

Preparation of layered double hydroxides and their applications as additives in polymers, as precursors to magnetic materials and in biology and medicine

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In recent years layered double hydroxides (LDHs), also known as hydrotalcite-like materials, have attracted considerable interest from both industry and academia. In this article, we discuss methods of preparing LDHs with an emphasis on the way in which particle size and morphology can be controlled with regard to specific target applications; scale-up of one such preparation procedure is also described. In addition, we review selected applications of LDHs developed by our own and other laboratories.

Introduction

Layered double hydroxides (LDHs) are a class of anionic clays whose structure is based on brucite ($\text{Mg}(\text{OH})_2$)-like layers in which some of the divalent cations have been replaced by trivalent ions giving positively charged sheets.^{1–3} This charge is balanced by intercalation of anions in the hydrated interlayer regions. In contrast to LDHs, most other layered materials have negatively charged sheets with charge-balancing cations in hydrated interlayer regions – examples include phyllosilicate clays and zirconium phosphates. LDHs can be represented by the general formula $[\text{M}^{\text{II}}_{1-x}\text{M}^{\text{III}}_x(\text{OH})_2]^{x+}(\text{A}^{n-})_{x/n}\cdot y\text{H}_2\text{O}$. The

identities of the divalent and trivalent cations (M^{II} and M^{III} respectively) and the interlayer anion (A^{n-}) together with the value of the stoichiometric coefficient (x) may be varied over a wide range, giving rise to a large class of isostructural materials. This flexibility in composition allows LDHs with a wide variety of properties to be prepared and is one of their most attractive features. The parent material of this class is the naturally occurring mineral hydrotalcite which has the formula $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3\cdot 4\text{H}_2\text{O}$ and LDHs are consequently also known as hydrotalcite-like materials. The structure of a typical LDH is shown⁴ in Fig. 1. In this article we first review some aspects of the synthesis of LDHs and then selected examples of their applications as additives in polymers, as precursors to magnetic materials and in biology and medicine. Space limitations preclude discussion of other important applications of LDHs, and their calcination products, in areas such as catalysis and environmental remediation and the reader is

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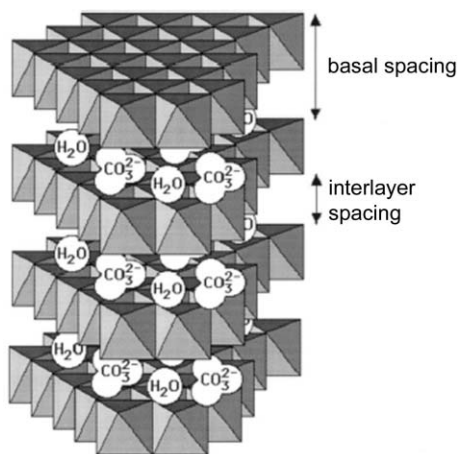


Fig. 1 Idealized structure of an LDH. Reprinted with permission from ref. 4. © Elsevier Science S.A.

referred to chapters 9–11 in a recent book for further information.³

Synthesis of LDHs

Control of particle size and particle size distribution

Both crystallite size and the distribution of crystallite size are important considerations for many potential applications of LDHs. For example, as discussed below, they can be used as additives in polymers for various purposes; in such cases the particle size of the LDH should be in the nanometer range and the particle size distribution should be narrow,^{5,6} if the presence of LDH additive is not to have an adverse effect on the mechanical properties and/or useful lifetime of the resulting polymer composite.

In our laboratory we have investigated a variety of means of controlling the crystallite size distribution of LDH materials.

LDHs are traditionally synthesized by coprecipitation reactions from aqueous solution.¹ The method of mixing and the pH during the nucleation and precipitation process can have a significant influence on the particle size of the resulting products. In the so-called variable pH precipitation process,¹ LDHs containing interlayer carbonate anions are prepared by adding a solution containing the desired divalent and trivalent metal cations to a solution of Na₂CO₃ until the pH of the reaction mixture reaches a specified value (typically around 10) and a solution of NaOH is then used to maintain the pH value until the precipitation is complete. More commonly used is the constant pH coprecipitation process at low supersaturation which involves simultaneous dropwise addition of mixed salt and base solutions to a reaction vessel at such a rate that the pH remains constant.¹ In either case, once mixing is complete the resulting suspension is subsequently aged at elevated temperatures. It is difficult to control the particle size and distribution of LDHs using either of these methods. Formation of crystallites involves two stages – nucleation and aging. The processes occurring while a crystal is undergoing aging in its mother liquor are very complex and can involve crystal growth, agglomeration, breakage, and other processes such as Ostwald ripening. Since the mixing process

of salt and alkali solutions takes a considerable time in the case of conventional coprecipitation at either high or low supersaturation, nuclei formed at the start of the addition process have a much longer period of time in which to begin aging than those formed at the end of the addition process. In other words, nucleation and aging take place simultaneously during the prolonged addition process. The inevitable consequence is that a wide dispersion of crystallite sizes is obtained after aging. It is therefore difficult to control the particle size and distribution of LDHs using the traditional coprecipitation methods.

We have recently reported⁷ a new method for the preparation of LDHs which involves a very rapid mixing and nucleation process in a colloid mill⁸ followed by a *separate* aging process. The colloid mill (see Fig. 2) consists of a conical rotor and a stator with a narrow gap (which can be varied in the range 2–10 microns) between them. A variable rotor speed in the range 3000–5000 rpm can be employed. The mixing takes place in a very short time in the liquid thin film between the rotor and stator leading to nuclei which have an equal length of time to grow prior to aging, resulting in a narrow range of particle diameter. In the colloid mill, particles are translated along the direction of flow, rotate and are translated perpendicular to the flow by a lift force (Fig. 3(a)).⁹ When particles rotating in same direction contact each other, their surfaces are moving in opposite directions (Fig. 3(b)). The lift forces concentrate particles near the rotor and increase the probability of particle–particle interactions (Fig. 3(c)) which means that agglomeration of the nuclei is inhibited and their size remains at a minimum. Subsequent aging allows the nuclei to grow together at approximately the same rate, giving a material containing particles with a narrow size distribution. We denote this the SNAS (separate nucleation and aging steps) method.

We have used the SNAS method to prepare LDHs of the type [Mg_{1-x}Al_x(OH)₂](CO₃)_{x/2}·yH₂O with different (Mg²⁺/Al³⁺) ratios.⁷ For each Mg²⁺/Al³⁺ ratio, the particle size distribution for the LDH material produced using the SNAS method was compared with that for LDHs produced by conventional precipitation at constant pH. TEM micrographs of the LDHs obtained using the two different synthesis methods are illustrated in Fig. 4 for samples with Mg²⁺/Al³⁺ = 2. The expected hexagonal plate-like nature of the crystallites is clearly apparent in each case. The average diameter of the platelets is smaller for the LDHs prepared

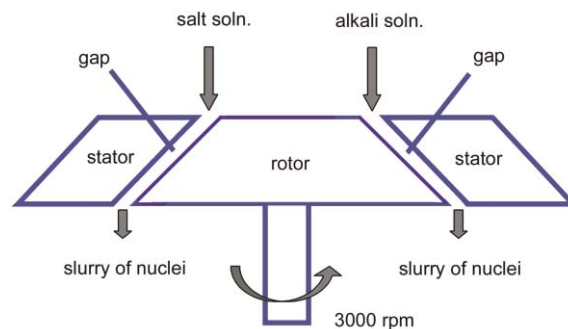


Fig. 2 Schematic illustration of a colloid mill.

