Efficient Separation of Terephthalate and Phthalate Anions by Selective Ion-Exchange Intercalation in the Layered Double Hydroxide $Ca_2Al(OH)_6 \cdot NO_3 \cdot 2H_2O$

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The brucite-like Ca^{2+}/Al^{3+} layered double hydroxide (LDH), $Ca_2Al(OH)_6 \cdot NO_3 \cdot 2H_2O$, was synthesized using the coprecipitation method. The dicarboxylate anion 1,4-benzenedicarboxylate can be selectively intercalated into the layered double hydroxide $Ca_2Al(OH)_6 \cdot NO_3 \cdot 2H_2O$ from an aqueous solution containing an equimolar mixture of the 1,2- and 1,4-benzenedicarboxylates. Time-resolved in situ energy-dispersive X-ray diffraction studies of the competitive intercalation reaction reveal that initially both the 1,2- and the 1,4-benzenedicarboxylates are intercalated in the LDH, followed by replacement of the 1,2-benzenedicarboxylate by the 1,4-isomer as the reaction proceeds. The final thermodynamic product is $Ca_2Al(OH)_6 \cdot [1,4\text{-}C_8H_4O_4]_{0.5} \cdot xH_2O$.

Introduction

Layered materials that are able to intercalate neutral guest molecules or to exchange interlayer inorganic or organic anions receive considerable attention. Although a variety of layered materials possessing cation-exchange properties are known (such as cationic clays or metal phosphates and phosphonates), layered materials that possess anion-exchange properties are comparatively rare.[1] Layered double hydroxides (LDHs) and synthetic anionic clays having hydrotalcite (HT) like structures have received attention in recent years due to their potential application in various technologies as anion exchangers, adsorbents, ionic conductors catalysts, and catalyst supports.[2−6] The structure of LDHs was first elucidated by Allmann for the MgFe-LDH (pyroaurite and sjögrenite)[7] and by Brown et al. for the MgAl-LDH (hydrotalcite and manasseite).[8] Layered double hydroxides can be structurally described as containing brucite ($Mg(OH)_2$) like layers in which some divalent metal cations have been substituted by trivalent ions to form positively charged sheets. The metal cations occupy the centers of octahedra whose vertices are hydroxide ions. These octahedra are connected to each other by edge sharing to form an infinite sheet. The cationic charge of the layers is compensated by the presence of hydrated anions between the stacked sheets.

LDHs can be represented by the general formula $[M^{II}_{(1-x)}M^{III}_{x}(OH)_2][A^{n-}_{x/n}] \cdot zH_2O$, where M^{II} and M^{III} are di- and trivalent metal cations, respectively, that occupy octahedral positions in hydroxide layers. The value of x ($x = M^{III}/(M^{II} + M^{III})$) ranges between 0.20 and 0.33 for the MgAl-LDH system,[9] and A^{n-} is the interlayer charge-compensating anion such as CO_3^{2-}, NO_3^{-}, Cl^{-}, etc. A large number of LDHs with a wide variety of $M^{II}-M^{III}$ cation pairs (e.g., Ca−Al) as well as an $M^{I}-M^{III}$ cation pair (e.g., Li−Al) with different anions in the interlayer and their physicochemical properties have been reported.[10−12]

The incorporation of organic guests into LDHs has received some attention previously, because of the potential uses of the inorganic−organic hybrids produced in catalysis, sorption, photochemistry, and electrochemistry.[13] The intercalation of anionic aromatic species has been the focus of several studies, and the uptake of naphthalenecarboxylate,[14] benzenedicarboxylate,[15] anthraquinonesulfonate,[16] and benxoate[17] by a variety of LDHs has been shown to occur efficiently. In this paper we describe a study of the intercalation properties of a CaAl-LDH, and report on the ability of the layered double hydroxide $Ca_2Al(OH)_6 \cdot NO_3 \cdot 2H_2O$ to undergo shape-selective intercalation reactions. $Ca_2Al(OH)_6 \cdot NO_3 \cdot 2H_2O$ has previously been shown to undergo a wide range of facile anion exchange reactions with a

