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New approach to the delamination of layered double hydroxides

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A new method for the delamination of layered double hydroxides (LDHs) is described: large quantities of LDHs containing glycine are rapidly delaminated in formamide, and the translucent colloidal solutions are stable to centrifuge and long-term storage.

Layered double hydroxides (LDHs), also known as hydrotalcite-like compounds or anionic clays, are a group of lamellar ionic solids that in terms of layer charge are the counterpart of cationic clay minerals. LDHs consist of positively charged metal hydroxide sheets based on the brucite structure with intercalated anions and water molecules. They can be represented by the general formula, $[M^{2+}{}_{1-x}M^{3+}{}_{x}(OH)_2][A^{n-}{}_{x/n}\cdot mH_2O]$ where M^{2+} and M^{3+} are di- and trivalent metal cations occupying octahedral positions within the hydroxide layers and A^{n-} is an interlayer anion compensating the charge on the layers.[1,2]

A large number of applications of LDHs based on the intercalation or exchange of specific guests have been described.[3–6] Guests that can be inserted into the galleries of the LDH are limited however in size as a result of the need to force the layers apart during exchange. An alternative approach to inserting guests would be *via* exfoliation of the LDH followed by condensation of the layers in the presence of a guest. Exfoliation, however, is difficult for LDHs because of the high charge density on the layers.[7] Recently, however, Adachi-Pagano *et al.*[8,9] have reported that delamination of the LDH may occur through the combined use of alcohols and a Zn–Al–dodecyl sulfate LDH under reflux conditions at 120 °C for 16 h. Although the method is effective it does not appear to be the result of a strong driving force for solvent inclusion into the gallery region—as might be expected if the layers are to be forced apart.

In the present study, our approach has been to create an environment within the LDH which would be particularly attractive to gallery uptake of solvent and consequential delamination. Specifically we make use of amino acid anions and polar solvents. We anticipated that there would be strong hydrogen bonding between the intercalated anions and polar solvent as well as between the solvent molecules themselves. These attractive interactions we felt would then lead to the penetration of large volumes of solvent and hence delamination.

Using this approach we have developed a method for delaminating LDHs, which allows delamination to takes place rapidly at room temperature as well as allowing much larger amounts of LDHs to be delaminated than previously reported.[8]

A range of amino acid/polar solvent combinations were investigated, including glycine, serine and L-aspartic acid as the amino acid with water, ethanol, acetone, formamide, ethylene glycol and diethyl ether as the solvent. Optimum results, possibly as a result of optimization of hydrogen bonding, were obtained using a glycine/formamide combination.

The LDHs containing the amino acid anions were prepared by coprecipitation.[10] Distilled and deionized water was used in all preparations. The water was also boiled immediately before use to minimize carbonate contamination. For the preparation of LDHs containing glycine, aqueous solutions of $Mg(NO_3)_2\cdot6H_2O$ and $Al(NO_3)_3\cdot9H_2O$ ($Mg^{2+}+Al^{3+}=0.5$ mol l^{-1}, Mg : Al ratios of 2 : 1, 3 : 1 and 4 : 1) were prepared. These were added drop-wise under flowing N_2 gas to an aqueous solution of glycine, previously adjusted to pH 10 by addition of NaOH solution. The molar amount of glycine in the solution was twice that of the nitrate. The vigorously stirred mixture was maintained at pH 10 by drop-wise addition of a NaOH solution. The resulting slurry was aged in a sealed container at 60 °C for 8 h, followed by cooling, washing several times with water and finally centrifuged. The products from these solutions are referred as (2 : 1), (3 : 1) and (4 : 1) Gly-LDHs. LDHs containing other amino acids were prepared using a similar approach.

