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The formation of ordered heterostructures during the intercalation of phosphonic acids into a layered double hydroxide

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The intercalation reactions have been studied using *in situ* energy dispersive X-ray diffraction; ordered second stage heterostructures were observed as intermediate phases, which is almost unprecedented for rigid layer host materials.

Layered double hydroxides (LDHs) are represented by the general formula $[M^{z+}_{1-x}M^{3+}_{x}(OH)_2]^{p+}(X^{n-})_{p/n}\cdot mH_2O$. Usually, $z = 2$; the exception to this is $[LiAl_2(OH)_6]X\cdot H_2O$. LDHs are superb ion exchange materials, and they find application in diverse areas such as heterogeneous catalysis,[1,2] separation science,[3–6] optical materials,[7,8] and as DNA reservoirs.[9,10]

Over recent years we have developed the use of energy dispersive X-ray diffraction (EDXRD) to carry out time-resolved, *in situ* diffraction studies on a range of intercalation reactions.[11–14] Using synchrotron radiation we are able to measure the complete powder XRD patterns of heterogeneous reaction mixtures in seconds. The time dependence of the integrated Bragg intensity data allows us to quantitatively determine the kinetics of the reaction; this technique also gives us the opportunity to observe any crystalline phases which may form during the course of these reactions.

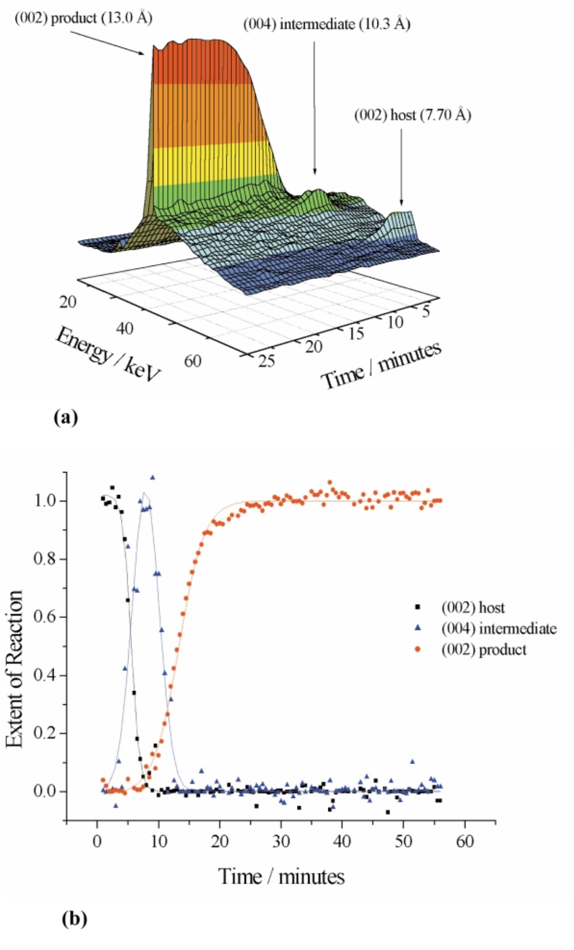

Fig. 1 Data showing the intercalation of methylphosphonic acid into $[LiAl_2(OH)_6]Cl\cdot H_2O$: **(a)** 3D stacked plot of the raw data (in EDXRD $d = \{hc\}/\{2E \sin\theta\}$) and **(b)** 2D plot showing the evolution in intensity of the host, intermediate and product peaks as calculated from the integrated intensities of the key Bragg reflections. The extent of reaction (α) is defined to be I_t/I_{max} where I_t is the intensity of a given peak at a time t and I_{max} is the maximum intensity of this peak.

Here we report a series of *in situ* EDXRD studies of the ion exchange intercalation of a number of phosphonic acids into the LDH $[LiAl_2(OH)_6]Cl\cdot H_2O$. Addition of 1.5 equivalents of either methyl, ethyl, phenyl or benzylphosphonic acid to a suspension of $[LiAl_2(OH)_6]Cl\cdot H_2O$ at pH 8 leads to rapid ion-exchange intercalation of the phosphonate anions. The products are isolated by filtration, and washed with an excess of deionised water and acetone. They have all been characterised by conventional powder X-ray diffraction, solid state ^{31}P NMR, transmission electron microscopy, elemental analysis, thermogravimetric analysis and infrared spectroscopy. The interlayer spacing ranges from 12.7 Å for methylphosphonic acid to 16.9 Å for benzylphosphonic acid. All the data are consistent with complete ion-exchange of the chloride ions and formation of monolayers of the phosphonic acid ions between the $[LiAl_2(OH)_6]^+$ layers.