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Table 1. Summary of the Elemental Microanalysis and Diffraction Data for the Intercalation Compounds

guest	stoichiometry	c lattice[a]/Å $d_{(002)}$/Å	elemental microanalysis obsd	elemental microanalysis calcd
NO_3^-	$Ca_2Al(OH)_6 \cdot NO_3 \cdot xH_2O$	$c = 17.4$	H, 3.31	H, 3.28
	$x \approx 2.0$	$d = 8.7$	N, 4.53	N, 4.56
1,2-BDA[b]	$Ca_2Al(OH)_6 \cdot [C_8H_4O_4]_{0.5} \cdot xH_2O$	$c = 29.6$, 21.8[c]	H, 4.40	H, 4.44
	$x \approx 4.0$	$d = 14.8$, 10.9[c]	C, 13.01	C, 13.22
1,4-BDA[b]	$Ca_2Al(OH)_6 \cdot [C_8H_4O_4]_{0.5} \cdot xH_2O$	$c = 26.8$	H, 4.39	H, 4.44
	$x \approx 4.0$	$d = 13.4$	C, 13.02	C, 13.22

[a] Based on a trigonal cell ($P\bar{3}c1$), a ≈ 5.74 Å. Values obtained from XRD data measurement on a Philips instrument. [b] BDA = benzenedicarboxylate. [c] The phase collapses on drying, giving a material with a c lattice of 21.8 Å [$d_{(002)} = 10.9$ Å].

variety of inorganic and organic guests.[18] benzenedicarboxylates are important starting materials in the synthesis of polyester polymers, and we have therefore investigated the possibility of separation of geometric isomers of the dicarboxylates, in particular the 1,4 (terephthalate) and 1,2 (phthalate) anions. In addition, we have studied the kinetics of these intercalation reactions using time-resolved in situ energy-dispersive X-ray diffraction.

Experimental Section

Synthesis of $Ca_2Al(OH)_6 \cdot NO_3 \cdot 2H_2O$. The starting LDH was prepared using the coprecipitation method at room temperature by reacting aqueous solutions containing a mixture of $Ca(NO_3)_2 \cdot 4H_2O$ (supplied by Aldrich) and $Al(NO_3)_3 \cdot 9H_2O$ (Aldrich) and a mixture of NaOH (BDH) and $NaNO_3$ (Aldrich) under a nitrogen atmosphere to avoid contamination by atmospheric CO_2. The Ca:Al atomic ratio in the starting solution was adjusted to 2.3:1. Typically, 17 g of $Ca(NO_3)_2 \cdot 4H_2O$ and 11.7 g of $Al(NO_3)_3 \cdot 9H_2O$ were mixed together in 80 mL of water, and the solution was added dropwise to a solution of 6.25 g of NaOH and 9.1 g of $NaNO_3$ in 44 mL water with vigorous stirring during precipitation. Once addition was completed, the resulting precipitate was stirred for 24 h at 80 °C. The solid was isolated by filtration and washed thoroughly with deionized water and acetone several times.

Synthesis of Benzenedicarboxylate Intercalates. The appropriate benzenedicarboxylic acid {$1,2\text{-}C_6H_4(CO_2H)_2$ and $1,4\text{-}C_6H_4(CO_2H)_2$} (supplied by Aldrich) was stirred with 1 equiv of NaOH in 5 mL of deionized water to prepare a solution of the disodium benzenedicarboxylate. A 150 mg sample of the $Ca_2Al(OH)_6 \cdot NO_3 \cdot 2H_2O$ host was then added to the solution (1.2-fold excess of the benzenedicarboxylate disodium salt), and the mixture was stirred overnight at 80 °C. The solid was isolated by filtration and washed thoroughly with water and acetone several times. Complete reaction was indicated by the absence of any Bragg peaks from the host lattice in the X-ray diffraction patterns and of nitrogen in the elemental microanalysis. A summary of the elemental microanalysis and X-ray diffraction data for the host and the intercalates is presented in Table 1.

