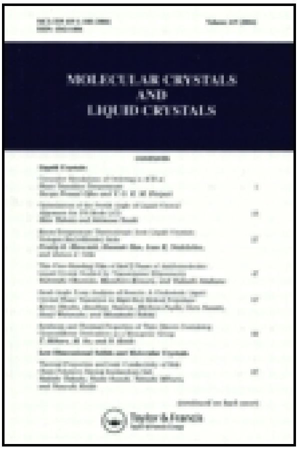

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Organic-Inorganic Hybrids Based on Anionic Clays

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Incorporation of terephthalate and benzenesulphonate anions in MgAl-LDHs with systematically varied layer charge (i.e., Mg/Al ratio) is studied. The orientation of the organic anions within the LDH interlayer is found to be strongly dependent upon the hydroxide layer charge.

Keywords: LDH; intercalation; anion-exchange; layered

INTRODUCTION

Layered materials that are able to intercalate neutral guest molecules or to exchange inorganic and organic ions for interlayer ions have attracted considerable attention.[1-4] Through the incorporation of a guest species into a layered host, novel solids may be engineered with desirable physical and chemical properties. Various layered materials such as clay minerals, graphite, transition metal dichalcogenides, and metal phosphates and phosphonates have the ability to act as host materials. These materials have been studied as potential catalysts, selective sorbents and hosts for nanoscale reactions.[5-9] A particularly attractive feature of such layered hosts is that they serve as templates for the creation of intercalated supramolecular arrays. Layered double hydroxides (LDHs), also known as anionic clays, are host-guest materials which, owing to their potential application in these and other areas, have recently gained much attention.[10-15]

An important group of LDHs may 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 divalent and trivalent cations, respectively; x is equal to the ratio $M^{3+}/(M^{2+} + M^{3+})$ and A is an anion of valence n. The structure of such LDHs may be described by considering the structure of brucite, $Mg(OH)_2$, which consists of Mg^{2+} ions co-ordinated octahedrally by hydroxyl groups. The octahedral units share edges to form infinite, charge neutral layers. In a LDH, isomorphous replacement of a fraction of the Mg^{2+} ions with a trivalent cation, such as Al^{3+}, occurs and generates a positive charge on the layers which necessitates the presence of interlayer, charge balancing, anions. Water of crystallisation also occupies the interlayer space of LDHs (Figure 1).

The charge density on the hydroxide layers of brucite-based LDHs is dependent upon the M^{2+}/M^{3+} ratio of the matrix cations in the layers. The anion-exchange capacity, and hence number of charge-balancing anions in the LDH, may therefore be controlled by varying the M^{2+}/M^{3+} ratio of the LDH. Here, incorporation of terephthalate and benzenesulphonate anions in MgAl-LDHs with systematically varied layer charge (i.e., Mg / Al ratio) is studied.

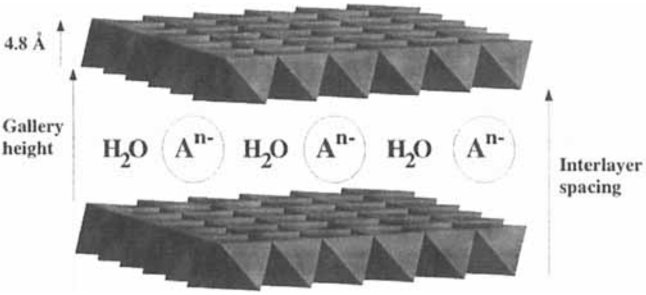

FIGURE 1 Schematic representation of the structure of a LDH.

SYNTHESIS AND CHARACTERISATION TECHNIQUES

The LDHs were prepared using the constant pH coprecipitation technique, as follows.[16] An aqueous solution (50 ml) containing 0.028 moles of $Al(NO_3)_3.9H_2O$ and 0.028xR moles of $Mg(NO_3)_2.6H_2O$ was added, in a dropwise manner, to 75 ml of a stirred aqueous solution containing either terephthalate or benzenesulphonate, at 65 °C. The pH of the solution containing the anion of interest was adjusted to 10 and maintained at this value during addition of the mixed metal nitrate solution, by the simultaneous addition of 1 M $NaOH_{(aq)}$. The resulting white precipitate was crystallised at 65 °C for approximately 18 hours, filtered and washed with hot deionised water.

