Towards understanding, control and application of layered double hydroxide chemistry†

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Layered double hydroxides (LDHs) have a vast number of potential applications in fields as diverse as separation chemistry, polymer additives and catalysis. They are facile and cheap to prepare, and are environmentally friendly. In this paper, some of the most exciting recent developments in LDH chemistry are discussed, with an emphasis on how we can control their chemistry and how in situ techniques can provide enhanced understanding of the nanoscopic processes involved in intercalation reactions.

1. Introduction

Layered double hydroxides (LDHs) are an unusual family of layered materials consisting of positively charged layers with charge balancing anions between the layers. The latter can be replaced by other species through an anion exchange process. Most LDHs may be represented by the formula $[M_2^{2+}M_3^{3+}(OH)_6]^{+\text{X}_1/2}$, for instance $[\text{Mg}_2\text{Al(OH)}_6]^{\text{NO}_3^{2-}}\gamma\text{H}_2\text{O}$ and $[\text{Ca}_2\text{Al(OH)}_6]^{\text{NO}_3^{2-}}\gamma\text{H}_2\text{O}$. These materials have a number of attractive properties including shape-selective ion exchange, and catalytic activity. Several excellent reviews on LDH chemistry have recently been published, and the interested reader is referred to these for more background information.

At present, little is known about the nanoscopic processes involved in intercalation. This is because few methods have been developed to monitor solid-state reactions in situ. Quenching studies (in which an aliquot of the reaction suspension is removed and the solid product recovered through filtration) have frequently proved to be unreliable. The material isolated is often atypical of the reaction matrix as a whole, having been affected by the quenching process. A non-invasive probe which can interrogate a typical intercalation process is required. It is also necessary to employ rapid data collection times in order that kinetic information may be obtained. X-Ray powder diffraction is a highly appropriate tool. It is non-invasive, and is a powerful characterisation technique when used in combination with ex situ analyses.

For in situ studies, the technique of energy dispersive X-ray diffraction (EDXRD) is employed. This allows the simultaneous observation of a wide range of $d$-spacings in as little as 10 s, even with small sample sizes. The simultaneous observation of the host material, any intermediate phases, and the product is possible. From these data, both qualitative and quantitative information regarding the mechanism and kinetics of a reaction can be obtained. A wide variety of reactions have been monitored using EDXRD, including the intercalation reactions of LDHs. Full details of the

† The HTML version of this article has been enhanced with colour images.

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Dermot O’Hare studied at Oxford University where he was awarded a BA in 1982 and a DPhil in 1985. Following his DPhil he was awarded a Royal Commission of 1851 Fellowship. After a year at CR&D Dupont, he returned to Oxford in 1987, being appointed to a permanent University position and fellowship at Balliol College in 1990. In 1998 he became a Professor. He has won a number of awards, including the Royal Society of Chemistry Sir Edward Frankland Fellowship, the Exxon European Chemical and Engineering Prize and the RSC Corday Morgan Medal and Prize. His scientific interests are wide ranging, including synthetic organometallic chemistry, intercalation chemistry, in situ diffraction studies and the synthesis of meso- and micro-porous solids.
EDXRD method, and of the models generally used to describe solid-state reaction processes, have been discussed in a recent review.\textsuperscript{12}

In this Feature Article, some highlights from recent research into LDHs will be showcased, with particular reference to how these data have afforded us an increased understanding of LDH chemistry, and how this may be exploited and controlled for advanced applications.

2. New synthetic methodologies

The exploration of new synthetic routes to produce novel LDHs and to gain morphological control of the LDH particles produced will be discussed in this section.