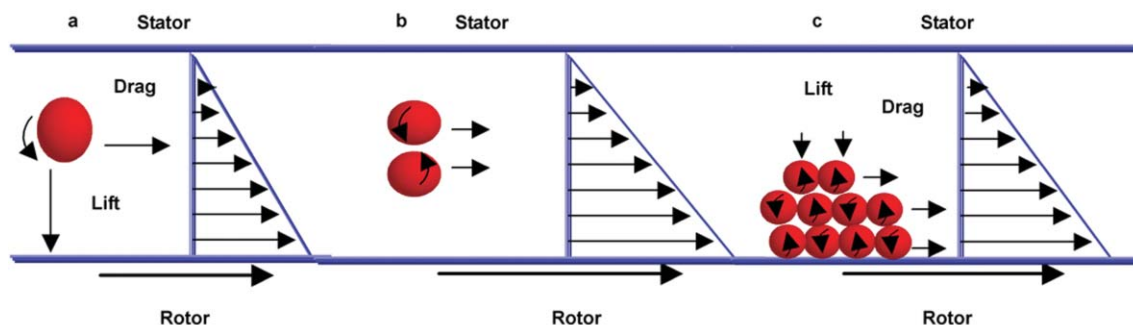


Fig. 3 Schematic illustration of forces operating in a colloid mill: (a) particles are translated along the direction of rotor and translated perpendicular to the flow by a lift force; (b) particles rotating in same direction contact each other with their surfaces moving in opposite directions; (c) lift forces concentrate particles near the rotor, increasing the probability of particle–particle interactions and minimizing agglomeration.

using the SNAS method and considerably more uniform in distribution than for the materials produced using the constant pH method. The diameters of the LDH crystallites produced using the SNAS method are in the range 60–80 nm. The particle size distribution of each of the LDH samples was determined by low angle laser light scattering. For each $\text{Mg}^{2+}/\text{Al}^{3+}$ ratio, the particle size distribution for the LDH material produced using the SNAS method is considerably narrower than that for the LDH sample produced by precipitation at constant pH; the latter generally show a bimodal distribution over a wide range. The particle size distribution by volume for samples with $\text{Mg}^{2+}/\text{Al}^{3+} = 2$ are shown in Fig. 5. Thus by having a rapid nucleation process in the colloid mill, followed by a separate aging process it is indeed possible to produce materials with a narrow range of crystallite sizes.

The SNAS method has also been successfully applied¹⁰ in the synthesis of Cu^{II} -containing LDHs, although well crystallized materials are difficult to prepare as a consequence of the Jahn–Teller distortion found in the coordination shell of Cu^{II} . Incorporation of Ni^{II} in the layers was found to improve the

crystallinity and structural stability of such LDHs. For the synthesis of $\text{Cu}/\text{Ni}/\text{Al}-\text{CO}_3$ and $\text{Cu}/\text{Ni}/\text{Mg}/\text{Al}-\text{CO}_3$ LDHs, materials with both smaller particle size and narrower distribution of particle size were obtained compared with those prepared using a conventional coprecipitation method, similar to the case for $\text{Mg}/\text{Al}-\text{CO}_3$ LDHs. We have also successfully employed this method in the synthesis of a variety of other materials including $\text{Mg}/\text{Al}-\text{NO}_3$ LDH,¹¹ $\text{Co}/\text{Al}-\text{CO}_3$ LDH,¹² $\text{Mg}/\text{Al}/\text{In}-\text{CO}_3$ LDH¹³ and $\text{Cu}/\text{Ni}/\text{Cr}-\text{CO}_3$ LDH.¹⁴

We have also developed¹⁵ a non-equilibrium crystallization procedure to operate in tandem with the SNAS method. In this process, the mixture emerging from the colloid mill is first aged in the conventional way. After a given time, another portion of mixed salt and alkali solutions is supplied simultaneously to the aging mixture, to ensure that the metal ions in the solution are always supersaturated. It is known¹⁶ that increasing concentration and/or decreasing temperature favor nucleation over crystal growth. Thus a high temperature and slow rate of introduction favor the adsorption of the added metal ions on the preformed crystal particles, rather than the formation of new nuclei. We have shown that $\text{Mg}/\text{Al}-\text{CO}_3$ LDHs with a

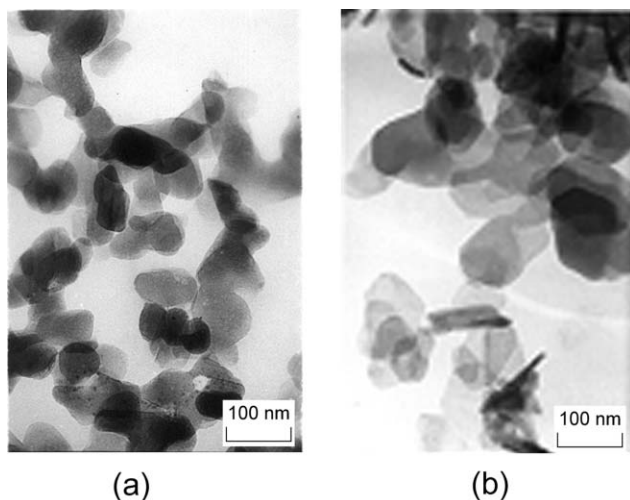


Fig. 4 Scanning electron micrographs of $\text{Mg}/\text{Al}-\text{CO}_3$ LDHs prepared by (a) the colloid mill (SNAS) method and (b) conventional precipitation at constant pH. Reprinted with permission from ref. 7. © ACS.

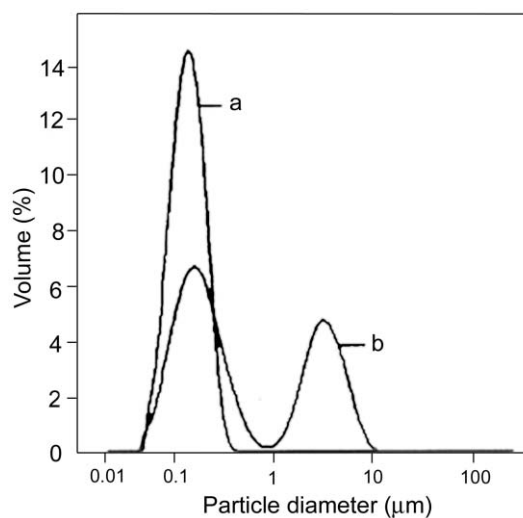


Fig. 5 Profiles of particle size distribution for $\text{Mg}/\text{Al}-\text{CO}_3$ LDHs prepared by (a) the colloid mill (SNAS) method and (b) conventional precipitation at constant pH. Reprinted with permission from ref. 7. © ACS.

stable composition and increased crystallinity can be prepared by this method.¹⁵ The particle size and its distribution can be controlled to some extent by changing the quantities of salts and alkali introduced.

