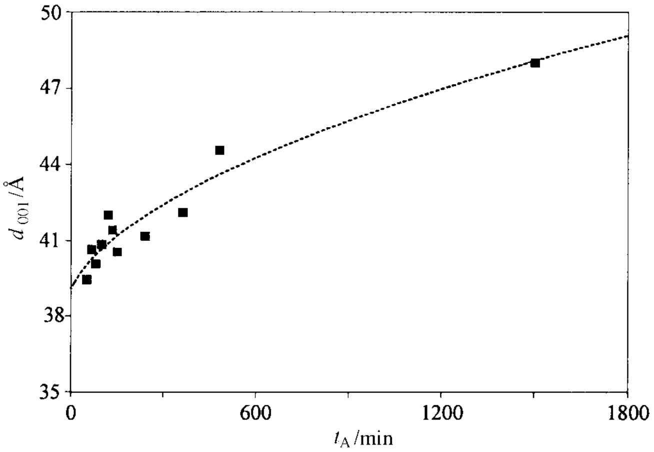

Fig. 3 Increase of the d_{001} spacing with ageing time of the precursor solution. The dotted line is a guide to the eye.

of the extrapolation lines are in all cases larger than 1.26 Å per carbon atom, indicating that the surfactants build up a tilted bilayer or a not fully interdigitated monolayer.

Fig. 3 exemplifies the influence of varying the ageing time t_A in the synthesis procedure described above (all these experiments were carried out with the addition of 5 ml of 2.5% ammonia solution). The layer spacing d_{001} increases with longer ageing times; for instance, $d_{001} = 39.4$ Å for $t_A = 50$ min and $d_{001} = 48.0$ Å for $t_A = 1500$ min.

Another synthesis also starts from Fe^{3+}, but uses highly diluted solutions. For example, adding 100 ml of a 0.007 M solution of $C_{12}S^-$ to 500 ml of a 0.01 M $FeCl_3$ solution results in the precipitation of a brown solid with a layer spacing of 34.8 Å [Fig. 1(*c*)].

The results can be explained on the basis of the hydrolytic chemistry of Fe^{III} solutions. Addition of a base or dilution forces deprotonation and hence hydrolysis:[6,7]

$$Fe(OH_2)_6^{3+} + H_2O \rightleftarrows Fe(OH)(OH_2)_5^{2+} + H_3O^+$$
$$Fe(OH)(OH_2)_5^{2+} + H_2O \rightleftarrows Fe(OH)_2(OH_2)_4^{+} + H_3O^+ \textit{ etc.}$$

In the case of a pure Fe^{III} solution, the low molecular weight species further condense to give species with higher nuclearity, *e.g.* the dimer,

$$2\,Fe(OH)(OH_2)_5^{2+} \rightleftarrows Fe_2(OH)_2(OH_2)_8^{4+} + 2H_2O$$

and finally a solid precipitate. Hence, we conclude that the condensation of low molecular weight precursors is the first step in the formation of the above described lamellar iron(hydro)oxyhydroxides species. Due to the low pH values, also after addition of ammonia, the rapid formation of bulk ironoxyhydroxide within 2 h is prevented. The condensation of the inorganic precursors into a two-dimensional array is only achieved in the second step by the addition of the surfactant solution. In terms of the cooperative templating mechanism proposed for the formation of mesostructured materials,[7,8] this involves the coordination of the negatively charged surfactants to the positively charged inorganic precursor molecules as an initiating reaction and the subsequent ordered self-assembly of these primary composites into solid lamellar composites. This model explains the increase in thickness of the inorganic layer with increasing pH and with increasing ageing time: both factors enhance the degree of condensation of the inorganic precursor species. Correspondingly, when the surfactant is added, larger inorganic precursors are taking part in the self-assembly process.

We have shown that novel synthetic methods allow the adjustment and variation of the thickness of iron(hydro)oxyhydroxide layers. With regard to the hydrolytic chemistry of transition metals, the outlined preparative routes should be applicable to the synthesis of similar metal oxyhydroxide–surfactant composites as well as to the synthesis of composites with a mixed-valence inorganic part.

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