2.1 Forcing conditions

LDHs are generally synthesised \textit{via} a coprecipitation route, involving the combination of mixtures of metal salts with pH control. In contrast, the family of LDHs [LiAl\(_2\)(OH)\(_6\)]\(_x\)\(\cdot\)\(_y\)H\(_2\)O (LiAl\(_2\)-X) is generally synthesised by the direct reaction of concentrated solutions of Li salts with Al(OH)\(_3\). Use of the gibbsite polymorph of Al(OH)\(_3\) yields an LDH in which the layers are stacked in an \textit{aba} sequence (the hexagonal form, h-LiAl\(_2\)-X). Use of the bayerite or nordstrandite polymorphs, however, produces a rhombohedral form of the LDH (r-LiAl\(_2\)-X) with an \textit{abca} layer stacking sequence.\textsuperscript{20–23} It will be seen later that this difference in layer stacking sequences is surprisingly important in the chemistry of the LiAl\(_2\)-X systems.

It proved very difficult to intercalate cations other than Li into Al(OH)\(_3\). However, Fogg \textit{et al.} recently showed that gibbsite may be activated by grinding in a ring or ball mill. When the activated Al(OH)\(_3\) is treated hydrothermally with a highly concentrated solution of a metal (M = Co, Ni, Cu and Zn) nitrate (10 M), a new family of LDHs is produced.\textsuperscript{24} These are structurally similar to the h-LiAl\(_2\)-X LDHs, except that only half the octahedral vacancies in the Al(OH)\(_3\) layers are filled after reaction: the new materials have the unprecedented composition \[\text{MAl}_4\text{(OH)}\text{NO}_3\text{]}\_y\text{H}_2\text{O} (\text{MAl}_4\text{-NO}_3).\] There are ordered cation vacancies in the layers (Fig. 1). The ion exchange chemistry of these materials has been thoroughly investigated, and is found to be similar to, but distinct from, that of the LiAl\(_2\)-X systems.\textsuperscript{25,26}

2.2 Morphological control

Modifying the traditional coprecipitation method of LDH synthesis is of interest, since this method produces an inhomogeneous distribution of particle sizes and shapes. Reverse micelle/microemulsion systems have been used to produce LDHs with novel particle morphologies.\textsuperscript{27,28} When a surfactant such as sodium dodecyl sulfate (NaDDS) is added to an organic solvent (e.g. isooctane), spherical reverse micelles will form with the hydrophobic chains pointing out into the solvent, and the hydrophilic heads clustered together. The addition of water causes the reverse micelles to swell, with water droplets trapped inside the polar core. These can be utilised as ‘nanoreactors’. Hu and O’Hare\textsuperscript{27} discovered that by dispersing a solution of Mg nitrate, Al nitrate, Na nitrate and NaOH into an isooctane/1-butanol/NaDDS system led to the synthesis of Mg\(_2\)Al LDHs with a novel ‘nanoplatelet’ morphology [Fig. 2(a)]. Modification of the synthesis by adding a triblock copolymer \[\text{HO(C}_2\text{H}_4\text{O)}\_n\text{(C}_3\text{H}_6\text{O)}\_m\text{(C}_2\text{H}_4\text{O)}\_n\text{H}\] at different stages of the reaction caused further changes in the morphology of the particles produced. Addition of the polymer at the start of the reaction led to structures with a belt-like morphology [Fig. 2(b)], whereas adding it after heating for 24 h produced rod-like structures [Fig. 2(c) and (d)].

From elemental microanalysis and EDX analysis, all three different morphologies were found to have the approximate formula [Mg\(_2\)Al(OH)\(_6\)]\(_y\)\(\cdot\)\(_2\)H\(_2\)O. The X-ray diffraction patterns were all consistent with the DDS anions being intercalated between the layers, giving an interlayer separation of ca. 26 Å. The nanoplatelets consist of 3–4 monolayers stacked together, and are approximately 200–300 Å in diameter. These platelets stack together into larger blocks without a specific morphology. The belt structures are a few hundred microns along the long axis; the cross-sectional dimensions are...
ca. 10 × 3 μm. The LDH layers are stacked perpendicular to the long axis. The rod-like structures are a few tens of microns in length, and a few hundred nanometres perpendicular to the long axis. The rods feature layers stacked along the long axis. The belts in particular can be easily exfoliated.