Control of composition of interlayer galleries

The interlayer galleries of LDHs contain both interlayer anions and water molecules and there is a complex network of hydrogen bonds between layer hydroxyl groups, anions and water molecules. The interlayer regions are substantially disordered and hydrogen bonds are in a continuous state of flux so that the precise nature of the interlayer is extremely complex.^{1–3} The ability to tune the supramolecular host–guest and guest–guest interactions is required for the development of many potentially interesting applications of LDHs, such as controlled drug release from, or the controlled stereochemistry of polymerization within, the interlayer galleries. In order to have the maximum control over the structure of the interlayer region, as well as be able to compare experimentally determined structures with the results of computer modelling,¹⁷ it is desirable that there should be only one type of interlayer guest anion present in the interlayer region. Unfortunately, this objective is often not easy to achieve in practice.

We have been particularly interested in the case of carboxylate-intercalated LDHs, for which many experimental^{18–20} and theoretical studies^{17,21} have been reported. Synthetic procedures for the intercalation of carboxylic acids into LDHs have been critically reviewed by Carlino.²² In coprecipitation reactions, co-intercalation of carbonate ions arising from atmospheric carbon dioxide is sometimes observed, even when the reaction is carried out under nitrogen. Even where carbonate contamination is prevented, the materials are often contaminated by precursor anions from the mixed salt solution.¹⁸ Alternatively, interlayer chloride or nitrate ions in LDH precursors can be replaced by carboxylate anions in an ion-exchange reaction, but exchange is often not complete.²³ A third method involves the calcination of LDH-carbonates at intermediate temperatures (450–500 °C) to give mixed metal oxides which on subsequent reaction with an aqueous solution of a carboxylate salt under nitrogen can reform the LDH layers with concomitant intercalation of carboxylate anions. In this case, the calcination conditions have a crucial effect on the purity and crystallinity of the resulting LDH carboxylate and must be optimized in each case.²² Furthermore, the strongly basic nature of the intermediate solids can lead to ready uptake of carbon dioxide, and in some cases, no reconstruction of the LDH phase is observed.²⁴

We have reported^{25,26} a general method for the preparation of carboxylate-pillared LDHs which does not suffer from any of the problems, such as competitive intercalation of carbonate or other anions, discussed above and is easy to carry out. The procedure involves dissolution of an LDH-carbonate precursor by addition of an aqueous solution of the appropriate carboxylic acid followed by re-precipitation of the LDH-carboxylate at variable pH. In contrast to the usual coprecipitation reactions, the re-precipitation does not need

to be carried out under nitrogen in order to prevent contamination by co-intercalated carbonate. Glutamate,²⁵ citrate, oxalate, tartrate and malate anion-pillared²⁶ M^{II}/Al LDHs (M^{II} = Mg, Zn, Ni) have been prepared by this procedure, illustrating its general applicability. The absence of other co-intercalated anions has been confirmed by elemental analysis, vibrational spectroscopy and qualitative analysis.

Control of particle morphology

When synthesized by conventional co-precipitation techniques, LDHs have a hexagonal platelet morphology as shown in Fig. 4 above,^{6,7} although the platelets are often aggregated into a “sand-rose” motif.⁶ Template-directed synthesis has been the object of much recent attention in the field of material science.²⁷ Using self-assembled aggregates as a template, inorganic minerals or materials can be directed to an ordered structure with specific morphology and size by replication of the structure of the self-assembled aggregates. Typically, reactions of inorganic precursors take place at the interface between the organic self-assembled aggregates and the solution, forming inorganic-organic composites. The templates commonly employed include peptides, polysaccharides, amphiphilic block polymers, Langmuir–Blodgett films, as well as microemulsions, vesicles, and micelles consisting of surfactants.

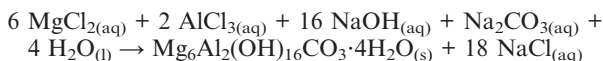
There have been only a few reports of the synthesis of LDHs using templates to date. It has been reported that when organic anions are adsorbed on the surface of LDHs causing the surface to be hydrophobic, the LDH crystallites will be assembled *via* hydrophobic interactions leading to unusual morphologies. Ogawa and Asai²⁸ reported the observation of curved thin flat sheets in LDHs pillared with cholesterate. Valim and co-workers observed²⁹ band-like structures which were attributed to aggregation of LDH particles in the presence of dodecyl sulfonate but Xu and Braterman³⁰ later suggested that similar bar-like and curved sheets formed by dodecyl benzene sulfonate LDHs were actually the result of hydrophobic interactions favoring growth along the *c* direction perpendicular to the layers. Leroux *et al.* have reported³¹ that when an LDH is precipitated in the presence of alginate, the biopolymer becomes intercalated between the layers and the resulting composite material has a tubular morphology.

We have recently shown³² that when Ni/Al–CO₃ LDHs are precipitated in the presence of the polysaccharide chitosan, materials with a curved fibre-like morphology are obtained. We have also been able to prepare³³ an Mg/Al–CO₃ LDH with a floccule or fiber-like morphology by co-precipitation at either constant or variable pH in a water-in-oil emulsion mixture composed of octane, water and sodium dodecyl sulfate; a material possessing similar chemical composition and properties to that synthesized using a conventional variable pH method, but showing higher surface area and a narrower distribution of mesopores, was obtained.

Large-scale production of LDHs using the SNAS method

The SNAS process for preparation of LDHs, based on the colloid mill as described above, has been successfully scaled up making use of a pilot plant facility (100 tonnes annum^{–1} scale)

in our laboratory, and two production lines have been established in Yixing in Jiangsu province (1000 and 10 000 tonnes annum⁻¹) and one in Dalian in Liaoning province (1000 tonnes annum⁻¹). The preparation of the parent LDH can be represented by the following equation:



In the case of Dalian, the plant is on the coast and the magnesium chloride is obtained from the bitterns remaining after crystallization of sodium and potassium chlorides from seawater. Previously there was no demand locally for magnesium chloride and the bitterns were regularly returned to the sea with adverse affects on the marine ecological balance. The sodium chloride solution formed as a by-product of LDH manufacture is electrolysed in an adjacent chloralkali plant, regenerating the majority of the sodium hydroxide solution required for the process. This results in an economical process with highly efficient use of resources and zero discharge.