Competitive Intercalation Reaction. For the competitive intercalation reaction, both benzenedicarboxylic acids and 2 equiv of NaOH were dissolved in 10 mL of deionized water to prepare a solution of the two disodium benzenedicarboxylates. A 150 mg sample of the $Ca_2Al(OH)_6 \cdot NO_3 \cdot 2H_2O$ host was then added to the solution, and the mixture was stirred overnight at 80 °C. The solid was isolated by filtration and washed thoroughly with water and acetone several times. The benzenedicarboxylate anions can be removed from the solid intercalate by ion exchange with Na_2CO_3. Typically, 150 mg of the intercalate was mixed with a 2-fold excess of Na_2CO_3 in 5 mL of D_2O, and the mixture was stirred at room temperature overnight. The suspension was then filtered and the filtrate retained for ^1H NMR studies (see below).

Materials Characterization. Powder X-ray diffraction (XRD) patterns were recorded on a Philips PW1710 diffractometer using Cu Kα radiation ($\lambda_1 = 1.5406$ Å and $\lambda_2 = 1.5444$ Å). For identification purposes, scans were performed at 0.02° (2θ) over the 2θ range 5−60° using 1 s/step.

^1H NMR spectra were recorded on a Brüker AM-300 spectrometer [^1H, 300 MHz]. Spectra were referenced internally using the residual solvent resonances relative to tetramethylsilane ($\delta = 0$ ppm).

The time-resolved in situ energy-dispersive X-ray diffraction (EDXRD) experiments were performed on Station 16.4 of the U.K. Synchrotron Radiation Source (SRS) at the Daresbury Laboratory, Cheshire. The SRS is a low-emission storage ring with an electron beam energy of 2 GeV. Station 16.4 receives usable X-ray flux in the range 15−120 keV with a maximum flux in the region of 3×10^{10} photons/s. EDXRD, using white-beam synchrotron-generated X-rays, permits the use of bulky sample cells because the high intensity of the incident radiation is sufficient to penetrate thick-walled vessels. Since diffraction data are measured by a fixed detector, only small windows are required for the passage of X-rays, and reaction cells can be constructed which resemble the laboratory apparatus in size and construction. Although the energy-discriminating detector is of inherently low resolution, the short data acquisition time (typically less than 1 min) allows the evolution or decay of well-resolved Bragg reflections to be monitored in real time, and thus kinetic data can be extracted for chemical processes under real reaction conditions. The experimental apparatus has been developed over a number of years by O'Hare et al. to allow the course of intercalation and hydrothermal reactions to be studied under real laboratory conditions using time-resolved in situ EDXRD.[19,20]

Results and Discussion

X-ray Powder Diffraction Data. The XRD pattern of the $Ca_2Al(OH)_6 \cdot NO_3 \cdot 2H_2O$ LDH (Figure 1) is similar to those previously reported by Reichle et al. for Mg/Al-LDHs.[21] This XRD pattern exhibits some common features of layered materials (e.g., narrow, symmetric, strong lines at low 2θ values and weaker, less symmetric lines at high 2θ values).[22] The (00l) reflections such as (002) and (004) are easily recognized. The (00l) reflections are characterized by high intensities combined with broad line shapes, indicating that the hydrotalcites are of relatively high crystallinity but form as very small crystallites. The diffraction maxima corresponding to diffraction by basal planes at 8.7 and 4.35 Å are similar to those previously reported in the literature and corresponding to a well-crystallized $Ca_2Al(OH)_6 \cdot NO_3 \cdot 2H_2O$ hydrotalcite-like structure.[23] Using the