The control of particle size and morphology is potentially of high importance for the production of nanocomposites, where one requires a stable, uniform dispersion of the inorganic component in the polymer matrix.

Several authors have achieved this by intercalation of macromolecules, and then exfoliation of the LDH. However, this can be difficult owing to the strength of the interactions between LDH layers. By modifying the ratios of the reactants used in the reverse microemulsion synthesis, O’Hare and co-workers have successfully synthesised LDH monolayers. These exist as particles of ca. 15 Å in height, and diameters of approximately 400 Å (Fig. 3).

The monolayers have the formula [Mg2Al(OH)6](DDS)yH2O. This suggests that the particles observed by AFM consist of single LDH layers coated in DDS anions to balance the charge. The monolayers can easily form stable dispersions in acrylate monomers. Hence, the development of homogenous LDH–polymer nanocomposites with improved properties should be possible.

Duan and co-workers adopted a different approach in their attempt to control LDH particle sizes and morphologies. A colloidal mill (Fig. 4) was employed to synthesise LDHs with separate nucleation and aging steps (SNAS). In the SNAS method, the different metal salts are mixed very rapidly in the mill (<2 min). The resultant slurry is subsequently aged. Thus, all the particles begin to form at the same time, and the growth time is the same for all particles. This is in contrast to standard coprecipitation methods, in which the solutions of the two metal salts are combined slowly: in this method the particles precipitate out at different times, and hence a range of particle sizes and morphologies are produced.

The SNAS method produces LDHs [e.g. [Mg2Al(OH)6]2-CO3:yH2O] with high crystallinity, and a much narrower range of particle sizes and shapes than those produced via a traditional coprecipitation approach.

### 3. Understanding intercalation

In order that we can begin to control reactions, tailoring the conditions to give desired outcomes, it is necessary to understand the intimate processes involved in intercalation. The EDXRD technique has been successfully employed to gain these insights.

#### 3.1 Kinetics and energetics

In favourable instances, intercalation reactions can be monitored over a range of temperatures and accurately be described using classical models for solid-state reaction processes. This is often the case for reactions of LiAl2-X and of the [Ca2Al(OH)6]NO3:yH2O LDH (Ca2Al-NO3). In contrast, [Mg2Al(OH)6]NO3:yH2O (Mg2Al-NO3) is found to react very rapidly, which precludes the calculation of kinetic parameters. In situ techniques have been applied to other LDHs, but this can be difficult owing to poor crystallinity.

A number of bicyclic and tricyclic carboxylate intercalates of LiAl2-Cl, Mg2Al-NO3 and Ca2Al-NO3 have recently been synthesised by Khan and O’Hare, and the reaction mechanisms were probed using in situ EDXRD. Examples of the guests incorporated are given in Fig. 5. EDXRD data from the intercalation of 1-AA into h-LiAl2-Cl are given in Fig. 6. The reaction is seen to proceed directly from the host (h-LiAl2-Cl) to the product (h-LiAl2-1-NAA). Extent of reaction, \( z = \frac{\text{Intensity at time } t}{\text{maximum intensity}} \), for any given reflection. The data are fitted with the Avrami equation: \( z = 1 - \exp(-kt)^n \), where \( k \) is the rate constant, \( t \) is

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**Fig. 3** AFM image of the LDH monolayers. Individual particles are marked A–F. Reproduced with permission from Chem. Commun., 2006, 287. © Royal Society of Chemistry, 2006.