Applications of LDHs as additives in polymers

LDHs as heat retention additives in horticultural plastic films

Horticultural crops are often grown under cover, in order to protect them from rain damage, low temperatures and pests. In temperate Europe, glass greenhouses are most commonly used, whereas expansion of agriculture in Asia has been mainly associated with the development of low cost plastic films.³⁴ Low density polyethylene (LDPE) is the most commonly used plastic in horticultural films because of its low cost, light weight and high visible light transparency. It has the disadvantage however that it has high transmission to radiated heat, leading to poor heat retention and low night-time temperatures. The heat retention properties of LDPE can be greatly improved by the addition of mineral fillers.³⁵ Requirements for heat retention additives include that they (i) enhance, or at least do not adversely affect, the lifetime or mechanical properties of the film, (ii) have high visible light transmission to allow for photosynthesis, (iii) have high transmission of solar heat energy (near-IR radiation in the range 1430–4760 cm⁻¹) to allow daytime warming and (iv) low transmission of black body radiated heat energy (mid-IR radiation in the range 710–1430 cm⁻¹) to minimize nighttime cooling. Whilst many inorganic materials have suitable IR absorption bands to meet – to varying extents – criterion (iv), unless the particles of the material have a small size with a narrow distribution, there will be a considerable reduction in visible light transparency³⁶ and an adverse effect on the mechanical properties of the film.⁶

In collaboration with the Harbin No. 5 Plastics Factory in N.E. China, we have carried out field trials over two winters with greenhouse films containing different additives including the mineral talc (currently used commercially in China), commercially available LDHs and an LDH produced by the SNAS process. The daily maximum and minimum temperatures in greenhouses made from the SNAS-LDH films are considerably higher than those observed using films containing

talc (by an average margin of 1.9 and 2.9 °C respectively); they are also higher than those observed with the films containing commercially available LDHs, which we believe is associated with the narrower particle distribution of the LDH which gives rise to an enhanced dispersion of the LDH in the polymer matrix.^{37,38}

The LDHs used in these trials all contained carbonate as the interlayer anion, but we are currently working on second-generation materials which contain mixtures of anions such as sulfate and carbonate which have a wider range of IR absorption bands and give films with further enhanced heat-retaining properties.³⁹

LDHs as flame retardants

The global market for flame retardants (FRs) is estimated to be \$2.4 billion with growth around 5% per year.⁴⁰ In recent years there has been increasing concern about the environmental hazards associated with halogen-containing FRs because of the toxicity of the products formed during a fire or when incinerating or recycling waste plastics. Indeed, brominated FRs such as polybrominated biphenyls (PBB) and polybrominated diphenyl ethers (PBDE) are to be phased out in the EU by July 2006 under the recently approved Restriction of Hazardous Substances Directive (RoHS). As a consequence, there has been considerable interest in halogen-free flame retardants and metal hydroxides such as aluminium hydroxide (ATH)⁴¹ and magnesium hydroxide (MH)⁴² are already in commercial use. In general, these materials reduce the flammability of the plastic by virtue of their endothermic decomposition which absorbs heat from the substrate and accompanying evolution of water vapor which dilutes the oxygen in the surroundings. The inorganic material is also thought to promote the formation of an expanded carbonaceous coating or char on the polymer which protects the bulk of the polymer from being exposed to air.^{41,42} In addition to improving resistance to ignition, a second key property of FRs is the ability to suppress smoke production if a fire does occur, because the majority of fatalities are a result of suffocation. Although metal hydroxides do have limited smoke suppressing properties,⁴³ other additives such as zinc borates (e.g. Firebrake[®] 415 (4ZnO·B₂O₃·H₂O)) or zinc hydroxystannate (ZHS) are often combined with MH or ATH⁴⁴ in order to enhance the smoke suppression.

Recent studies⁴⁵ have shown that an LDH with the formula Mg₄Al₂(OH)₁₂CO₃·3H₂O has better flame retardant properties than either ATH or MH and that the layered structure may play a key role in this respect. We have focused on the preparation of second generation LDH FRs with enhanced properties such as smoke suppression by either modification of the layers or intercalation of different anions. For example, we have demonstrated⁴⁶ that a borate-pillared LDH may be prepared by a simple procedure involving reaction of boric acid with an LDH in the carbonate form. The interlayer region contains polymeric triborate anions of the type [B₃O₄(OH)₂]_n⁻ with –B–O–B– chains of BO₄ units oriented parallel to the layers with each BO₄ unit forming a hexagonal B₃O₃ ring with two BO₃ units. Two key fire retardant properties for different LDHs with ethylene vinyl acetate

Table 1 Flame retardant properties of different LDH fillers (60 wt%) with EVA-28

Filler	LOI (%) ^a	Smoke density
None	21.3	187.4
Mg/Al-CO ₃	30.0	133.1
Mg/Al-borate	29.2	102.9

^a Limiting Oxygen Index (see text).

(EVA) as the polymer component are given in Table 1. The limiting oxygen index value (LOI) represents the minimum concentration of oxygen (expressed as percent by volume) in a mixture of oxygen and nitrogen that will support flaming combustion of a material that is initially at room temperature. The LOI values for the resins containing carbonate- and borate-pillared LDHs are comparable and significantly higher than that of the pure resin, indicating that addition of the LDHs has reduced the flammability of the material.

Most noteworthy however, is that whilst addition of the LDH-carbonate gives a reduction in smoke density during combustion, the borate-pillared LDH has significantly better smoke suppressant properties. The smoke density of the borate-pillared LDH/EVA composite is 45% lower than that of the pure resin. The powder XRD patterns of the composites of EVA with the LDH-carbonate and the borate-pillared LDH before heating are virtually identical to those of the respective LDH phases indicating that dispersion in the polymer has not disrupted the layer structure of the LDHs. After heating at 700 °C, the LDH-carbonate composite decomposes to give a material with an X-ray pattern corresponding to that of a poorly crystalline MgO phase, as is well known for such LDHs in the absence of polymer.¹ In contrast however, the material produced by decomposition of the LDH-borate composite has a diffraction pattern corresponding to that of fairly well crystalline Mg₂B₂O₅ which makes a major contribution to the flame retardant and smoke inhibiting effects. Scanning electron micrographs of the composites of EVA with the LDH-carbonate and the borate-pillared LDH after heating in air at 700 °C are shown in Fig. 6(a) and (b), respectively. Comparison of the two micrographs clearly indicates that the LDH-borate forms a more complete protective layer which has been suggested⁴⁷ to be the basis of smoke inhibiting action of flame retardants. When used as a flame retardant with PVA, the synergistic effect between the borate anions uniformly distributed in the interlayer region and the host layers gives

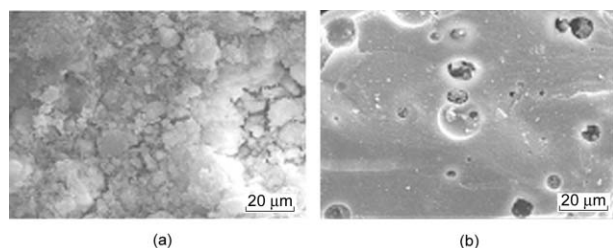


Fig. 6 Scanning electron micrographs of composites of EVA with (a) Mg/Al-CO₃ LDH and (b) Mg/Al-borate LDH after heating in air at 700 °C. Reprinted with permission from ref. 46. © Clay Minerals Society.

rise to enhanced smoke-suppressant properties compared to the LDH-carbonate precursor without compromising the flammability of the material. We have also recently found that the flame retardancy of LDHs can be modified by tuning the composition of the layers as well as that of the interlayer galleries. Thus for example, ternary LDHs of the type Zn/Mg/Al-CO₃ have better flame retarding properties than binary Mg/Al-CO₃ LDHs.⁴⁸