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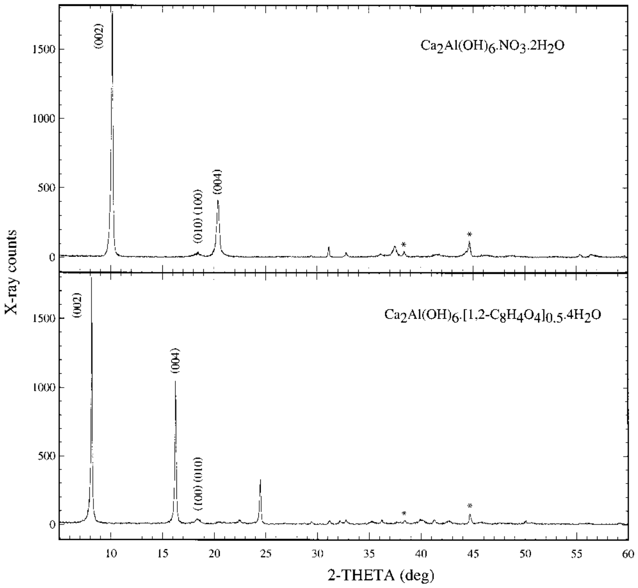

Figure 1. Powder X-ray diffraction patterns of $Ca_2Al(OH)_6 \cdot NO_3 \cdot 2H_2O$ (top) and $Ca_2Al(OH)_6 \cdot [1,2\text{-}C_8H_4O_4]_{0.5} \cdot 4H_2O$ (bottom). The asterisks indicate reflections due to the sample holder.

structure determined by Renaudin and Francois from single crystals of the compound, the lattice parameters were calculated as $c = 17.40(2)$ Å and $a = 5.74(1)$ Å in the space group $P\bar{3}c1$.[24] The former corresponds to 2 times the layer-to-layer distance, while the latter is related to the average metal−metal distance within the layers. The structure can be described by the stacking sequences of planes $-(NO_3^-,H_2O)-[Ca_4Al_2(OH)_{12}]^{2+}-(NO_3^-,H_2O)-$ parallel to the c axis. Two adjacent $[Ca_4Al_2(OH)_{12}]^{2+}$ layers are separated by a distance of 8.7 Å. The equivalent distance is only 7.55 Å in the carbonate intercalate.[24] This difference of 1.1 Å is due to the orientation of the planar anionic groups (perpendicular to the layer for NO_3^- and parallel to the layers for CO_3^{2-}).

Treatment of $Ca_2Al(OH)_6 \cdot NO_3 \cdot 2H_2O$ with an aqueous solution of the disodium salt of the phthalic acid (1,2-benzenedicarboxylic acid) yields the first-stage intercalate $Ca_2Al(OH)_6 \cdot [1,2\text{-}C_8H_4O_4]_{0.5} \cdot xH_2O$. The measured interlayer separation of 10.9 Å is consistent with the location of the guest ions between the $[Ca_2Al(OH)_6]^+$ layers. The XRD pattern of the $Ca_2Al(OH)_6 \cdot [1,2\text{-}C_8H_4O_4]_{0.5} \cdot xH_2O$ is shown in Figure 1. Similarly, treatment of $Ca_2Al(OH)_6 \cdot NO_3 \cdot 2H_2O$ with an aqueous solution of the disodium salt of the terephthalic acid (1,4-benzenedicarboxylic acid) yields the first-stage intercalate $Ca_2Al(OH)_6 \cdot [1,4\text{-}C_8H_4O_4]_{0.5} \cdot xH_2O$. The elemental microanalytical and diffraction data for the intercalates are summarized in Table 1.

Selective Ion-Exchange Reactions. When an equimolar aqueous solution of the phthalate and terephthalate disodium salts is stirred with a suspension of $Ca_2Al(OH)_6 \cdot NO_3 \cdot 2H_2O$ for 1 h, the X-ray powder diffraction pattern is very similar to that of a sample prepared by direct intercalation with pure disodium terephthalate. There is no evidence for any Bragg reflections assignable to the other intercalated phase. This observation suggests that the terephthalate anion is selectively intercalated in $Ca_2Al(OH)_6 \cdot NO_3 \cdot 2H_2O$.

