

Terephthalate Intercalated Layered Double Hydroxides: Use of AFM to Study the Influence of Temperature on Crystallite Morphology

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INTRODUCTION.

Layered double hydroxides (LDHs) are an important class of layered materials which have attracted much industrial and academic attention due to the diversity of potential compositions and corresponding range of physical and chemical properties which may result including a number of interesting inherent features such as anion exchange and ease of reconstruction following mild thermal decomposition (see Layered Double Hydroxides: Present and Future, Evans and Slade (2006)). Structural Previously known for their applications as catalysts, adsorbent materials and anion exchangers recent attention has highlighted other applications including the controlled release of pharmaceutical excipients and in materials design such as in composite organic - inorganic materials or as a source of positively charged metal hydroxide sheets (see Evans and Duan (2005), Choy et al.2007).

The structure of an LDH is similar to that of brucite, $Mg(OH)_2$, in which magnesium hydroxide octahedra come together by edge sharing to form sheets which subsequently stack to form a layered solid. In LDHs, however, layers are composed of more than one metal species, of different valencies leading to the development of a positive layer charge. Overall charge neutrality is maintained by the incorporation of hydrated anions into the interlayer space. These anions interact electrostatically with the metal hydroxide layers and are exchangeable, the extent of exchangeability depending on the strength of the layer - anion interaction (see book Layered Double Hydroxides: Present and Future). Terephthalate is an interesting anion because of its rigidity (extensive e-delocalisation), bifunctionality (meaning it can interact with both LDH layers) and

hydrophobicity. Terephthalate intercalated LDHs are important precursors in the synthesis by anion exchange of many functionalised LDHs (see Nijs et al.). In this way, LDH composites containing catalytically active species such as molybdates, tungstates, chromates and ferrates have been prepared. These LDHs have been subsequently used to catalyse liquid phase processes such as esterification and epoxidation reactions. Terephthalate containing LDHs are commonly prepared by the standard route of coprecipitation but the terephthalate anion may also be introduced into LDHs via anion exchange or during the rehydration of a mildly calcined precursor LDH (Kagunya et al., 1994).

The interlayer spacing in terephthalate intercalated LDHs, as for other LDHs containing organic anions (e.g. benzoate, DDS) is determined by the arrangement of the anion within the interlayer which in turn is dependent on the space available to the anion. Three distinct arrangements have been identified, the extended arrangement (where all of the terephthalate are thought to be vertically aligned, corresponding basal spacing ≈ 14 Å), a collapsed arrangement (anions aligned horizontally, basal spacing ≈ 8.5 Å) and an interstratified arrangement (when the two extreme anion orientations coexist, basal spacing ≈ 22.4 Å). It is possible to manipulate the anion orientation by varying the interlayer water content (e.g. by thermal treatment or by varying the relative humidity) and LDH layer charge (determined during synthesis) enabling reversible conversion from the vertical to the horizontal arrangement (Kooli et al., 1996). Although changes in anion orientation have been studied crystallographically, to our knowledge the influence in changing anion orientation on the crystallite morphology

has not previously been investigated. Here we report the use of atomic force microscopy (AFM) to study the influence of thermal treatment on terephthalate intercalated LDH crystallites. Special attention was focused on improving the LDH crystallinity during synthesis in order to facilitate observation of structural changes.

EXPERIMENTAL DETAILS.

Mg-Al TA containing LDHs were prepared by a method adapted from the work of Lyi et al. involving coprecipitation of the metal nitrates in the presence of the TA⁻ anion, induced by the thermal decomposition of hexamethylenetetramine (HMT) (Lyi et al.,2004). A 50 ml aqueous solution containing $Mg(NO_3)_2 \cdot 6H_2O$ (0.015 mol), $Al(NO_3)_3 \cdot 9H_2O$ (0.0075 mol), terephthalic acid (0.03 mol) and HMT (0.020 mol) was heated hydrothermally at 140 °C for 24 hours. The resulting solid product was collected by filtration, washed with distilled water and ethanol and dried at 80 °C. Products were characterized by PXRD, FTIR, SEM and AFM. The crystal structure of the resulting LDH product was studied as a function of temperature using an appropriate stage fitted to a Pan Alytical diffractometer. The sample temperature was also varied *in situ* during AFM experiments using a heating stage.

RESULTS AND DISCUSSIONS.