LDHs as stabilizing agents for PVC and other polymers

Chlorine-containing polymers such as poly(vinyl chloride) PVC undergo an autocatalytic dehydrochlorination reaction under the influence of elevated temperatures or UV radiation. Since the HCl originating from the de-hydrochlorination of the PVC chains is believed to sustain this autocatalytic process, stabilizers that irreversibly bond HCl can thus inhibit the degradation. Heavy metal compounds such as cadmium stearate or lead stearate are currently used for this purpose; alternatives are required however in the light of environmental concerns associated with the use of heavy metals. LDHs have been employed to good effect and, indeed, the largest current commercial application of LDH materials is in the polymer industry, mainly to stabilize PVC.⁴⁹

Kyowa Chemical Industries of Japan were the first to demonstrate that adding Mg/Al LDHs to PVC in combination with other additives such as zinc stearate and tin maleate leads to an enhancement in thermal stability of the resin.⁵⁰ The role of the LDH in absorbing HCl was confirmed experimentally by Van der Ven *et al.* who measured⁵¹ the capacity of LDHs having the same M^{II}/M^{III} ratio and different counter-ions to react with HCl gas and found a linear correlation between increasing HCl capacity and thermal stability of the LDH in the order SO₄²⁻ < Cl⁻ < OH⁻ ~ NO₃⁻ < CO₃²⁻ < C₁₇H₃₅COO⁻. They suggested that the reaction between the LDHs and the HCl generally occurs in a two-step process: firstly, the interlayer anions react with the HCl gas, and, secondly, the LDH layers themselves react with the HCl giving complete destruction of the LDH structure and formation of metal chlorides.

We have recently demonstrated⁵² that an Mg/Al-CO₃ LDH with Mg/Al = 2 has a better stabilizing effect on PVC than LDHs with higher Mg/Al ratios. This LDH contains the highest quantity of interlayer CO₃²⁻ ions but the lowest overall HCl absorption capacity, suggesting that the reaction of HCl and CO₃²⁻ ions is more important than the reaction of HCl with the layers in stabilizing the PVC against thermal degradation. We have also shown⁵³ that LDHs containing interlayer maleate anions have superior heat stabilizing properties to mixtures of carbonate-containing LDHs and tin maleate; as for the borate-pillared LDH flame retardant discussed above, this again demonstrates the efficacy of a uniform distribution of the active components in a polyfunctional material.

LDHs as stabilizing agents for pigments in polymers

Organic dyes are extensively used in the textile and polymer industries, but suffer from limited UV and/or oxygen and thermal stability. Ways of enhancing their stability continue to

attract a great deal of interest and there has been considerable work on intercalation of cationic dyes in zeolites, aluminosilicate clays, and metal(IV) phosphonates.⁵⁴ The resulting materials also have potential applications in nonlinear optics provided that they have sufficient thermal and optical stability under relatively strong laser irradiation.⁵⁵

Several examples of the intercalation of anionic organic dyes in LDHs have also been reported in the literature.^{56–58} The stability to heat and light of the resulting intercalated materials has not generally been investigated however. We have recently reported¹¹ the intercalation of a large anionic azo pigment into an LDH host by ion-exchange of an Mg/Al-NO₃ LDH precursor with a solution of C.I. Pigment Red 48:2 (the calcium salt of 4-((5-chloro-4-methyl-2-sulphophenyl)azo)-3-hydroxy-2-naphthalenecarboxylic acid), in ethane-1,2-diol. The UV-visible diffuse reflectance spectra of C.I. Pigment Red 48:2 itself show marked changes after heating at 200 °C and above, whereas there are no significant changes in the spectra of the intercalated pigment after heating at temperatures up to 300 °C, indicating that the thermostability is markedly enhanced by intercalation in the LDH host. Furthermore, the pigment-intercalated LDHs exhibits much higher photostability to UV light than the pristine pigment. When the pigment and pigment-intercalated LDH were separately incorporated in polypropylene composites, the thermo- and photostability of the composite containing the intercalated pigment were also higher than that of the composite containing the pure pigment. We have investigated the origin of the increased thermal and photostability of the intercalated pigment.¹¹ The stability of an intimately ground physical mixture of the pigment and the LDH-nitrate precursor is comparable to that of the free pigment and far inferior to that of the intercalated pigment; the enhanced stability is therefore a result of intercalation rather than being an artifact of heating/equilibration/light absorption properties associated with mixing of the two components. Azo pigments such as C.I. Pigment Red 48:2 are known⁵⁹ to exist as keto-hydrazone and phenoxy-azo tautomers as shown in Fig. 7. On the basis of single-crystal X-ray diffraction, C.I. Pigment Red 48:2 and related calcium salts are known to exist largely as the keto-hydrazone tautomer in which the carboxylate, sulfonate and keto groups are all coordinated to calcium. We have carried out PM3 semi-empirical SCF-MO calculations¹¹ which suggest that the phenoxy-azo tautomer is energetically favored

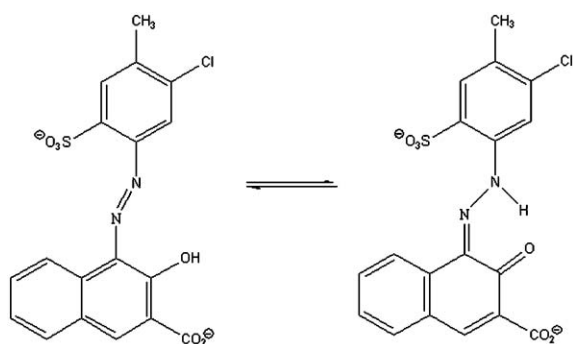


Fig. 7 Structure of the two tautomeric anions of C.I. Pigment Red 48:2.

in the absence of coordination to calcium and that the phenoxy hydrogen is involved in intramolecular hydrogen bonding to the azo nitrogen (calculated H...N distance 0.171 nm). The IR data for the intercalated anion are consistent with this model and further suggest that the carboxylate group bridges adjacent hydroxyl groups of one layer by means of strong hydrogen bonds whilst the sulfonate group is hydrogen bonded to the opposite layer. It is known⁵⁹ that photooxidation of azo dyes involves attack by photochemically generated singlet oxygen and that the hydrazone tautomer is more readily attacked than the azo form. Furthermore, for related azo dyes in solution it has been shown that the presence of intramolecular hydrogen bonding of the type we propose in the intercalated pigment can protect the chromophore from attack by ¹O₂. This suggests that the enhanced photostability of intercalated C.I. Pigment Red 48:2 compared with the pristine pigment is not merely due to the physical barrier associated with intercalation between the layers, but is also related to the effect of intercalation on the structure of the anion.