The percentage of each isomer intercalated in $Ca_2Al(OH)_6 \cdot NO_3 \cdot 2H_2O$ during the competition reaction was determined by solution ^1H NMR. When the reaction is completed, the intercalated ions (terephthalate and/or phthalate) can be ion-exchanged out of the solid by addition of an aqueous solution of Na_2CO_3, yielding the carbonate intercalate $[Ca_2Al(OH)_6]_2 \cdot CO_3 \cdot 5H_2O$. Integration of the *CH* resonance assignable to each isomer of the solution ^1H NMR of the washing reaction was used to confirm the selectivity of the reaction and to quantify the relative amount of intercalation for each isomer. Thus, the selectivity for the terephthalate intercalation was estimated to be in excess of 95%.

We have also investigated the selective intercalation of these dicarboxylates using time-resolved in situ energy-dispersive X-ray diffraction. These experiments showed that the intercalation occurs very rapidly at 80 °C (completion reached in less than 2 min). It should be noted that the elevated temperature is required to produce a highly crystalline intercalate. To slow the reactions sufficiently to allow us to study them in detail, it was necessary to add the guest solution to an aqueous suspension of the host lattice in a dropwise manner via a syringe pump. While this experiment prevents us from a quantitative kinetic analysis of the data, it does reveal a number of important insights into these reactions. Figure 2a shows a 3D plot of EDXRD patterns as an aqueous solution of the disodium salt of the phthalic acid was added to $Ca_2Al(OH)_6 \cdot NO_3 \cdot 2H_2O$ at a rate of 0.1 mL min^{-1}. At the early stage of the reaction, the crystalline starting phase ($Ca_2Al(OH)_6 \cdot NO_3 \cdot 2H_2O$) is observed, which exhibits a Bragg reflection centered at 8.7 Å. On continued addition of the dicarboxylate ions, the first-stage intercalate $Ca_2Al(OH)_6 \cdot [1,2\text{-}C_8H_4O_4]_{0.5} \cdot xH_2O$ crystalline phase rapidly appears in the EDXRD. This material has an interlayer spacing of 14.8 Å corresponding to the (002) of the phthalate intercalate (it should be noted that the *d* spacing of this reflection changes when the material is dried; see Table 1). Continued addition of the phthalate solution results in the precipitation of a solid with a strongest Bragg reflection of 11.2 Å. Calcium phthalate, prepared by direct reaction between phthalic acid and calcium nitrate solution, exhibits its strongest Bragg reflection at exactly the same *d* spacing, and we suggest it is this compound that is formed on continued addition of phthalic acid. Figure 2b shows the normalized integration peak intensities of the reaction taking place. This illustrates the rapidity of the intercalation reaction and also that the phase with the 11.2 Å reflection is formed at the expense of the intercalate. The intercalate is clearly unstable in the presence of excess phthalic acid. Experiments in the laboratory confirmed this; if $Ca_2Al(OH)_6 \cdot NO_3 \cdot 2H_2O$ is stirred with a 10-fold excess of sodium phthalate ,then complete destruction of the LDH takes place. Identical behavior was observed with terephthalate.

Figure 3a shows a stack plot of EDXRD data obtained during a competition reaction using $Ca_2Al(OH)_6 \cdot NO_3 \cdot 2H_2O$ and an equimolar solution of sodium phthalate and sodium terephthalate at 80 °C (2 mole excess of