In order to systematically vary the layer charge of the product LDHs, the amount of $Mg(NO_3)_2$ used in the mixed metal nitrate solution was adjusted such that R = 1.0, 1.5, 2.0, 2.5, 3.0 or 3.5, for each of the charge-balancing anions studied. A constant pH of 10 was chosen for the synthesis, as it has been reported that this value gives product LDHs with Mg / Al ratios similar to the initial value of R used.[16]

It is important to realise that, using this procedure, the concentration of nitrate in the reaction mixture increases as the value of R increases. At higher values of R, therefore, the competition between the anion of interest and nitrate to be incorporated into the LDH is highest. The incorporation of impurity nitrate anions into the product LDHs is therefore more probable at higher values of R. Kooli *et al.* used a two-fold excess of terephthalate or benzoate above the necessary stoichiometric amount required for charge neutrality of the LDH.[16] Despite the two-fold excess, it was found that a significant amount of nitrate was incorporated into the products. For this reason, a ten-fold excess of the charge-balancing anion of interest was used in the present work for the preparations with R = 1.0, 1.5 and 2.0. A twenty-fold excess was used for the preparations with R = 2.5, 3.0 and 3.5.

Room-temperature powder X-ray diffraction (PXRD) patterns were recorded in reflection geometry using a Philips PW1710 diffractometer with Cu Kα radiation (λ = 1.5418 Å). A nickel filter was used to remove Cu Kβ radiation. A step-scan from 2.5 to 70° (2θ) with a step size of 0.03° (2θ) at a rate of one step per second was used for data collection. Data were collected from finely-ground samples pressed into a glass sample holder. All the PXRD patterns were recorded after allowing the samples to equilibrate in air at room temperature for 24 hours following drying for 24 hours at 65 °C.

CHARACTERISATION

MgAl(terephthalate) LDHs

The PXRD patterns of the MgAl(terephthalate) R(x) LDHs may be indexed on the basis of a rhombohedral lattice with a hexagonal unit cell (Table 1).

Table 1. Unit-cell parameters and corresponding

R	*a* / Å	*c* / Å	Interlayer spacing / Å
1.0	3.003(7)	41.9(2)	14.0
1.5	3.026(6)	42.2(2)	14.1
2.0	3.03(1)	42.7(2)	14.2
2.5	3.043(8)	68.0(3)	-
3.0	3.05(1)	24.6(2)	8.2
3.5	3.060(8)	24.4(1)	8.1

Indexing based on a rhombohedral lattice with a hexagonal unit cell. Values in parentheses are the estimated standard deviations.

For the R(1.0), R(1.5) and R(2.0) LDHs, the observed interlayer spacing is approximately 14 Å (*c* / 3), which corresponds to a gallery height of 9.2 Å, following subtraction of the hydroxide layer thickness of 4.8 Å. This gallery height is consistent with a vertical orientation of the terephthalate anion with respect to the hydroxide layers (denoted as the expanded (E) interlayer arrangement, Figure 2).[16] For the R(3.0) and R(3.5) LDHs, the measured interlayer spacing is approximately 8.2 Å, which corresponds to a gallery height of 3.4 Å and, therefore, an approximately horizontal arrangement of the terephthalate anion with respect to the hydroxide layers of the LDH (denoted as the collapsed (C)) interlayer arrangement, Figure 2).[16]

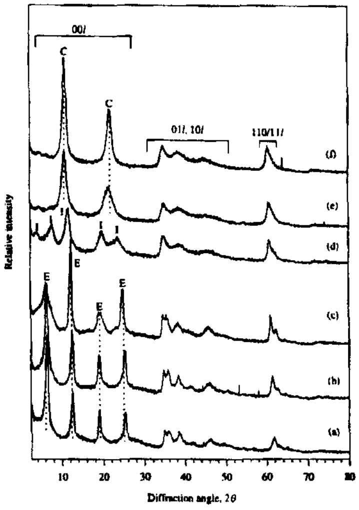

FIGURE 2. PXRD patterns of MgAl(terephthalate) R(x) LDHs: (a) R(1.0); (b) R(1.5); (c) R(2.0); (d) R(2.5); (e) R(3.0) and (f) R(3.5). E, C and I indicate basal reflections due to the Expanded, Collapsed or Interstratified interlayer arrangement, respectively (see text).

For the R(2.5) LDH, the measured *c*-parameter corresponds to a layer repeat distance of 22.6 Å – approximately the sum of the 14.0 and 8.2 interlayer spacings. The layer repeat distance for the R(2.5) LDH is interpreted, therefore, as arising from interstratification of the 14.0 and 8.2 Å interlayers (denoted as the interstratified (I) arrangement, Figure 3).[16-18] The interstratified arrangement thus consists of an approximately regular alternation of expanded and collapsed interlayers.

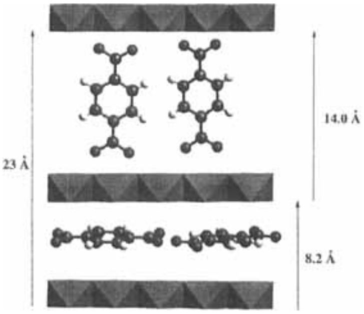

FIGURE 3. Schematic representation of the different interlayer arrangements of MgAl(terephthalate) LDHs

MgAl(benzenesulphonate) LDHs

The PXRD patterns of the MgAl(benzenesulphonate) R(x) LDHs are compared in Figure 4. The breadth and low intensity of the non-basal reflections (01*l* or 10*l*) prevents complete indexing of the patterns and satisfactory determination of the stacking sequence of the layers, thus suggesting a turbostratic disordering of the layers.