Applications of LDHs as precursors to magnetic materials

Cation order-disorder phenomena in LDHs

The extent of long-range or short-range ordering of the cations within the layers of LDHs has been widely discussed in the literature and contradictory conclusions have been drawn. Although interesting in its own right as a theoretical problem, the arrangement of cations is also of practical significance since where LDHs are used as catalysts themselves,⁶⁰ or as precursors to catalysts⁶¹ or other materials, it should be advantageous to have a homogeneous distribution of cations without segregation of 'lakes' of separate cations. Any long-range order in the distribution of cations is difficult to observe experimentally by powder XRD because of high pseudo-symmetry, micro-crystallinity and stacking faults. Although the evidence for and against long-range cation ordering in LDHs is somewhat inconclusive,⁶² there is much stronger evidence for local ordering of cations. In particular, the presence of M^{III}-O-M^{III} linkages is believed to be unfavorable from the point of view of charge repulsion (the so-called cation avoidance rule).⁶³ EXAFS is a powerful tool for studying local cation ordering. In the case of Mg_nFe^{III}-CO₃ LDHs with nominal values of *n* = 2, 3 and 4 for example, it has been shown⁶³ that Fe^{III} cations never (within the detection limits of EXAFS) occupy neighboring sites and a number of other EXAFS studies have confirmed that local ordering with absence of M^{III}-O-M^{III} linkages is a feature of LDHs.⁶⁴

Many materials are prepared from mixtures of precursors and ineffective or incomplete mixing can have an adverse effect on the properties of the resulting material. Since LDHs can be prepared with a wide range of component ions, they offer the possibility of preparing new functional materials from a *single* solid precursor which can be prepared in a *pure* state in which the cations are *uniformly distributed* on an atomic level.

Synthesis of $M^{II}M^{III}_2O_4$ spinels from LDH precursors

Spinel of the type $M^{II}M^{III}_2O_4$ continue to attract a great deal of interest because of their many practical applications.^{65,66} LDHs are potential precursors to such spinels since both involve mixtures of divalent and trivalent cations. Calcination of LDHs at intermediate temperatures (450–600 °C) affords poorly crystalline mixed metal oxides,^{1,3} which are converted⁶⁷ to spinels above about 750 °C. The spinel phases are generally mixed with the oxide of the divalent metal however.^{1–3} This reflects the fact that in LDHs, the ratio M^{II}/M^{III} is typically¹ in the range 2–4 whereas in a spinel the required ratio is $M^{II}/M^{III} = 0.5$. The presence of oxidizable cations in the LDH generally leads to reduced decomposition temperatures, and more importantly, offers the potential to tailor the composition of the thermal decomposition products.⁶⁸ For example,⁶⁹ calcination of a $Co^{II}Fe^{III}-CO_3$ LDH with $Co^{II}/Fe^{III} \sim 2$ at moderate temperatures (350 °C) affords a mixed spinel of the type $Co^{II}Co^{III}_xFe^{III}_{2-x}O_4$ ($x \sim 1$) resulting from partial oxidation of Co^{II} , which on further heating (750 °C) segregates to give a mixture of two spinel phases $Co^{II}Fe^{III}_2O_4$ and $Co^{II}Co^{III}_2O_4$; a further increase in calcination temperature to 1100 °C results in decomposition of the latter to give $Co^{II}O$. The interconversion of LDH and spinel phases containing cobalt has been extensively studied by Zeng and co-workers. For example, calcination of Co^{II}/Co^{III} LDHs containing interlayer nitrate and carbonate anions⁷⁰ at temperatures as low as 150–250 °C gives $Co^{II}Co^{III}_2O_4$ spinel phases.^{71,72} In addition to oxidation by calcination in air, they have also shown that calcination of $Co^{II}/Co^{III}-NO_3$ LDHs in an oxygen-free atmosphere can also afford $Co^{II}Co^{III}_2O_4$ spinel phases; in this case, the interlayer nitrate anions act as oxidant.⁷³ The formation of spinel phases of the type $Mg_xCo^{II}_{1-x}Co^{III}_2O_4$ ($x = 0.0–0.9$) by low-temperature (<300 °C) calcination of $Mg/Co^{II}/Co^{III}$ LDH phases has also been reported.^{74,75}

We have been particularly interested in the use of iron-containing LDHs as precursors to ferrite spinels, which are amongst the most widely used magnetic materials.⁷⁶ The efficacy of these materials depends on their microstructural properties which are sensitive to the mode of preparation.⁶⁶ To take magnesium ferrite, $MgFe_2O_4$, as an example, the conventional ceramic method of preparation⁷⁷ involves calcination of mixtures of precursors (MgO or $MgCO_3$ and Fe_2O_3) at temperatures of 1100 °C or above. High temperatures are required in order to prepare a single homogeneous phase but if the temperature is too high there can be problems with phase separation and non-stoichiometry.⁷⁸ A variety of wet chemical methods have also been proposed, including coprecipitation from aqueous solution, sol–gel synthesis and use of micellar microemulsions; in these cases however, it is difficult to prevent contamination of the product by cations from the precipitants or organic residues from the precursors.⁷⁹ We have reported⁸⁰ the preparation of LDHs of the type $[Mg_{1-x-y}Fe^{II}_yFe^{III}_x(OH)_2]^{x+}(CO_3^{2-})_{x/2} \cdot yH_2O$. These are precursors to pure spinels when $(1 - x - y):(x + y) = 0.5$, since the Fe^{2+} ions are oxidized on calcination in air to give Fe^{3+} ions, thus overcoming the deficiency of trivalent ions. The saturation magnetization of the spinel produced in this way has a much higher value ($\sigma_s = 34.6 \text{ emu g}^{-1}$) than that of

$MgFe_2O_4$ produced by conventional ceramic methods (26.4 emu g^{-1}).

LDHs possess several advantages as a precursor to ferrite spinels which are responsible for the enhanced saturation magnetization. Use of a single precursor with the cations uniformly distributed facilitates the synthesis of a homogeneous spinel phase. The close structural relationship between the LDH precursor and its calcination products is also a key factor. Rebourt *et al.* have shown⁶⁷ that the poorly crystalline mixed metal oxide obtained by collapse of the layered structure on heating an LDH at around 400 °C can best be described as a spinel-like phase. This phase preserves the particle morphology of the LDH,⁸¹ suggesting a topotactic transformation. Indeed, on further heating, the (110) reflection of the LDH transforms to the (440) spinel reflection in a topotactic manner.⁶⁷ The structural formula of magnesium ferrite is usually written as $(Mg_{1-c}Fe^{III}_c)[Mg_cFe^{III}_{2-c}]_4\{O^{2-}\}_4$, where the round and square brackets denote sites of tetrahedral (A) and octahedral [B] coordination respectively and where c represents the degree of inversion.⁷⁷ In an idealized topotactic transformation, the metal ions in the LDH layers undergo a diffusionless transformation to the spinel phase, in which one third of the metal ions change their octahedral coordination to tetrahedral with retention of their original statistical distribution.^{74,82,83} In this case the spinel derived from the LDH precursor with $Mg:(Fe^{II} + Fe^{III}) = 0.5$ would be expected to have the formula $(Mg_{0.33}Fe_{0.67})[Mg_{0.67}Fe_{1.33}]_4O_4$, which is close to the experimental value calculated from the relative areas of the Mössbauer subspectra *viz.* $(Mg_{0.29}Fe_{0.71})[Mg_{0.71}Fe_{1.29}]_4O_4$; this supports the hypothesis of a topotactic transformation.

