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Journal of Solid State Chemistry 179 (2006) 3562–3567

JOURNAL OF SOLID STATE CHEMISTRY

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Alkaline hydrolysis of dimethyl terephthalate in the presence of $[\mathrm{LiAl_2(OH)_6}]\mathrm{Cl}\cdot 2\mathrm{H_2O}$

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Received 7 June 2006; received in revised form 10 July 2006; accepted 18 July 2006

Abstract

The alkaline hydrolysis of dimethyl terephthalate (DMT) in the presence of $[\mathrm{LiAl_2(OH)_6}]\mathrm{Cl}$ has been investigated to demonstrate a possible application of anion exchange facility of layered double hydroxides (LDHs) to control chemical reactions. The results show that (i) in the alkaline hydrolysis of DMT in the presence of $[\mathrm{LiAl_2(OH)_6}]\mathrm{Cl}$, most of the interlayer $\mathrm{Cl^-}$ of $[\mathrm{LiAl_2(OH)_6}]\mathrm{Cl}$ is quickly replaced by $\mathrm{OH^-}$ in the alkaline solution because the LDH host favors $\mathrm{OH^-}$ more; (ii) the alkaline hydrolysis of DMT in the presence of $[\mathrm{LiAl_2(OH)_6}]\mathrm{Cl}$ is faster than the reaction of DMT and $[\mathrm{LiAl_2(OH)_6}]\mathrm{OH}$; (iii) The hydrolysis of DMT in a buffer solution of $\mathrm{pH}\approx 8$ takes longer time to reach equilibrium than the alkaline hydrolysis of DMT in the presence of $[\mathrm{LiAl_2(OH)_6}]\mathrm{Cl}$. It is believed that the selective anion exchange chemistry of the LDH plays a key role in storage and controlled release of active reactant, that is, $\mathrm{OH^-}$, thus make the hydrolysis proceeds in a controlled way.

Keywords: Layered double hydroxide; Anion exchange; Dimethyl terephthalate; Hydrolysis; Reaction control

1. Introduction

Layered double hydroxides (LDHs) are formed by substitution of part bivalent metal in brucite-like $M(\mathrm{OH})_2$ for trivalent metal cations, or by intercalation of monovalent and bivalent cations into the vacancies in gibbsite, $\mathrm{Al(OH)_3}$ [1–4]. The former has a generalized formula of $[M_xM'_y(\mathrm{OH})_{2(x+y)}]^{y+}A^{n-}{}_{y/n}\cdot m\mathrm{H_2O}$, where M and M' are bivalent and trivalent metal cations, respectively, A^{n-} an interlayer anion with n negative charges, x, y, m are numbers; the latter has a formula of $[M^{n+}{}_x\mathrm{Al_2(OH)_6}]^{nx+}\ A^{m-}{}_{nx/m}\cdot l\mathrm{H_2O}$. When M is a monovalent cation, only $[\mathrm{LiAl_2(OH)_6}]A^{n-}{}_{1/n}\cdot m\mathrm{H_2O}$ have been found so far; when M is a bivalent cation, $[M\mathrm{Al_4(OH)_{12}}]A^{m-}_{2/m}\cdot l\mathrm{H_2O}$, where $M = \mathrm{Zn^{2+}}$, $\mathrm{Cu^{2+}}$, $\mathrm{Ni^{2+}}$ and $\mathrm{Co^{2+}}$ were synthesized [5]. The interlayer anions A^{n-} include a wide variety of inorganic or organic species, such as common inorganic anions ($\mathrm{Cl^-}$, $\mathrm{OH^-}$, $\mathrm{CO_3^{2-}}$, etc.), carboxylates [3] (include drug molecule [6]), complex anions [7], even $\mathrm{C_{60}}$ [8] and bioactivity molecules (such as nucleoside monophosphates [9], DNA molecules [10]).

Crystallographic researches reveal that LDHs have positively charged hydroxide layers which are formed by edge sharing of $[M(\mathrm{OH})_6]$ octahedra, in which there are strong chemical bonds and thus make the layers rigid to anion exchanges; interlayer anions to balance the positive charges, also, some co-crystallized water molecules. The hydroxide layer and interlayer components may be connected by electrostatic and/or van der Waals interactions and/or hydrogen bonds.

