ChemComm

Delamination of layered double hydroxides by use of surfactants

Mariko Adachi-Pagano, Claude Forano* and Jean-Pierre Besse

Laboratoire des Matériaux Inorganiques, CNRS ESA 6002, Université Blaise Pascal, 63177 Aubière Cedex, France. E-mail: forano@chimtp.univ-bpclermont.fr

Received (in Oxford, UK) 29th November 1999, Accepted 29th November 1999

Delamination of the layered double hydroxide structure $[Zn_2Al(OH)_6][C_{12}H_{25}SO_4{\cdot}nH_2O]$ was realized by dispersion in butanol; translucent colloidal solutions are stable for at least 8 months with oriented LDH materials with extended crystallite size being obtained; the results presented here suggest that total delamination occurs in the colloidal solution.

Delamination of low dimensional solids is of tremendous practical importance in applications ranging from polymer reenforcement,[1] self assembling monolayers (SAM) and Langmuir–Blodgett film preparation[2] or emulsion stabilizations.[3] Dispersions of clay minerals have been studied more extensively owing to their extended swelling properties and a great ability to undergo surface modification with organophilic cations.[4] Exfoliation of other layered structures such as MoS_2, layered phosphates and metal oxides have also been achieved by manipulation of the interlayer interactions.[5]

Layered double hydroxides (LDHs) are layered materials constituted by a stacking of positive hydroxylated layers $[M^{2+}{}_{1-x}M^{3+}{}_x(OH)_2]^{x+}$ separated by interlayered anionic species and water molecules $[X^{q-}{}_{x/q}{\cdot}nH_2O]$. They are known for their unique anion exchange properties and their rich chemistry which make them good catalysts or catalyst precursors.[6] However, the high charge density of the LDHs layers and the high content of anionic species and water molecules result in strong interlayer electrostatic interactions between the sheets and significantly hydrophilic properties. Such dense interlamellar hydrogen bonding networks lead to a tight stacking of the lamellae. The rigid spheroidal 'sand rose' morphology of intergrown platelets prevents both accessibility to the major part of the surface or exfoliation of the sheets in water or in any other non-aqueous solvents. However, exchange of inorganic anions by organophilic anions, such as fatty acid salts or anionic surfactants proceeds readily.[10] This leads to a substantial modification of the surface properties, from hydrophobic to hydrophilic. Moreover, the van der Waals interlayer interactions introduced by the introduction of such species weakens the stacking of the layers and favours interactions with non-aqueous solvents.

The purpose of this study was to develop a method of delamination of LDHs which will lead to a novel generation of LDH based materials in which the total surface of the layered compound will be rendered accessible for chemical reactivity or for the preparation of new porous or oriented materials. The delaminated structure of the $Zn_2Al(OH)_6Cl{\cdot}2H_2O$ LDH phase ([Zn–Al]) would reach a theoretical specific surface aera of 800 $m^2\ g^{-1}$, while the experimental BET measured surface areas reach only 10–50 $m^2\ g^{-1}$.

We have already reported the influence of organic solvents (ethanol, methanol, acetone, ethylene glycol, glycerol) on the modification of the surface and porosity properties of LDHs.[7] However, complete delamination of LDHs has, as yet not been reported. Now successful LDH delamination has been achieved using various anionic surfactants and we report, for the first time, stable colloidal solutions of LDHs. In this study, we demonstrate total delamination of the [Zn–Al] LDH using dodecyl sulfate (DS) as an anionic surfactant and butanol as the dispersant.

The $Zn_2Al(OH)_6Cl{\cdot}2H_2O$ LDH precursor ($[Zn_2Al–Cl]$) was prepared by the coprecipitation method previously described by Bonnet *et al.*[9] The preparation of the surfactant modified LDH ($[Zn_2Al–DS]$) was realized by the anion exchange reaction in deionised water of 1.00 g of $[Zn_2Al–Cl]$ with a 1.54 molar excess (1.34 g) of sodium dodecyl sulfate (Across). Intercalation of the surfactant was monitored by X-ray diffraction (Siemens D501 X-ray powder diffractometer, Cu-Kα radiation) and FTIR spectroscopy (Perkin-Elmer-FTIR16PC). The chemical formulae of the various compounds were calculated from elemental analysis. In all cases, the Zn/Al ratio was 2.2 and for the DS exchanged LDH, S/Al was equal to 0.98 in accord with total exchange of the Cl anions.

Intercalation of dodecyl sulfate in $Zn_2Al(OH)_6Cl{\cdot}2H_2O$ leads to the expanded phase $Zn_2Al(OH)_6(C_{12}H_{25}SO_4){\cdot}nH_2O$ ($[Zn_2Al-DS]$) with an increase of the basal spacing from 0.77 to 2.52 nm (Fig. 1) as reported in the literature.[12] The particle widths for both precursor and modified LDHs were measured by SEM (Cambridge Stereoscan 360, 20 kV, at Techinauv S.A). The measured thickness of $[Zn_2Al–Cl]$ platelets was 0.05 μm, corresponding to a stacking of *ca.* 60 layers, while expansion of the basal spacing for $[Zn_2Al-DS]$ leads to lamellae thickness of 0.15 μm. The number of stacked layers is retained after anion exchange confirming that the anion exchange proceeds by a topotactic mechanism.