Formation of an Mg-Al (TA) LDH was successfully achieved using HMT to nucleate LDH precipitation. A PXRD pattern representative of the LDH products obtained is shown in Figure 1. The most intense basal reflection observed, at $6.4^\circ 2\theta$ (13.8 Å), corresponds to that expected for the extended arrangement of TA anions. FTIR confirmed the presence of TA⁻ in the product with characteristic COO⁻

palabras clave: Microscopio de Fuerza Atomica, hidroxidos duplos lamelares, Presion, Terephthalate.

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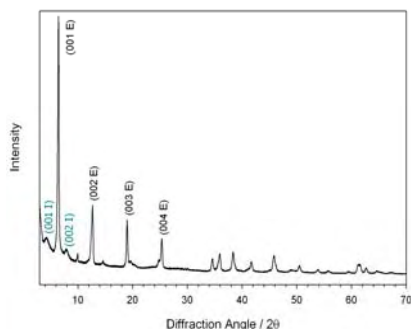


fig 1 PXRD pattern of material resulting from synthesis with HMT.

vibrations observed at 1380 and 1565 cm^{-1} . SEM images (Fig. 2) show that the LDH product is composed of large plate-like crystallites of predominantly hexagonal morphology. Some intergrowth of LDH crystallites is noted.

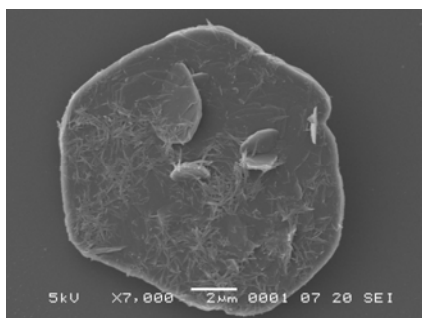


fig 2. SEM image typical of Mg-Al (TA) LDH crystallites prepared using HMT.

An *in situ* study by PXRD of the effect of varying temperature on the LDH crystal structure confirmed previous observations of a change in the anion orientation. The development of reflections corresponding to an interstratified arrangement (as indicated by the reflection at $4^\circ 2\theta$) was observed after heating to 50°C . This phase was found to be predominant at 75°C above which a change in anion orientation towards the collapsed phase was observed (Figure 3).

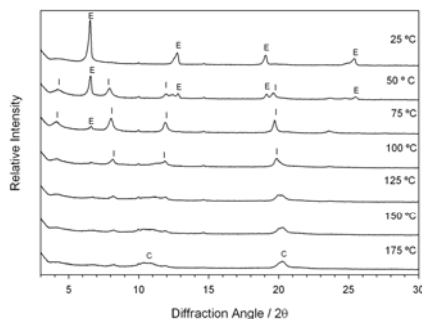


fig 3 Variation in PXRD pattern of LDH after stepwise increase to temperature indicated. E = extended, I = interstratified and C = collapsed anion orientation.

In situ AFM studies of the LDH crystallites imaged at different temperatures have also revealed interesting results. A decrease in the height profile, which may be logical

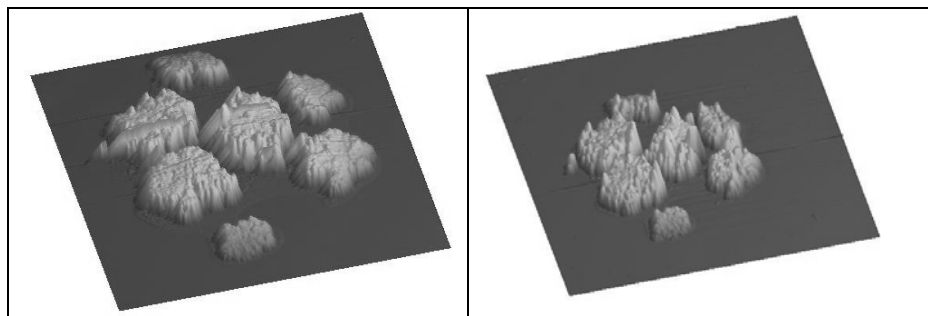


fig 4. AFM images acquired in tapping mode of a group of TA intercalated LDH crystallites before (left) and after (right) heating to 125°C for 1 hour.

following a collapse of the anion orientation is sometimes observed but also in several cases evidence for changes in the crystallite morphology in the form of crystallite growth has been observed following sample heating to 125°C . Figure 4 compares the 3D representations of the AFM height images (same height scale) of a group of LDH crystallites recorded in tapping mode before and after heating. Clear morphological differences can be observed before and after thermal treatment (this is particularly noticeable for the central crystallite).

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