The solid state ^{31}P MAS NMR spectra of the new intercalates exhibit single ^{31}P resonances. The chemical shift in each case is intermediate between the shifts expected for the mono- and dianionic forms of the relevant phosphonic acids. The data suggest that there is fast proton exchange between the co-intercalated mono- and dianions. In the case of methylphosphonic acid (MPA) the ^{31}P chemical shift suggests that the $MePO_3H^-$: $MePO_3^{2-}$ ratio is *ca.* 2 : 1. Combining the spectroscopic and analytic data we can derive the chemical composition to be $[Li_{0.84}Al_2(OH)_6](MePO_3)_{0.19}(MePO_3H)_{0.46}\cdot 2.6H_2O$.

The rates of intercalation of the different phosphonic acids into this LDH have also been determined. At room temperature the $t_{1/2}$ values range from less than 30 s to 160 s for methylphosphonic acid and phenylphosphonic acid respectively. Detailed analyses of the crystallisation growth curves suggest that these are 2D diffusion controlled reactions.

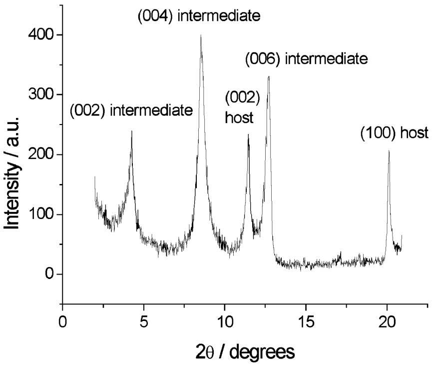

Fig. 2 Powder XRD pattern of a quenched sample showing the presence of a second stage intermediate in the intercalation of MPA.

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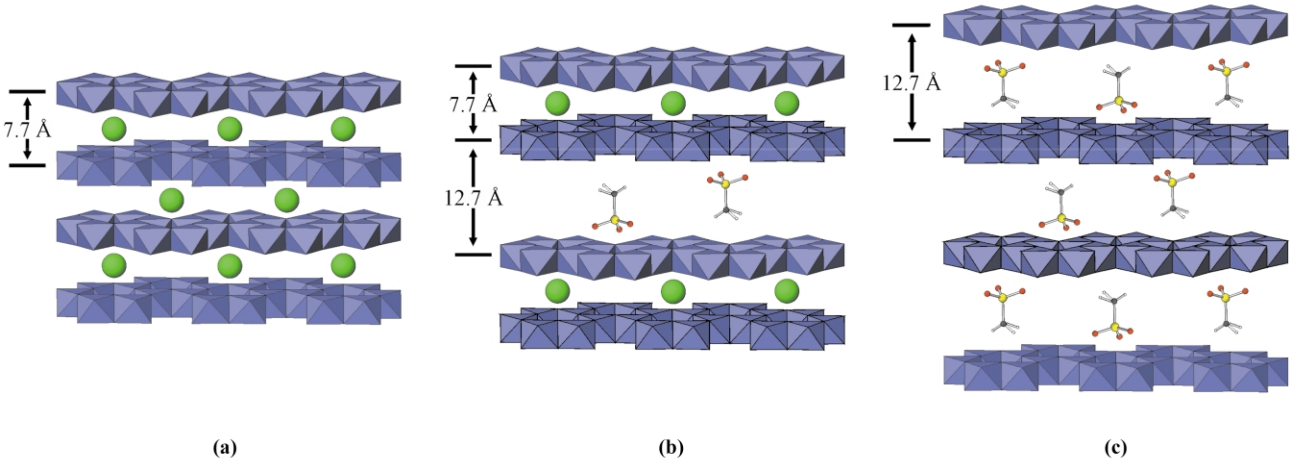

Fig. 3 Schematic showing the intercalation of methylphosphonic acid: **(a)** The host lattice, $[LiAl_2(OH)_6]Cl{\cdot}H_2O$; **(b)** the second stage intermediate with alternate layers occupied by methylphosphonic acid and Cl^- anions; **(c)** the first stage product with all interlayer regions occupied by methylphosphonic acid.

We have monitored the intercalation reactions while slowly adding a solution of the phosphonic acid guest species to a suspension of the host. This slow addition limits the rate of reaction to the speed of guest addition, which we hoped would facilitate the observation of transient intermediate phases. Fig. 1 shows the *in situ* EDXRD data obtained when MPA was slowly added to a suspension of $[LiAl_2(OH)_6]Cl{\cdot}H_2O$ in water at pH 8.

Remarkably, the data reveal that the intercalation reaction proceeds from the host to the product *via* a transient crystalline intermediate phase. For MPA intercalation in $[LiAl_2(OH)_6]Cl{\cdot}H_2O$ the intermediate is fully formed after about 8 min.