Dispersion of $[Zn_2Al–DS]$ in water, methanol, ethanol, propanol or hexane under reflux conditions leads to unstable suspensions which settle after a few hours and only a minor part of the material was dispersed. Dispersion in methanol appears to be kinetically controlled by the slow replacement of water molecules by methanol. After one week stirring, *ca.* 50% of the LDH can be exfoliated. By contrast, reflux in butanol at 120 °C for 16 h leads to a translucent colloidal solution, which remains stable for at least 8 months. Up to 1.5 g of $[Zn_2Al–DS]$ per liter of butanol can be dispersed. Similar results have been obtained with higher alcohols such as pentanol and hexanol.

The size of the LDH colloids was measured by dynamic light scattering (Zetasizer–Malvern instrument). The mean equiva-

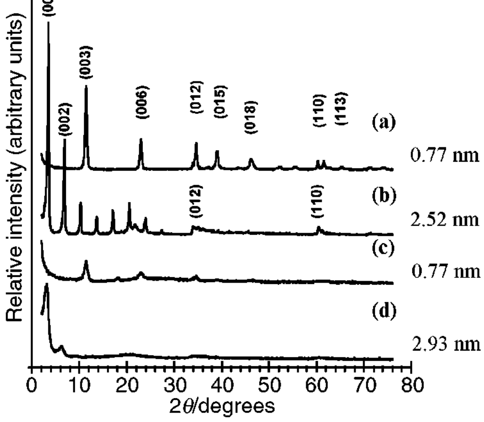

Fig. 1 Diffraction patterns of (a) $[Zn_2Al–Cl]$, (b) $[Zn_2Al–DS]$, (c) $[Zn_2Al–Cl]_{recov}$, (d) $[Zn_2Al–DS]_{recov}$.

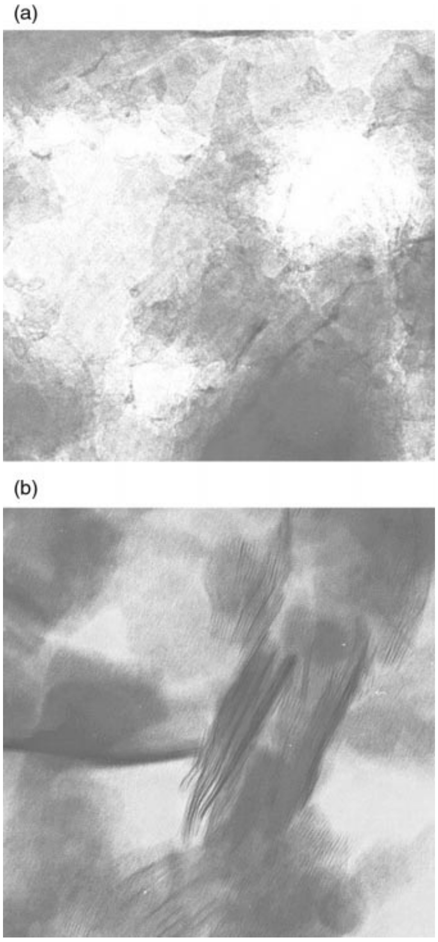

Fig. 2 TEM micrographs of [Zn_2Al–DS] dispersed in (a) butanol and (b) ethanol.

lent spherical diameter (d_s) is *ca.* 140 nm, smaller than the width of the hexagonal sheets measured by SEM (200 nm). Transmission electron micrographs of [ZnAl–DS] particles recovered from the colloidal solution [Fig. 2(a)] show assemblies of dispersed platelets all oriented parallel to the grid surface and confirm that delamination has occurred at the layer level while aggregates of stacked sheets are observed for the same materials dispersed in ethanol [Fig. 2(b)]. This argues in favour of a total delamination in butanol.

We note that the hydration state of the modified LDH is a critical parameter. Delamination was only observed when the organo-LDH compounds were previously dried under vacuum at room temperature for 1 day but not when a freshly wet prepared LDH was used or if the [Zn_2Al–DS] was thoroughly dried under vacuum at 80 °C for 4 h. Such intense drying leads to a new DS containing LDH phase with a smaller basal spacing of 1.68 nm corresponding to a tilted intertwined DS single layer. This LDH displays a densely packed structure which is resistent to exfoliation. It appears that the use of butanol with a boiling point higher than that of water and reflux conditions allows for a rapid replacement of all the intercalated water molecules by the solvent molecules. This seems to be the key process to completely exfoliate of the solid material.