Those crystallographic arrangements make LDHs undergo a wide range of facile anion exchange reactions, which have already been used in many applications [11,12]. However, what has been interesting to us is that the anion exchange reactions have a high degree of selectivity, which can be used as novel separation chemistry, especially for separation of isomeric anions [11,13]. In this paper, we are trying to demonstrate that this selective anion exchange chemistry can also be used to control chemical reactions, the idea is as follows [1]:

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0022-4596/$ - see front matter
doi:10.1016/j.jssc.2006.07.038

It is a well-known fact that there are anionic reactants, products, byproducts, or intermediates in many of the known reactions. The anions may play very important roles, and therefore control of their concentration can lead to control of the whole reaction. On the other hand, those important anions may be sealed in the interlayer space of LDHs and thus be isolated from other reactants. Therefore, by adding a LDH into a reaction system and by selectively exchanging the important reactive anions into the interlayer space of the LDH, the reaction can be definitely controlled.

There are two ways to control reactions with the anionic reactant or product. Suppose a reaction with anionic reactant and product can be represented by

$$AY + Z^- \rightleftharpoons AZ + Y^-. \tag{1}$$

While the selective anion exchange reaction of a LDH can be represented by Eq. (2) (where LDH_X represents a LDH with an interlayer anion X):

$$\mathrm{LDH\_}X + W^- \rightleftharpoons \mathrm{LDH\_}W + X^-. \tag{2}$$

When X^- in Eq. (2) is Z^- in Eq. (1), the coupling of them two becomes:

$$AY + W^- + \mathrm{LDH\_}Z \rightleftharpoons AZ + Y^- + \mathrm{LDH\_}W. \tag{3}$$

Therefore, adding W^- makes Z^- being released in a controlled way, thus controls reaction (1). According to the sequence of the reactions, this is a controlled release-reaction process. This is the first way.

When W^- in Eq. (2) is Y^- in Eq. (1), the coupling of them will give

$$AY + Z^- + \mathrm{LDH\_}X \rightleftharpoons AZ + X^- + \mathrm{LDH\_}Y. \tag{4}$$

In that way, the anionic product of Eq. (1) is intercalated into the interlayer space and be isolated from reaction (1), thus decreasing the possibility of its reverse reaction and may also make the whole reaction faster. According to the sequence of the reactions, this is a reaction-intercalation separation process. This is the second way.

It should be remembered that W^- may be Y^- in reaction (3), and Z^- may be the same anion as X^- in reaction (4). In both cases, they make the same reaction as

$$AY + \mathrm{LDH\_}X \rightleftharpoons AX + \mathrm{LDH\_}Y. \tag{5}$$

In this paper, we would like to demonstrate this idea by the following reactions: the first one is the alkaline hydrolysis of dimethyl terephthalate (short as DMT, and the terephthalate anion is noted as TP^{2-}):

$$\mathrm{DMT} + 2\mathrm{OH}^- \rightarrow 2\mathrm{MeOH} + \mathrm{TP}^{2-}. \tag{6}$$

The second ones are the anion exchange reactions of $[LiAl_2(OH)_6]Cl \cdot 2H_2O$ (short as $LiAl_2$_Cl, similar notation is used for other interlayer anions in the following context. For example, $LiAl_2$_OH means $[LiAl_2(OH)_6]OH \cdot 2H_2O$). There are three possible reactions in this system:

$$[\mathrm{LiAl_2(OH)_6}]\mathrm{Cl} + \mathrm{OH}^- \rightleftharpoons [\mathrm{LiAl_2(OH)_6}]\mathrm{OH} + \mathrm{Cl}^-, \tag{7}$$

$$2[\mathrm{LiAl_2(OH)_6}]\mathrm{Cl} + \mathrm{TP}^{2-} \rightleftharpoons [\mathrm{LiAl_2(OH)_6}]_2\mathrm{TP} + 2\mathrm{Cl}^-, \tag{8}$$

$$2[\mathrm{LiAl_2(OH)_6}]\mathrm{OH} + \mathrm{TP}^{2-} \rightleftharpoons [\mathrm{LiAl_2(OH)_6}]_2\mathrm{TP} + 2\mathrm{OH}^-. \tag{9}$$

2. Experimental section

2.1. Reagents

All the starting materials used in this paper are of analytical reagent with a purity of better than 99%, and used without further treatments.