The powder X-ray diffraction (PXRD) pattern of an air-dried (3 : 1) Gly-LDH, with a 0.81 nm basal spacing, is shown in Fig. 1(a). (A moist sample gave a larger value of 1.01 nm confirming the presence of glycine within the layers.) Stirring 0.03 g of this material in 10 ml of formamide resulted in a clear colloidal dispersion. The reaction was extremely fast being completed within a few minutes. Fig. 1(b) shows the XRD pattern for a viscous 1 : 1 (by vol) mixture of the LDH in formamide. Only a broad reflection associated with the support glass slide is observed, with the absence of LDH reflections indicating loss of the original crystalline structure. Reaction

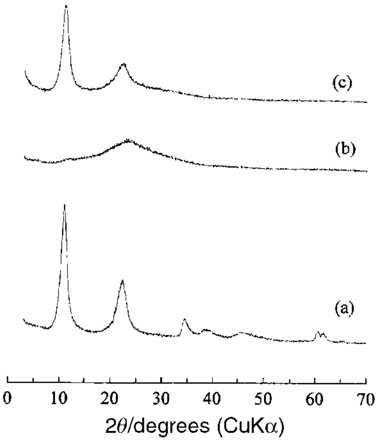

Fig. 1 PXRD patterns for (3 : 1) Gly-LDH (a) after preparation and drying in air, (b) 1 : 1 mixture with formamide indicating absence of LDH reflections and (c) of a material obtained by repeated addition of droplets of a completely delaminated mixture.

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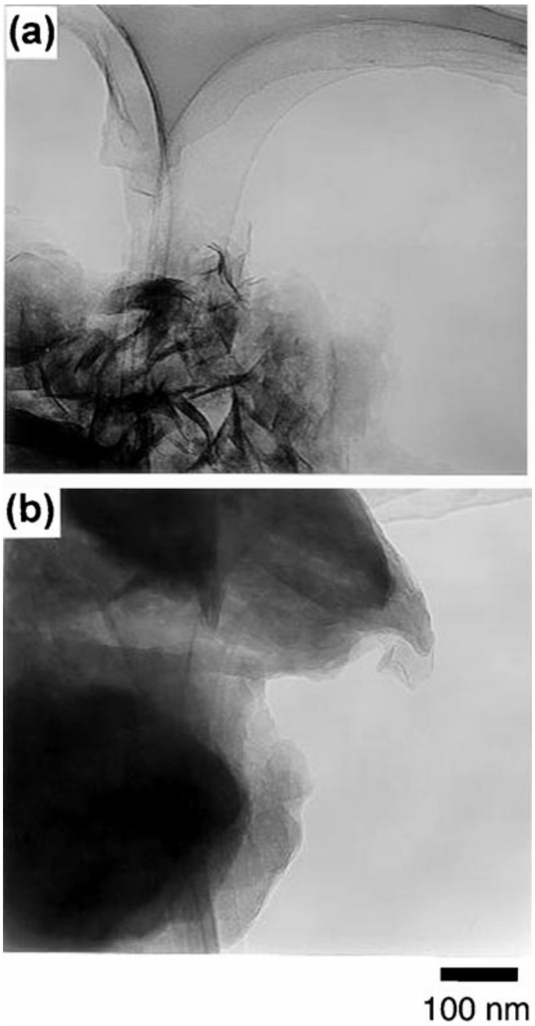

Fig. 2 TEM micrographs of (3 : 1) Gly-LDH (a) before dispersion in formamide and (b) recovered from the colloidal solution.

was too rapid to observe any intermediate expanded states. Repeated deposition of droplets of a 0.03 g/10 ml mixture onto a glass slide (dried at 25 °C), however, resulted in the creation of a crystalline LDH as evidenced in Fig. 1(c). The absence of reflections other than basal ones indicates that the deposited LDH platelets are highly oriented parallel to the surface of the glass slide. Clearly, dispersion in formamide had resulted in the separation of the LDH layers. The transmission electron microscope (TEM) images shown in Fig. 2 also confirm that delamination has occurred. The plate-like crystallites of the original (3 : 1) Gly-LDH are randomly oriented before dispersion in formamide (Fig. 2(a)), but the TEM image of the material recovered from the colloidal solution shows that all crystallites are highly oriented (Fig. 2(b)). This was in sharp contrast to LDHs containing other amino acids and carbonate anions which did not show any change in morphology. For the (3 : 1) and (4 : 1) Gly-LDHs up to 3.5 g of LDH could be delaminated per liter of formamide. This is to be compared with the value of 1.5 g l^{-1} of butanol reported for the Zn–Al–dodecyl sulfate LDH.[8]