When butanol is removed from the colloidal solution by evaporation (120 °C) or by lyophilization, a new LDH phase ([Zn_2Al–DS]$_{recov}$) is obtained with larger size and well oriented platelets as shown by an SEM micrograph [Fig. 3(a)]. This extended bidimensional orientated material displays a basal spacing of 2.93 nm in accord with incorporation of butanol in the interlamellar spaces. The typical 'sand rose' morphology of the LDH precursor is then lost and a thin film of LDH is obtained.

Comparison between FTIR spectra of the oriented LDH and [Zn_2Al–DS], particularly in the 400–1800 cm^{-1} wavenumber range in with unchanged lattice vibrations are superimposed on surfactant vibrations, confirms that the LDH structure is retained after delamination. When NaCl or Na_2CO_3 are added to the colloidal solution, flocculation of particles occurs and reversible back anion exchanges to give [Zn_2Al–Cl]$_{recov}$ and [Zn_2Al–CO_3]$_{recov}$ results (Figs. 1, 3(b)). The recovering of LDH structures under solvent extraction or precipitation confirms the presence of delaminated LDH in the colloidal solution.

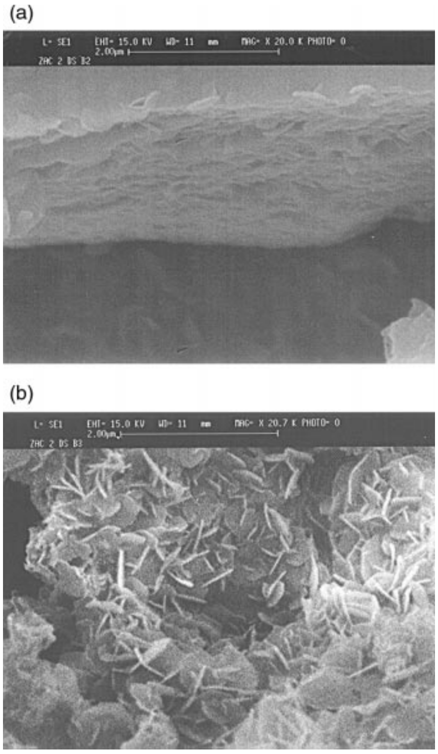

Fig. 3 SEM micrographs of (a) [Zn_2Al–DS]$_{recov}$ and (b) [Zn_2Al–CO_3]$_{recov}$.

The preparation of colloidal solutions of LDHs appears to be of substantial importance for the development of novel chemistry of the LDHs. It is now possible to develop the chemistry of LDHs in non-aqueous media, *e.g.* for electrochemistry applications. Ultrathin films based on LDHs can now easily be prepared by a soft chemistry route. Preparations of novel based-LDH materials with improved chemical or porosity properties are now envisaged through interstratified LDH/LDH, LDH/clay, LDH/polymer or nanoporous LDH/SiO_2 materials.

Notes and references

1 A. Usuki, Y. Kojima, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi and O. Kamigaito, *J. Mater. Res.*, 1993, **8**, 1179.
2 T. E. Mallouk, H. N. Kim, P. J. Ollivier and S. W. Keller, *Supramolecular Comprehensive Chemistry*, Pergamon, Oxford, 1996, p. 189.
3 I. Dekany, F. Berger, K. Imrik and G. Lagaly, *Colloid Polym. Sci.*, 1997, 681.
4 T. Permien and G. Lagaly, *Clays Clay Miner.*, 1995, **2**, 229.
5 A. J. Jacobson, *Comprehensive Supramolecular Chemistry: Colloidal dispersion of compounds with layer and chain structures*, ed. G. Alberti and T. Bein, Elsevier, Oxford, 1996, vol. 7, p. 315.
6 F. Cavani, F. Trifiro and A. Vaccari, *Catal. Today*, 1991, **11**, 173.
7 F. Malherbe, C. Forano and J. P. Besse, *Microporous Mater.*, 1997, **10**, 67.
8 A. De Roy, C. Forano, K. El Malki and J. P. Besse, *Synthesis of Microporous Materials*, ed. L. Occelli and H. Robson, Van Nostrand, Reinhold, 1992, vol. 2, p. 108.
9 S. Bonnet, C. Forano, A. De Roy, J. P. Besse, P. Maillard and M. Momenteau, *Chem. Mater.*, 1996, **8**, 1962.
10 M. Meyn, K. Beneke and G. Lagaly, *Inorg. Chem.*, 1990, **29**, 5201.
11 S. Sundell, *Acta. Chem. Scand., Ser. A*, 1971, **31**, 799.
12 A. Clearfield, M. Kieke, J. Kwan, J. L. Colon and R. C. Wang, *J. Inclusion Phenom. Mol. Recognit. Chem.*, 1991, **11**, 361.

Communication a908251d