**Fig. 4** Schematic diagram of the colloidal mill used by Duan et al.

**Fig. 5** Examples of some cyclic carboxylates which have been intercalated: (a) 1-adamantane acetate (1-AA); (b) 5-norbornene-2-carboxylate (5-NC); (c) 1,3-adamantane diacetate (1,3-ADA).
The intercalation of a number of organic carboxylate \( (e.g. \text{1,4-benzenedicarboxylate}) \) and sulfonate \( (e.g. \text{1,5-naphthalenedisulfonate}) \) species into the novel MAI\(_2\)-NO\(_3\) LDHs has been investigated using EDXRD.\(^{25}\) It was discovered that in all cases bar one the reaction proceeds directly from the host to the product. The carboxylates were observed to react very quickly, with the products being formed within a few minutes at room temperature. The intercalation of maleate into CuAl\(_2\)-NO\(_3\) proceeded via a more hydrated intermediate; once this had formed some water was subsequently extruded to give the final product.

For MAI\(_2\)-NO\(_3\) \( (M = \text{Zn, Cu, Co}) \), the intercalation of sulfonates occurred much more slowly, taking \( ca. \) 30–60 min to reach completion at 50 °C. In contrast, the reactions of NiAl\(_2\)-NO\(_3\) with the organic sulfonates occurred much more rapidly, at similar rates to carboxylate intercalation.

Furthermore, the reaction mechanisms were found to be very different. In the \( M = \text{Zn, Cu and Co} \) systems, nucleation control is operational, and the rate-limiting step is the expansion of the interlayer spaces to accommodate the new guests. In the \( M = \text{Ni} \) case, the reaction is diffusion-controlled. As soon as the guest species reach the host they can intercalate: the reaction barrier being observed is that inhibiting movement of guests through the solvent (water).

### 3.2 Divergent mechanisms

In a number of cases, intercalation reactions occur too rapidly to be modelled using the Avrami equation. In such cases, one may still follow the reaction \textit{in situ} by adding a solution of the guest dropwise to a suspension of the host. This limits the rate of reaction to the rate of addition, and therefore no kinetic parameters may be calculated. However, mechanistic information may still be obtained. In fact, it turns out that a number of these rapid reactions are interesting mechanistically.

The energy barrier to an intercalation reaction may be reduced by a process known as staging. This is a phenomenon in which some interlayer regions are completely vacant while other regions are fully or partially occupied. The number of layers between successively filled or partially filled layers defines the order of staging. The traditional models describing staging involve the layers having a degree of flexibility.\(^{38,39}\) LDHs have relatively rigid layers,\(^{40}\) and so staging is rare.

Drits \textit{et al.}\(^ {41}\) have reported a hydrotalcite-based mineral found in a saline deposit in Soviet Central Asia that has interlayers which alternately contain SO\(_4^{2-}\) and CO\(_3^{2-}\).

Fogg \textit{et al.} discovered that the intercalation of a variety of carboxylic acids into h-LiAl\(_2\)-Cl proceeds via a then-unprecedented second-stage intermediate. This features alternate interlayer regions occupied by Cl\(^-\) and carboxylate anions [seen later in Fig. 11(b)].\(^ {42}\) Similar results have also been observed for the intercalation of some phosphonate anions into this LDH.\(^ {43,44}\) Data for the intercalation of methylphosphonate (MPA) at pH 8 are shown in Fig. 8. Methyl-, ethyl- and benzylphosphonate all intercalate via this two-stage mechanism, whereas phenylphosphonate intercalates in a direct, one-step mechanism. However, for the rhombohedral analogue, r-LiAl\(_2\)-Cl, a one-step mechanism is operational for the intercalation of all four phosphate anions.
Data for MPA are given in Fig. 9(a). Experiments were also performed with other LiAl$_2$-X materials (X = NO$_3$ and Br). It was observed that staging intermediates are never seen where X = NO$_3$ [Fig. 9(b) and (c)], but where X = Br, second-stage intermediates are formed with certain organic anions [MPA, fumarate and succinate in particular: Fig. 9(d)]. Therefore, both the interlayer anion and the stacking sequence of the layers play a profound role in determining the mechanism of the reaction.