Furthermore the fact that the spinel is produced from a single solid precursor rather than a mixture of two or more precursors means that the calcination process requires a much shorter time, leading to a lower chance of side-reactions occurring. We have also extended this process to other spinels⁸⁴ such as $CoFe_2O_4$ and $NiFe_2O_4$. In each case, the saturation magnetization of the as-prepared ferrites is significantly higher than that of ferrites made by conventional methods.

We have also reported⁸⁵ an alternative way of producing LDH precursors with M^{II}/Fe^{III} ratios appropriate for formation of MFe_2O_4 spinel ferrites involving intercalation of iron-containing guests such as $[Fe(CN)_6]^{3-}$. On calcination, the iron from the interlayer anions is incorporated in the spinel phase along with the iron originally in the layers and is not converted to a separate iron oxide phase.

A third method of preparing pure spinel phases from LDHs involves exploiting the amphoteric nature of zinc oxide in order to overcome the mismatch in M^{II}/M^{III} ratios between LDHs and spinels. We have shown⁸⁶ that $Zn/Fe^{III}-SO_4$ LDHs with different Zn/Fe^{III} ratios can be prepared from zinc and iron(II) precursors. Calcination at 500 °C or higher affords a mixture of ZnO (zincite) and $ZnFe_2O_4$ spinel phases. The former may be removed by dissolution in aqueous $NaOH$ resulting in the formation of a pure zinc ferrite phase. Removal of ZnO is accompanied by substantial increases in both surface area and pore volume. Magnetic measurements and Mössbauer spectroscopy indicate that the zinc ferrite has the thermodynamically stable normal spinel structure, which is

antiferromagnetic; no evidence of a metastable ferrimagnetic phase⁸⁷ was obtained. Although the magnetic properties are comparable to those of a sample of zinc ferrite prepared by a conventional co-precipitation route followed by calcination under the same conditions, the new method gives a material which is a superior catalyst for the photocatalytic degradation of phenol with an active lifetime longer than that of the zinc ferrite prepared by the conventional route.⁸⁶ In the latter case, loss of activity is believed to result from adsorption of intermediate oxidation products such as hydroquinone, catechol and benzoquinone which inhibits phenol adsorption. Competitive adsorption of these intermediate products is presumably less significant in the case of the LDH-derived zinc ferrite as a consequence of its higher porosity, which allows for easier diffusion of these products away from the initial adsorption site. The LDH-derived zinc ferrite also exhibits a higher selectivity to low molecular weight oxidation products than the co-precipitated catalyst.

Applications of LDHs in biology and medicine

Recently, considerable attention has been focused on the intercalation of biomolecules into LDHs.⁸⁸ In addition to pharmaceuticals and enzymes which are discussed in more detail below, these include amino acids and peptides,^{18,89,90} vitamins,⁹¹ DNA and other nucleosides,^{92–95} ATP,⁹⁶ and polysaccharides such as alginate,³¹ chitosan³² and carrageenans.⁹⁷ Choy and co-workers have demonstrated that nano-sized LDHs can be effective delivery carriers for drugs and genes by hybridization with DNA and c-antisense oligonucleotide (As-myc).⁹⁸ A strong suppression of cell growth (65%) was observed when HL-60 leukemia cells were incubated with 20 μM (As-myc)–LDH hybrid. The LDH itself was found to be non-cytotoxic against HL-60 cells. Consequently, LDHs can act as a new type of inorganic carrier that is completely different from existing nonviral vectors in terms of its chemical bonding and structure. Recently, Choy *et al.* also reported that bioinorganic DNA–LDH nanohybrids could be used as a genetic molecular coding system⁹⁹ and a molecular-level coding method utilizing DNA base pairs as code units was systemized. The system consists of four steps: encoding, encrypting, decrypting and decoding. The nanohybrids were found to provide a potential solution to the inherent problems that hamper DNA molecular coding systems. In addition, LDHs are able to concentrate selectively and organize organic molecules.^{100–102} For example, Pitsch *et al.* reported that glycolaldehyde phosphate intercalated in LDHs from highly dilute aqueous solution can condense to racemic aldotetrose-2,4-diphosphates and aldohexose-2,4,6-triphosphates,¹⁰² which has led to speculation about the possible role of LDHs in chemical evolution and the origins of life.

In general, most biomolecules are chiral and their optical activity is readily lost by racemization under relatively mild conditions.¹⁰³ As is well known, the chirality usually influences the properties and efficacy of drugs; as a rule, one enantiomer has the desired therapeutic effect whilst the other has none, or is even harmful. Methods of conserving the chirality of bioactive materials have therefore been widely investigated.¹⁰³ We have studied the effect of intercalation in LDHs on the rate of

racemization of chiral species. For example, L-Tyrosine (4-hydroxyphenylalanine, represented as L-Tyr) is a non-essential amino acid that is normally synthesized in the body from phenylalanine. Deficiencies in L-Tyr have been associated with depression and L-Tyr supplements in the diet have shown a beneficial effect.¹⁰⁴ L-Tyr is also used in the treatment of dementia, vitiligo and in easing the adverse effects of stress.¹⁰⁵ In addition to racemization, L-Tyr also undergoes oxidation to a quinone¹⁰⁶ and intercalation of the amino acid in an LDH host may reduce the rate of both of these processes. The structure of L-Tyr is very similar to that of pharmaceuticals used in the treatment of Parkinson's disease such as L-dopa (L-3,4-dihydroxyphenylalanine); the amino acid can therefore also serve as model for the more expensive drugs in intercalation studies.

We have shown¹⁰⁷ that intercalation of L-Tyr into NiAl, MgAl and ZnAl LDHs by coprecipitation stabilized the amino acid with respect to racemization under the influence of sunlight, high temperature and ultraviolet light. The layered host may therefore have potential application as a “molecular container” for storing or transporting unstable chiral biomolecules or pharmaceutical agents. The thermal decomposition of the L-Tyr intercalated NiAl-LDH was investigated in detail by means of *in situ* HT-XRD, *in situ* FT-IR and TG-DTA. Loss of interlayer water occurs between room temperature and 150 °C while decomposition of intercalated L-tyrosine and dehydroxylation of the host layers begin at about 250 °C and 300 °C respectively.

We have found that such *in situ* studies can give valuable information about the decomposition of LDHs intercalated with organic guests. Conventional *ex situ* studies have the disadvantage that mixed oxides derived from LDHs may rehydrate and reconstruct to the original structure at ambient temperature in air.¹⁰⁸ *In situ* IR spectroscopy has previously been employed to provide structural information about the dehydroxylation and decarbonation processes in LDHs.¹⁰⁸ High-temperature XRD has been used as an *in situ* technique to investigate the decomposition and reconstruction mechanism of Mg/Al–CO₃ LDHs,¹⁰⁹ and thermally metastable phases not observed by conventional XRD were characterized.