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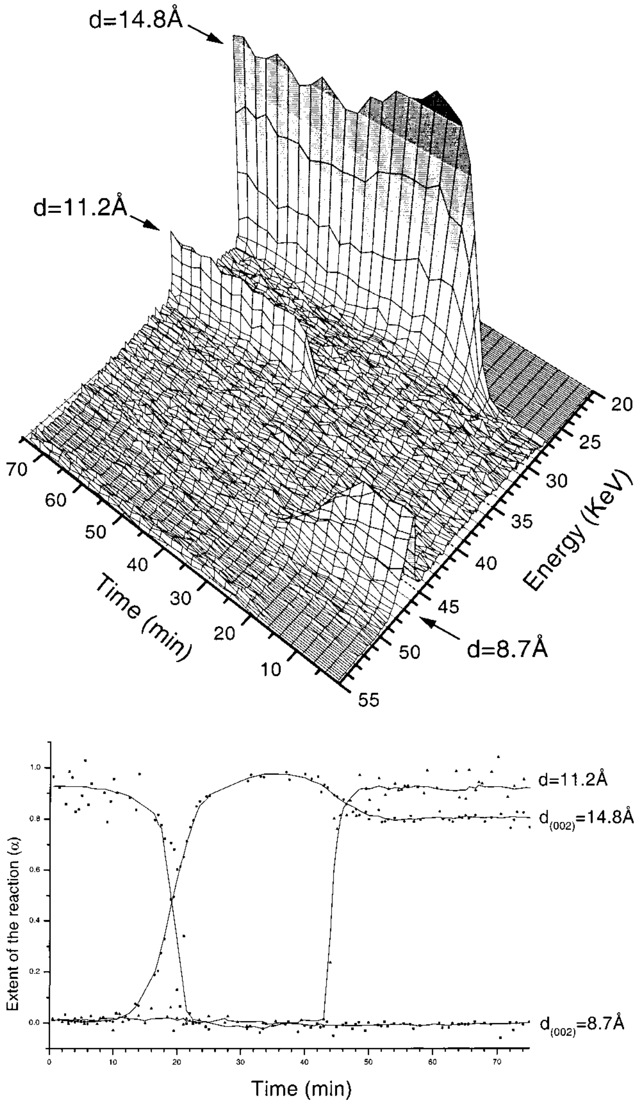

Figure 2. (a, top) 3D stacked plot showing the time-resolved, in situ EDXRD data recorded during the reaction between $Ca_2Al(OH)_6NO_3{\cdot}2H_2O$ and a solution of sodium 1,2-benzenedicarboxylate. (b, bottom) Extent of reaction vs time obtained by measurement of the integrated intensities of the Bragg reflection in the EDXRD for the reaction between $Ca_2Al(OH)_6NO_3{\cdot}2H_2O$ and a solution of 1,2-benzenedicarboxylate. ■ and ● indicate the intensities of the (002) reflection of the host and intercalate, respectively. ▲ indicates the strongest Bragg peak intensity of calcium phthalate.