In situ EDXRD studies have been performed to investigate this material: it was found that the formation of a second-stage product has a higher activation energy than the direct conversion of h-LiAl$_2$-Cl to the first-stage product, h-LiAl$_2$-4-NP (ca. 70 and 42 kJ mol$^{-1}$ respectively). This demonstrates unequivocally that the 4-NP heterostructure is a thermodynamically stable species, and that the alternating distribution of interlayer anions might be more properly described as interstratification rather than staging.

A recent collaboration between Leroux, Taviot-Guého and O’Hare has aimed to explore the chemistry of some second-stage materials. It was previously noted by Pisson et al. that second-stage intermediates are formed during the intercalation of succinate and tartrate into Zn$_2$Al-Cl, Zn$_2$Cr-Cl and Cu$_2$Cr-Cl.$^{35}$ After an in situ study, it proved possible to isolate the second-stage materials using a quenching approach. The chemistry of some second-stage intercalates of Zn$_2$Cr-Cl (Zn$_2$Cr-Cl/succ. and Zn$_2$Cr-Cl/tart.) was then investigated. In situ EDXRD was used to monitor the reactions of these systems with solutions of adipate and fluoride ions. A remarkable segregation effect was observed. When Zn$_2$Cr-Cl/succ. or Zn$_2$Cr-Cl/tart. were reacted with adipate, the adipate first replaces the organic succinate (tartrate) anions, forming a new second-stage intermediate, Zn$_2$Cr-Cl/adip. Upon continued addition of adipate, the Cl anions are replaced, and the product retrieved from the reaction is the first-stage adipate intercalate. This is shown in Fig. 10.

Experiments were also performed in which the second-stage Zn$_2$Cr-Cl/succ. and Zn$_2$Cr-Cl/tart. materials were reacted with a solution of F$^-$ ions. It was seen that the F$^-$ ions initially replace the chloride anions in the interlayer space, before replacing the organic species. These results are summarized schematically in Fig. 11. A remarkable segregation between the organic and inorganic ions is operational here.

A similar segregation phenomenon is observed for the 4-NP heterostructure; reaction of this with stoichiometric amounts of some carboxylates (e.g. phthalate) leads to the isolation of the h-LiAl$_2$-Cl/carboxylate second-stage intercalate.

4. LDHs for advanced applications

4.1 Bionanohybrids as storage and delivery matrices

Much of the interest in LDHs arises because of their potential in industrial applications. One principal area that has been the focus of intense research in recent years is the use of LDH host matrices as storage and delivery devices for biologically important species. A number of important bioactive species are based on carboxylic acids, and hence are suitable for intercalation into LDHs. Furthermore, the wide variety of cations that can comprise an LDH mean that it is facile to produce biocompatible materials.

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**Fig. 8** Time-resolved in situ EDXRD data showing the course of the ion exchange reaction between h-LiAl$_2$-Cl and MPA at pH 8: (a) 3D stacked plot and (b) extent of reaction vs. time plot showing the host 002 (■), intermediate 004 (▲) and product 002 (●) reflections. Reproduced with permission from Chem. Commun., 2003, 1816. © Royal Society of Chemistry, 2003.
A variety of drugs, including those in Fig. 12, have been incorporated into LDHs. It is a long-term goal of pharmaceutical scientists to develop so-called ‘controlled release formulations’ (CRFs). These are advantageous over current methods of drug delivery: instead of taking doses of the drug regularly at given time intervals, CRFs allow the patient to take only one tablet far less frequently. Delivery of the drug is slow and sustained, and an effective and non-toxic concentration of the drug may be retained in the body over a long period of time.

With traditional formulations, the drug concentration is in the effective region for a relatively short period of time, either side of which the concentration may be dangerously high or ineffectively low.