The influence of layer charge was investigated by adding 0.07 g portions of air-dried Gly-LDHs to 1, 10 and 20 ml of formamide. The (3 : 1) Gly-LDH appeared to have the optimum layer charge amongst those tested. For the (2 : 1) Gly-LDH only partial delamination occurred even after addition of 20 ml formamide. The colloidal solutions that were obtained were stable for at least 3 months or to centrifuge treatment at 3500 rpm. For the (3 : 1) Gly-LDH gel formation took place after addition of only 1 ml of formamide.

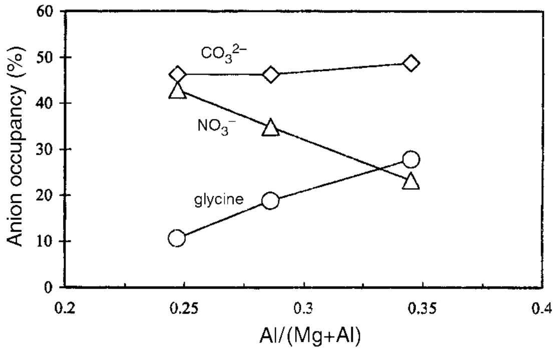

Fig. 3 Variation in anion compositions as a function of Mg/Mg+Al ratio, showing decreased organic anion presence with increased Mg : Al ratio.

Table 1 Mg : Al atomic ratio and anion content in various Gly-LDHs

		Anion content/mol × 10^{-3} g^{-1}		
Sample	Mg : Al ratio	Glycine	Nitrate	Carbonate
(2 : 1) Gly-LDH	1.90 : 1.00	1.29	1.08	1.13
(3 : 1) Gly-LDH	2.50 : 1.00	0.74	1.37	0.91
(4 : 1) Gly-LDH	3.05 : 1.00	0.38	1.51	0.81

The extent of drying also has a major impact on the delamination process. A (3 : 1) Gly-LDH air-dried sample was further dried at 80 °C for 24 h. This sample did not completely delaminate in 20 ml formamide, with a small portion of powder remaining intact. Incomplete delamination was also observed for a moist (3 : 1) Gly-LDH sample obtained just after centrifuge treatment. Clearly an optimum hydration state exists for successful delamination.

The values of the Mg : Al ratio (measured by EDTA titration) are shown in Table 1 along with C, H and N contents (by combustion analysis). A gravimetric method using nitron ($C_{20}H_{16}N_4$) was used in order to determine the nitrogen content arising specifically from nitrate anions. Anion occupancies are shown in Fig. 3, with charge occupation corresponding to:

$$\text{charge occupation} = \text{quantity of anion} \times \text{valence} / \sum (\text{valence} \times \text{quantity of anion}) \times 100\%$$

As frequently noted the Mg : Al ratios for the precipitated materials are lower than in the initial solutions.[11–14] The percentage layer charge compensated by carbonate is essentially the same for all the products. With increasing Mg : Al ratio, however, the glycine content falls and the nitrate content increases. Contamination by carbonate could occur during coprecipitation and washing, because the high pH of the solutions will readily adsorb atmospheric CO_2. Competition between the monovalent glycine and nitrate anions at lower charge density on the host layers will result in the preferential uptake of the smaller anions. The implications of layer charge, anion composition and extent of hydration on delamination are currently being investigated.

An interesting observation concerns the stability of the dispersion after formation. Ten milliliters of a formamide mixture, in which the (3 : 1) Gly-LDH was completely delaminated, was mixed with 10 ml of water. No re-sedimentation occurred and the mixture was stable to centrifuge treatment. Clearly the delaminated mixture is stable in a mixture of formamide/water and ion exchange of large anions should be possible. We are currently investigating such possibilities.

The delamination process described here opens up a range of possible applications in the preparation of microporous and mesoporous solids as well as nanocomposites based on LDHs.

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