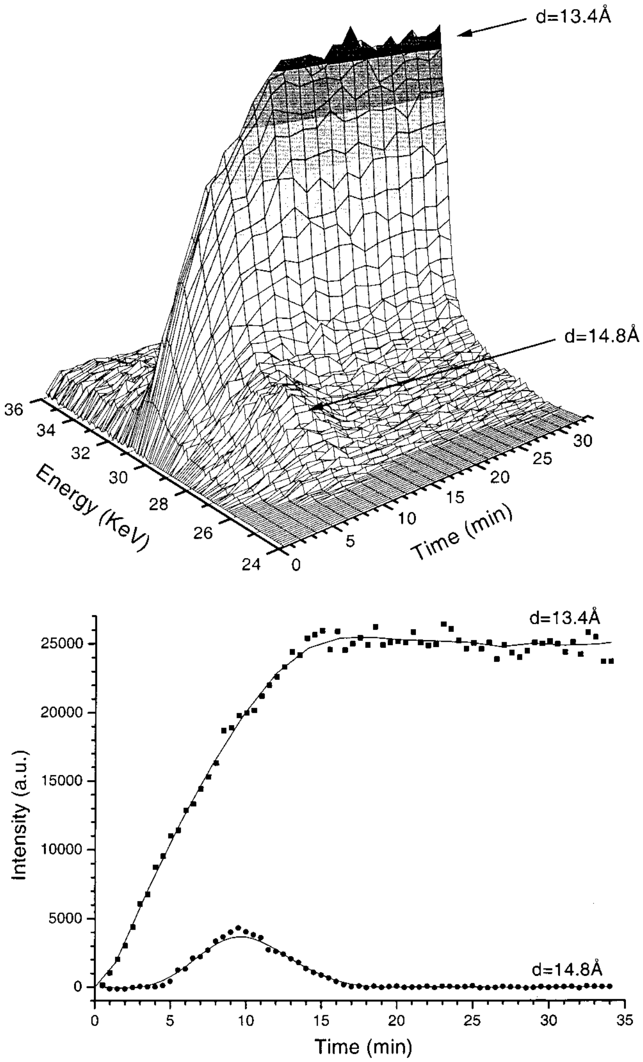

Figure 3. (a, top) 3D stacked plot showing the time-resolved, in situ EDXRD data recorded during the competition reaction between $Ca_2Al(OH)_6NO_3{\cdot}2H_2O$ and a solution of equimolar amounts of 1,2-benzenedicarboxylate and 1,4-benzenedicarboxylate. (b, bottom) Extent of reaction vs time obtained by measurement of the integrated intensities of the Bragg reflection in the EDXRD of the reaction between $Ca_2Al(OH)_6NO_3{\cdot}2H_2O$ and a solution of equimolar amounts of 1,2-benzenedicarboxylate and 1,4-benzenedicarboxylate. ■ and ● indicate the intensities of the (002) reflection of the terephthalate and phthalate intercalates, respectively.

each anion). A syringe pump was used to supply a solution of the benzenedicarboxylates to a suspension of the solid host at a rate of 0.1 mL min^{-1}. The reaction was found to be very rapid under these conditions, and the host Bragg reflection had decayed totally before data collection was commenced. Figure 3b shows the integrated peak intensities of the data. As soon as data collection is begun, Bragg reflections of two distinct intercalate phases (the terephthalate with a reflection at 13.4 Å and the phthlate with a reflection at 14.8 Å) appear and increase in intensity. The 14.8 Å Bragg reflection is present only for ~15 min total, while that of the terephthalate intercalate steadily increases in intensity and at the end of the process is the sole Bragg reflection observed. We deduce that, during the competition intercalation reaction between phthalate and terephthalate, two distinct intercalates are initially formed, but the phthalate intercalate is a kinetic product which undergoes exchange with the terephthalate in solution so that the ultimate sole product is the terephthalate intercalate. This proposed sequence is summarized in Figure 4.

Previous work in our group has shown that the lithium aluminum layered double hydroxide $[LiAl_2(OH)_6]Cl{\cdot}H_2O$ also exhibits selective ion-exchange reactions with dicarboxylate anions.[12] Work by others has shown that isomers of anthraquinone sulfonate may be selectively intercalated into ZnAl-LDHs.[16] The work described in this paper has allowed a model for a competition intercalation to be proposed. For the case of phthalate and terephthalate we propose that, for both hosts, the terephthalate intercalate is the thermodynamically more stable product, so separation of the two isomers is possible. We are currently investigating the intercalation behavior of other layered hydroxides and