O’Hare and co-workers investigated drug intercalates of the h-LiAl₂-Cl, Mg₂Al-NO₃ and Ca₂Al-NO₃ materials as CRFs for release into the bowel. It was discovered that the host used had a profound effect on the release profile. The release of 4-biphenylacetic acid (4-Bip⁻) at pH 7.5 is shown in Fig. 13, and a summary of the release data for several drugs is given in Table 1.
Release occurs very much faster for Mg\textsubscript{2}Al-4-Bip than for the Ca-containing analogue. The effect of the host may also be seen in Table 1.

Choosing the right combination of host and guest allows the release time to be varied between 0.5 and 35 min. It is important to note that it is difficult to determine trends; the release data cannot be easily correlated to the charge density of the layers or to the size of the drug molecule. A number of competing factors are operational, and deconvoluting these is non-facile. However, the data do suggest that by employing the right combination of host and guest, release times in the order of hours (which is the target for these systems to be practically useful) could be attained.

Choy et al. have made very significant contributions to this area. Mg\textsubscript{2}Al-NO\textsubscript{3} was successfully employed to intercalate folic acid and methotrexate (MTX), both commonly used to treat cancer sufferers.\textsuperscript{50} An \textit{in vitro} bioassay was used to demonstrate that in the initial stages after administration of the drug, Mg\textsubscript{2}Al-MTX has a significantly higher efficacy.

![Fig. 11](image1.png)

**Fig. 11** Schematic diagram illustrating the selective intercalation chemistry of the Zn\textsubscript{2}Cr-Cl/succ. material. (a) Zn\textsubscript{2}Cr-Cl/adip., synthesised through reaction of Zn\textsubscript{2}Cr-Cl/succ. with adipate; (b) Zn\textsubscript{2}Cr-Cl/succ.; (c) Zn\textsubscript{2}Cr-Fl/succ., produced \textit{via} the reaction of Zn\textsubscript{2}Cr-Cl/succ. with fluoride.

![Fig. 12](image2.png)

**Fig. 12** Some of the drug molecules which have been intercalated into LDHs: (a) 4-biphenylacetic acid; (b) Diclofenac; (c) Gemfibrozil; (d) 2-propylpentanoic acid.

![Fig. 13](image3.png)

**Fig. 13** Profiles for the release of 4-Bip\textsuperscript{2-} from Ca\textsubscript{2}Al-4-Bip (■) and Mg\textsubscript{2}Al-4-Bip (●) into simulated intestinal fluid (pH = 7.5).

![Fig. 13](image4.png)

**Fig. 13** Profiles for the release of 4-Bip\textsuperscript{2-} from Ca\textsubscript{2}Al-4-Bip (■) and Mg\textsubscript{2}Al-4-Bip (●) into simulated intestinal fluid (pH = 7.5).

**Table 1** Release data for selected drug ions at pH 7.5. The data given are the time (min) taken for 90% of the intercalated drug to be released.

<table>
<thead>
<tr>
<th>Drug, X</th>
<th>LiAl\textsubscript{2}-X</th>
<th>Mg\textsubscript{2}Al-X</th>
<th>Ca\textsubscript{2}Al-X</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diclofenac</td>
<td>4</td>
<td>22</td>
<td>6</td>
</tr>
<tr>
<td>Gemfibrozil</td>
<td>5</td>
<td>12</td>
<td>35</td>
</tr>
<tr>
<td>Ibuprofen</td>
<td>2.5</td>
<td>13</td>
<td>12</td>
</tr>
<tr>
<td>Tolufenamic acid</td>
<td>21</td>
<td>0.5</td>
<td>20</td>
</tr>
<tr>
<td>Naproxen</td>
<td>9</td>
<td>2.5</td>
<td>5.5</td>
</tr>
<tr>
<td>4-Biphenylacetic acid</td>
<td>2</td>
<td>2</td>
<td>15</td>
</tr>
</tbody>
</table>
against tumor cells than MTX alone. This could be because the LDH matrix allows MTX to pass through the cell membrane more effectively, and also prevents decomposition of the drug in the cell plasma. However, it is not clear exactly how this could occur. The LDH is not simply acting as a delivery matrix, but is also improving the efficiency of the drug. A novel recent development is the synthesis of LDHs intercalated with β-cyclodextrins. These bowl-like molecules can be used to contain lipophilic drug molecules, thereby increasing the stability, water solubility and bio-availability of these drugs.