In the laboratory we have repeated these experiments and quenched the reaction when the concentration of the intermediate phase should be greatest. The powder XRD spectrum of the quenched material is shown in Fig. 2. The major Bragg reflections can be indexed on a cell with a *c*-parameter of 40.8 Å. Hence, d_{002} = 20.4 Å. This value is consistent with the formation of a structure in which the methylphosphonic acid is only intercalated between every other LDH layer. Such a material would be predicted to have a d_{002} equal to the sum of d_{002} of $[Li_{0.84}Al_2(OH)_6](MePO_3)_{0.19}(MePO_3H)_{0.46}{\cdot}2.6H_2O$ (12.7 Å) and d_{002} of the host, $[LiAl_2(OH)_6]Cl{\cdot}H_2O$ (7.7 Å). The elemental analysis of the isolated phase shows it to contain both Cl and phosphonic acid, in the approximate ratio 1 : 1, again consistent with a second stage intermediate.

The phenomenon in which some regions of a layered host material are fully or partially occupied by guest molecules while other regions are empty is commonly referred to as staging. The *n*th stage intercalate has every *n*th layer occupied by guest; the intermediate discussed above is therefore a 2nd stage intercalate. Staging compounds can form as intermediates where the fully intercalated product is a first stage intercalate.

Staging was first observed in graphite and has been studied in great detail. The accepted Dumas–Herold model of staging in graphite has the guest ions populating each layer equally but forming ordered domains by bending the graphite layers. In rigid layered hosts, bending of the layers is not possible, and it is thought that ordered heterostructures such as that shown in Fig. 3(b) must be forming. This behaviour is extremely rare in rigid layered hosts such as LDHs, having been seen only once before with the intercalation of dicarboxylates into $[LiAl_2(OH)_6]Cl{\cdot}H_2O$.[14] In addition, the transient nature of the intermediates often makes them hard to detect, so rapid *in situ* EDXRD studies were critical for our observation of this behaviour. A schematic showing the intercalation of methylphosphonic acid is presented in Fig. 3.

The intercalation of benzylphosphonic acid was also followed using *in situ* EDXRD. Again, the reaction was observed to proceed from the host to the first stage product *via* a second stage intermediate. After filtration and washing, the product was determined by powder XRD to have an interlayer spacing of 16.9 Å. The formula was determined to be $[Li_{0.89}Al_2(OH)_6](PhCH_2PO_3)_{0.15}(PhCH_2PO_3H)_{0.58}{\cdot}2.2H_2O$ by elemental analysis. Quenching the reaction where the concentration of intermediate is expected to be greatest allows isolation of a phase with a *d*-spacing of 23.5 Å, which is again consistent with a second stage intermediate.

In summary, the intercalations of phosphonic acids into the layered double hydroxide $[LiAl_2(OH)_6]Cl{\cdot}H_2O$ are diffusion controlled reactions and in the cases of methyl and benzylphosphonic acids proceed *via* a crystalline intermediate. Initially an ordered heterostructure is formed in which alternate layers are occupied by guest phosphonate anions and Cl^-. This intermediate is then converted into a fully intercalated first stage product.

Notes and references

1 V. R. L. Constantino and T. J. Pinnavaia, *Catal. Lett.*, 1994, **23**, 361.
2 A. Corma, V. Fornes, F. Fey, A. Cervilla, E. Llopis and A. Ribera, *J. Catal.*, 1995, **152**, 237.
3 A. M. Fogg, J. S. Dunn, S.-G. Shyu, D. R. Cary and D. O'Hare, *Chem. Mater.*, 1998, **10**, 351.
4 A. M. Fogg, V. M. Green, H. G. Harvey and D. O'Hare, *Adv. Mater.*, 1999, **11**, 1466.
5 L. Lei, F. Millange, R. I. Walton and D. O'Hare, *J. Mater. Chem.*, 2000, **10**, 1881.
6 F. Millange, R. I. Walton, L. X. Lei and D. O'Hare, *Chem. Mater.*, 2000, **12**, 1990.
7 H. Tagaya, S. Sato, T. Kuwuhara, J. Kadokawa, K. Masa and K. Chiba, *J. Mater. Chem.*, 1994, **4**, 1907.
8 M. Ogawa and K. Kuroda, *Chem. Rev.*, 1995, **95**, 399.
9 J. H. Choy, S. Y. Kwak, Y. J. Jeong and J. S. Park, *Angew. Chem., Int. Ed.*, 2000, **39**, 4042.
10 J. H. Choy, J. S. Park, S. Y. Kwak, Y. J. Jeong and Y. S. Han, *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A*, 2000, **341**, 425.
11 A. M. Fogg and D. O'Hare, *Chem. Mater.*, 1999, **11**, 1771.
12 D. O'Hare, J. S. O. Evans, A. Fogg and S. O'Brien, *Polyhedron*, 2000, **19**, 297.
13 J. S. O. Evans, S. J. Price, H. V. Wong and D. O'Hare, *J. Am. Chem. Soc.*, 1998, **120**, 10837.
14 A. M. Fogg, J. S. Dunn and D. O'Hare, *Chem. Mater.*, 1998, **10**, 356.