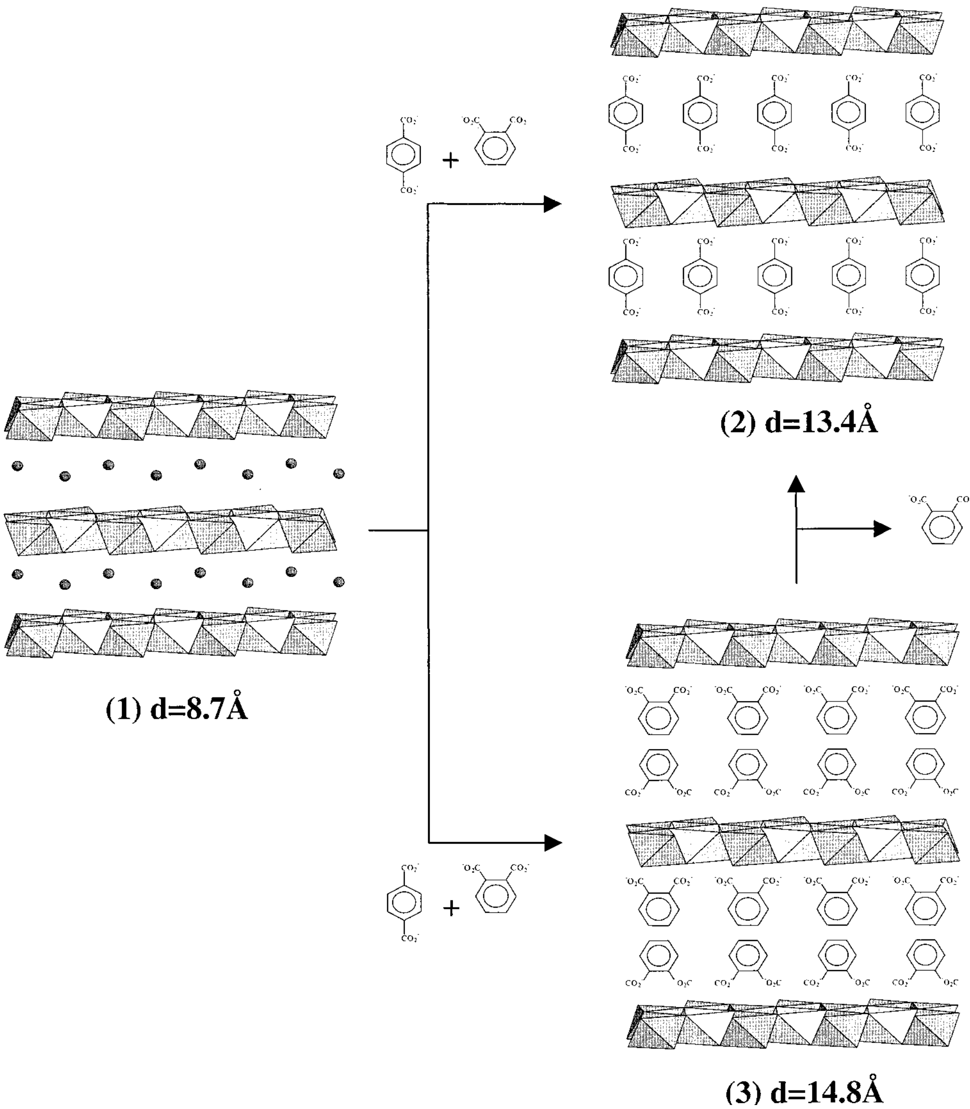

Figure 4. Schematic representation showing the kinetic $Ca_2Al(OH)_6 \cdot [1,2\text{-}C_8H_4O_4]_{0.5} \cdot 4H_2O$ (**3**) and thermodynamic $Ca_2Al(OH)_6 \cdot [1,4\text{-}C_8H_4O_4]_{0.5} \cdot 4H_2O$ (**2**) intercalate phases formed during the competition reaction with $Ca_2Al(OH)_6NO_3 \cdot 2H_2O$ (**1**).

extending our work to other dicarboxylates and solvents, with the aim of understanding the origin of the selectivity.

Summary

The layered double hydroxide $Ca_2Al(OH)_6 \cdot NO_3 \cdot 2H_2O$ undergoes selective ion exchange with a solution of 1,4- and 1,2-benzenedicarboxylate anions. The process gives >95% 1,4-benzenedicarboxylate intercalate, and thus provides an efficient low-temperature means of separation and also the purification of these isomers. Monitoring the process in situ using energy-dispersive X-ray diffraction reveals that initially both isomers are taken up by the layered double hydroxide to produce a mixture of two intercalate phases. The 1,2-benzenedicarboxylate intercalate phase is metastable in the reaction medium and undergoes further ion exchange with 1,4-benzenedicarboxylate anions to ultimately produce a pure 1,4-benzenedicarboxylate intercalate of the LDH.

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