Nucleotides and DNA have also been intercalated into LDHs. Data from cellular uptake experiments show the transfer efficiency of the bionanohybrids to be as much as 25-fold greater than that of the nucleotide alone. Further experiments have shown that vitamins may also be intercalated and discharged in a controlled fashion. In vivo studies have determined that LDH particles have little systematic effect at low doses, and thus are likely to be suitable as drug delivery matrices.

O’Hare and co-workers have studied the intercalation of a number of agrochemicals, such as those in Fig. 14. Similarly to the intercalation of drugs, modification of the host and guest led to widely different release profiles. It was generally observed that release occurs more slowly from the LiAl2-X intercalates than from the Mg2Al-X and Ca2Al-X analogues. Studies are ongoing to optimise the materials for industrial applications.

4.2 Possibilities in separation science

Interestingly, LDHs have been shown to be highly effective for separating mixtures of isomeric guest ions. For instance, Fogg et al. observed that if h-LiAl2-Cl is reacted with an equimolar mixture of 1,2-, 1,3- and 1,4-benzenedicarboxylate (BDC), 1,4-BDC is intercalated with close to 100% selectivity, and the other anions remain in solution. Analogous results were obtained with a mixture of fumarate and maleate, where the intercalate contained only fumarate. Additionally, Millange et al. discovered that Ca2Al-NO3 can also effect the separation of 1,2- and 1,4-BDC; only the 1,4-BDC anions are intercalated. In situ EDXRD was used to determine that the selectivity is governed by thermodynamic factors. Initially, all the guest isomers intercalate, and subsequently the less favourable guest(s) are de-intercalated, and replaced by the thermodynamically favoured species.

Further work has revealed that this selective property is very general, and LDHs may be used to separate large numbers of isomeric organic species, including naphthalenesulfonates, pyridinecarboxylates, and toluate isomers. A very recent study considered all the possible isomers of a variety of substituted benzoates (XC8H4COO-, where X = F, Cl, Br, OH, OMe, NO2, CO2Me, NH2, NMe2). Reactions were performed with a range of isomeric mixtures, and it was noted that generally the selectivity series is 4-isomer > 3-isomer > 2-isomer. Molecular modelling was used to determine the dipole moments of each of the guests; the 4-isomer has the greatest dipole moment and the 2-isomer the smallest. It is postulated that the greater the difference in the dipole moments of the isomeric guests, the higher the selectivity for the isomer with the greatest dipole moment. A greater dipole moment is likely to lead to stronger electrostatic interactions between the host and guest.

The new LDHs MAl4-NO3 have been investigated for their selective properties. All four materials show broadly similar selectivity trends to the related LiAl2-Cl system. 1,4-BDC is intercalated with almost 100% selectivity over the 1,2-isomer. Similarly, 2-naphthalenesulfonate (NS) is intercalated almost exclusively over 1-NS. Reactions were investigated over a range of temperatures (rt to 100 °C) using several solvent systems (water, water/acetone and water/THF), which were shown to cause subtle changes to the selectivity. More interestingly, the competitive intercalation of 1,5 and 2,6-naphthalenedisulfonate (NDS) was found to be highly sensitive to the temperature and solvent used for reaction. For the ZnAl4-NO3 system, in water at room temperature the intercalate contains ca. 55% 2,6-NDS. However, when the reaction is performed at 100 °C, the selectivity for 2,6-NDS is only 27% (Fig. 15). Using a water–acetone mixture (1:1) at 100 °C reduces the amount of 2,6-NDS incorporated even further to 7%. Similar results have been seen for LiAl2-Cl, Mg2Al-NO3 and Ca2Al-NO3.