The interlayer spacing of the LDHs may be determined, however, from the positions of the basal reflections (Table 2). In addition, the reflection at approximately 61-63° (2θ), may be indexed as the 110 reflection of a hexagonal lattice, from which the *a*-parameter of the unit cell may be determined ($a = 2d_{110}$).

Table 2. PXRD data for MgAl(benzenesulphonate) R(x) LDHs.

R	a / Å[a]	Interlayer spacing / Å
1.0	3.02(1)	15.4(1)
1.5	3.02(1)	15.7(1)
2.0	3.03(1)	15.4(1)
2.5	3.03(1)	15.3(1)
3.0	3.05(1)	-
3.5	3.06(1)	8.5(1)[b]

[a] Determined from the *d*-spacing of the 110 reflection. [b] This value is the interlayer spacing of the major LDH phase. Values in parentheses are the estimated standard deviations.

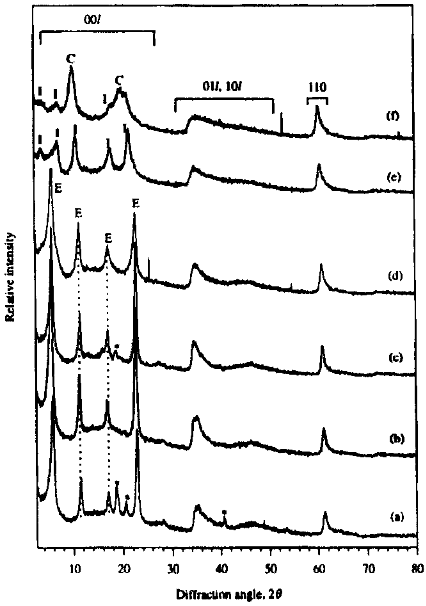

FIGURE 4. PXRD patterns of MgAl(benzenesulphonate) R(x) LDHs: (a) R(1.0); (b) R(1.5); (c) R(2.0); (d) R(2.5); (e) R(3.0) and (f) R(3.5). E, C and I indicate basal reflections due to the Expanded, Collapsed or Interstratified interlayer arrangement, respectively (see text).

The observed interlayer spacings of the R(1.0) to R(2.5) LDHs (approximately 15.4 Å), corresponds to a gallery height of 10.6 Å following subtraction of the hydroxide layer thickness of 4.8 Å. This gallery height, similar to that generally reported for LDHs containing interlayer benzoate anions,[16] is consistent with an approximately vertical bilayer arrangement of the benzenesulphonate anions with respect to the hydroxide layers (denoted as the expanded (E) interlayer arrangement, Figure 4).[16,19] In such an arrangement, the sulphonate groups are attached to the hydroxide layers and the phenyl rings form a hydrophobic region in the mid-plane of the gallery. It is possible, therefore, that the observed turbostratic disorder is a consequence of the relatively weak association between adjacent layers (i.e., interactions between the phenyl rings).

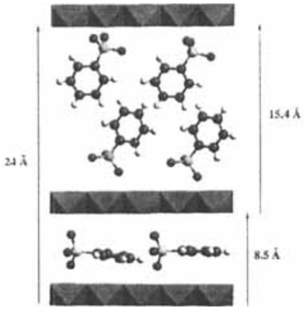

FIGURE 5. Schematic representation of the different interlayer arrangements of MgAl(benzenesulphonate) LDHs.

For the R(3.5) LDH, the most intense basal reflections correspond to an interlayer spacing of approximately 8.5 Å and therefore a gallery height of 3.7 Å, indicating a horizontal orientation of the benzenesulphonate anions with respect to the hydroxide layer (denoted as the collapsed (C) interlayer arrangement, Figure 4).

For the R(3.0) LDH the basal reflections corresponds to a layer repeat distance of 24.4 Å – approximately the sum of the 15.4 and 8.5 Å interlayer spacings, indicating the existence of an interstratified arrangement of these component interlayers (denoted as the interstratified (I) arrangement, Figures 4 and 5). It should be noticed that weak reflections due to the interstratified phase are also present in the PXRD pattern of the R(3.5) LDH, in addition to the more intense reflections from the collapsed phase.

CONCLUDING REMARKS

Previous work [16,18] had shown that interstratification is possible in MgAl-LDHs containing terephthalate or benzoate. In particular, it was demonstrated that dehydration of an intercalate at elevated temperature resulted in an interstratified intermediate between expanded and collapsed interlayer arrangements. The present work extends the study to show that, under relatively well-defined conditions of hydration, significant variation in local microstructure can occur as the layer charge is varied. This phenomenon clearly has an impact on the nature of the PXRD patterns obtained for organo-LDHs.

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