Temperature-programmed reduction (TPR), temperature-programmed desorption (TPD), and temperature-programmed decomposition (TPDE) are powerful techniques used widely in the study of catalysts and surface mediated reactions.¹¹⁰ As most intercalated LDHs release volatile products during thermolysis and TPDE measurements reflect that with a characteristic chromatograph signal, the technique may provide considerable insight into the nature of the decomposition process. Furthermore, GC-MS can be used to analyze the composition of the evolved gas. We recently reported¹¹¹ the first example of the use of combined TPDE and GC-MS measurements in the investigation of intercalated LDH species with the aim of providing more evidence about the nature of the decomposition process than is available from conventional thermogravimetry-differential thermal analysis (TG-DTA). We chose to investigate the mechanism of thermolysis of L-aspartic acid (L-Asp) intercalated in Mg/Al-LDHs. The thermolysis of L-Asp LDH was found to be quite different from that of the pristine L-Asp and characterized by

three steps: the first from room temperature to 150 °C can be attributed to the loss of both adsorbed and interlayer water, accompanied by the destruction of the hydrogen bonding network and a decrease in basal spacing; the second step (250–350 °C) involves the polymerization and deamination of L-Asp ions in the interlayer of LDH and dehydroxylation of the brucite-like layers; the third step in the temperature range 350–450 °C corresponds to dehydroxylation of the brucite-like layers as well as further decomposition of interlayer materials. Solid-state ^{13}C MAS NMR spectroscopy confirms that polymerization is the only reaction occurring when L-Asp is heated at 220 °C, while both polymerization and deamination of L-Asp ions in the interlayer of LDH take place after calcination at the same temperature. These observations may indicate that constriction of the L-Asp anions in the limited interlayer space of LDHs results in different chemical properties.

We have also shown by means of similar *in situ* studies that the thermal stability of other biomolecules such as (+)-6-methoxy- α -methyl-2-naphthalene acetic acid (naproxen)¹¹² and cyclodextrins¹¹³ can be increased by intercalation in LDH matrices.

The earliest medical applications of LDHs were mainly as antacid and antipepsin agents.^{114,115} They have also been suggested for the removal of phosphate anions from the gastrointestinal fluid with the aim of preventing hyperphosphatemia.¹¹⁶ LDHs have other potential applications in medicine however, especially in pharmaceutical formulations. Current trends in pharmaceutical technology require formulations to be able to maintain pharmacologically active drug levels for long periods avoiding repeated administration, and/or to localize the drug release at its pharmaceutical target. The interlayer region of LDHs may be considered a microvessel in which an anionic drug may be intercalated and protected from the action of light and oxygen as discussed above. After administration of the intercalation compound, the drug may be released *via* a deintercalation process, occurring because of ion-exchange or displacement reactions. The rate of drug diffusion out of the LDH intercalation compound will depend on the strength of the host–guest interaction, the rigidity of the layers and the diffusion path length.

The viability of this approach has been demonstrated in our laboratory and elsewhere. For example, a variety of anionic drug molecules, including members of the non-steroidal anti-inflammatory drug (NSAIDs) family such as ibuprofen,¹¹⁷ indomethacin¹¹⁸ and fenbufen¹¹⁹ as well as 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP)¹²⁰ which is a drug for osteoporosis, have been intercalated into Mg/Al LDHs. In the case of ibuprofen (IBU), for example, Ambrogi *et al.*¹¹⁷ compared the results of dissolution tests for LDH-intercalated IBU at pH 7.5 with those obtained using a physical mixture of LDH-Cl and IBU as well as the commercial formulation Neo-Mindol (containing ibuprofen sodium salt), in simulated intestinal fluid. It was found that the latter two samples gave an immediate release of total drug content, whilst LDH-IBU released 60% of the drug after 20 min and 100% after 100 min. They suggested that the mechanism of modified drug release was based on the ion-exchange process of the IBU anion intercalated in the lamellar host and phosphates contained in

the buffer solution used as model intestinal fluid. In another example, O'Hare and co-workers intercalated a series of pharmaceutically active compounds including diclofenac, gemfibrozil, IBU, naproxen, 2-propylpentanoic acid, 4-biphenylacetic acid and tolfenamic acid into LDHs.¹²¹ Their results confirm that the intercalation of pharmaceutically active compounds that form stable anions is a feasible approach for the storage and subsequent controlled release of bioactive agents

As a consequence of their basic character however, unmodified LDHs are unsuitable as a practical oral drug delivery system because they will be destroyed in the stomach where the pH is 1.2. We have recently prepared¹²² a core-shell material as a drug delivery system. An LDH intercalated with a non-steroidal anti-inflammatory drug, fenbufen, as the core was coated with enteric polymers, Eudragit[®] S100 or Eudragit[®] L100, as a shell, giving a composite material which shows effective controlled release of the drug under *in vitro* conditions which model the passage of a material through the gastrointestinal tract, suggesting the potential practical applicability of LDHs in orally-administered controlled release drug delivery systems.

There has also been recent interest in using tailored LDHs as supports for immobilization of enzymes. We have shown²⁵ that penicillin G acylase (PGA) may be immobilized in an LDH pre-pillared with glutamate anions. Subsequent reaction of the amino groups of the immobilized glutamate ions with a glutaraldehyde linker followed by addition of PGA affords the immobilized enzyme. The activity, thermal stability, pH stability and operational stability of the immobilized enzyme in the hydrolysis of penicillin G solution were assayed. It was found that the immobilized enzyme has better thermal stability and acid resistance than native enzyme. It has also been demonstrated that another enzyme, lipase, may be immobilized in LDHs which have been pre-expanded with surfactants such as sodium dodecyl sulfate¹²³ or dioctyl sodium sulfosuccinate.¹²⁴ The activity of the enzyme in the esterification of oleic acid with 1-butanol was assayed and it was found that both thermal stability and resistance to organic solvents such as hexane was enhanced after immobilization.

Electrochemical sensors have been increasingly important in continuous monitoring in health care and environmental applications. Mousty and co-workers¹²⁵ have shown that enzymes immobilized on LDHs are attractive materials for use in such electrochemical sensors. Thus urea biosensors have been developed by immobilization of urease within LDHs¹²⁶ and the co-immobilization of glucose oxidase and horseradish peroxidase in a redox-active Zn/Cr-LDH pre-intercalated with 2,2'-azinobis(3-ethylbenzothiazoline-6-sulfonate) gives a material which can be employed in the determination of glucose.¹²⁷ Finally, a comparison of LDHs and laponite, a synthetic cationic clay, as supports for biosensors based on polyphenol oxidase showed that the LDH support was superior in terms of both sensitivity and storage stability.¹²⁸

Conclusions

In this article we have demonstrated how the physical and chemical properties of layered double hydroxides may be

tailored to produce functional materials with the properties required for specific applications. Control of particle size and its distribution during the synthesis procedure facilitates the formation of materials which are highly effective as polymer additives for applications such as heat retention in horticultural films. The broad range of compositional flexibility of both layers and interlayer galleries facilitates the preparation of multifunctional materials with applications in a wide diversity of areas such as flame retardants with high smoke suppressing properties and PVC stabilizers. Furthermore, the fact that the cations in the layers are uniformly distributed without 'lakes' of separate cations being formed, leads to their effective use as precursors to magnetic spinel-type materials. Finally, their generally non-toxic natures allows the formulation of materials with applications in the storage, delivery and controlled release of pharmaceuticals and other biomolecules.

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