These separations are facile to perform, and the LDHs used are easy and cheap to make. This approach to separation...
should be amenable to large-scale application, and is therefore very attractive to industry. It should be emphasised that the high degree of separation of the isomers achievable is of great industrial importance. For instance, the 1,4-isomer of benzenedicarboxylate is the monomer used for polyester synthesis. Benzenedicarboxylates are produced from the oxidation of xylenes derived from crude oil. These xylenes are produced in mixtures. The separation of the useful 1,4-isomer from other species is therefore vital. At the present time, this is normally achieved by selective crystallisation or adsorption of the xylene isomers. However, these methods are relatively ineffective. Naphthalenesulfonates are important organic synthons. They are produced in a similar way to the benzenedicarboxylates, and their separation is also very difficult to achieve using conventional methods.

Another important class of raw materials for industry which are commonly synthesised as mixtures are nitrophenols (NPs). These are used in the manufacture of pharmaceuticals, dyestuffs and agrochemicals, among other applications. It has recently been demonstrated that h-LiAl₂Cl may be used to selectively remove 4-nitrophenolate from a mixture of the 2-, 3- and 4-isomers. Studies were also performed into the feasibility of using this system to separate mixtures of 4-NP and 2,4-dinitrophenolate. The solvent and host LDH used had a significant effect on the selectivity observed.

4.3 Improved polymers

The desirability of producing LDHs with small, regularly sized particles was stressed in Section 2.2. It has been found that LDHs synthesised using the SNAS process are more effective additives for polymers than those synthesised commercially. For instance, in Asia, low density polyethylene is frequently used in the manufacture of greenhouses. Duan and co-workers have performed field trials using polymers with different additives: the mineral talc, a commercially available LDH, and additives for polymers than those synthesised commercially. For instance, in Asia, low density polyethylene is frequently used in the manufacture of greenhouses. Duan and co-workers have performed field trials using polymers with different additives: the mineral talc, a commercially available LDH, and an LDH prepared using the SNAS method. It was found that both the daily maximum and minimum temperatures are produced in a similar way to the benzenedicarboxylates, and their separation is also very difficult to achieve using conventional methods.

Another important class of raw materials for industry which are commonly synthesised as mixtures are nitrophenols (NPs). These are used in the manufacture of pharmaceuticals, dyestuffs and agrochemicals, among other applications. It has recently been demonstrated that h-LiAl₂Cl may be used to selectively remove 4-nitrophenolate from a mixture of the 2-, 3- and 4-isomers. Studies were also performed into the feasibility of using this system to separate mixtures of 4-NP and 2,4-dinitrophenolate. The solvent and host LDH used had a significant effect on the selectivity observed.

**Conclusions**

It has been shown that by systematic modification of the synthesis strategy, LDHs with novel stoichiometries and particle morphologies and sizes may be formed. This latter development is of profound importance for the generation of polymers with improved physicochemical properties. It has frequently been proven that the composition of the LDH layers alters the chemistry of the materials, and hence a new family of LDHs is also of immense importance. The use of X-ray diffraction to study the intercalation reactions of LDHs in situ, in real time, has produced some significant insights into the reaction mechanisms. In general, the reactions proceed directly from the host to the product, and the rate-limiting step is the expansion of the interlayer space to accommodate the new guests. In a few cases where the reaction proceeds very rapidly at room temperature, however, the reaction proceeds via an unusual second-stage intermediate. The stacking sequence of the layers and the initial interlayer anion are seen to have a profound effect on the mechanism of intercalation into LiAl₂-X systems. The second-stage materials are of interest for the preparation of multifunctional materials. Finally, the potential to use LDHs in pharmaceutical and agrochemical applications, as well as in separation science and as polymer additives, has been demonstrated.

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**References**