2.2. Measurements

Powder X-ray diffraction patterns were recorded on a Philips X'Pert Pro diffractometer equipped with X'celerator detector using CuKα radiation (40 kV, 40 mA); the electrical conductivity of the reaction mixtures was measured by using a Shanghai REX DDS-11A conductivity meter.

2.3. Synthesis of $[LiAl_2(OH)_6]Cl$

$[LiAl_2(OH)_6]Cl$ was prepared by using a reported method [14] with a little modification. Under nitrogen atmosphere, 10 g of $Al(OH)_3$ ($\approx$0.128 mol) was stirred with a solution of LiCl (30.98 g, $\approx$0.512 mol) in 60 mL of distilled water at 95 °C for 24 h. The solid was then isolated by filtration and washed three times with boiled distilled water and acetone and dried in a vacuum desiccator at room temperature.

2.4. Synthesis of $[LiAl_2(OH)_6]OH$

$[LiAl_2(OH)_6]OH$ was prepared with a similar method [15], in which $LiOH \cdot H_2O$ (13.55 g, $\approx$0.323 mol) in 50 mL of boiled distilled water replaced the solution of LiCl. After the mixture was stirred at 95 °C for 24 h, the solid was filtered out, washed and dried as above.

2.5. The alkaline hydrolysis of DMT and the abstraction of TP^{2-} by anion exchange reaction of $[LiAl_2(OH)_6]Cl$

Solid DMT of 297.7 mg was dissolved in 75 mL of 2:1 mixture solvent (v/v) of ethanol and water. Then, 122.6 mg of NaOH in 25 mL of the same solvent was added to the DMT solution as soon as possible. The mixture was kept at 30 or 70 °C under fine stirring, and its conductivity was measured until it does not change any more.

Then 663.5 mg of $[LiAl_2(OH)_6]Cl$ was added to the solution according to n(DMT): n(NaOH): n($[LiAl_2(OH)_6]Cl$) = 1:2:2 and stirred at the same temperature for 10 h. The solid was then filtered out, washed and dried as above.

2.6. Alkaline hydrolysis of DMT in the presence of $[LiAl_2(OH)_6]Cl$

In this reaction, the materials used are all the same as the above alkaline hydrolysis of DMT except $[LiAl_2(OH)_6]Cl$ was also added according to $n(DMT):n(NaOH):n([LiAl_2(OH)_6]Cl) = 1:2:2$. This design is to make the reactions take place under the same conditions. The difference is only that $[LiAl_2(OH)_6]Cl$ was added together with the solution of NaOH, and conductivity of the mixture was not followed because it was found that conductivity is no longer a good index for the reaction extent. The mixture was kept at 30 °C for 19 h, or was kept at 70 °C for 1, 2, 3, 4, 5, 6, 7, 8, 10, 11, 13, 14, 17, 19 h, respectively, and then the solid was filtered, washed and dried as above for XRD measurements.

2.7. Hydrolysis of DMT in a slightly alkaline buffer solution

Here, 26.6 mg of KH_2PO_4 and 1123.5 mg of Na_2HPO_4 were dissolved in 100 mL 2:1 mixture solvent (v/v) of ethanol and water to prepare a buffer solution. A total of 357.2 mg of solid DMT sample was dissolved in 20 mL of the same solvent, then was added to the buffer solution and stirred at 70 °C, and its conductivity was measured until it did not change any more.

2.8. Reaction of DMT with $[LiAl_2(OH)_6]OH$

Here, 120.8 mg of solid DMT sample was dissolved in 40 mL 2:1 mixture solvent (v/v) of ethanol and water, then 268.7 mg of $[LiAl_2(OH)_6]OH$ was added to the DMT solution according to $n(DMT): n([LiAl_2(OH)_6]OH) = 1:2$ and stirred for 48 h at 30 or 70 °C, respectively. The solid was then filtered out, washed and dried as above.

The above reaction was repeated with 72.7 mg NaCl added ($n(DMT):n(NaCl): n([LiAl_2(OH)_6]OH) = 1:2:2$ and all others remained unchanged.

3. Results and discussion

3.1. Characterization of $[LiAl_2(OH)_6]X$ ($X = Cl^-$ and OH^-)

Powder X-ray diffraction patterns of $[LiAl_2(OH)_6]Cl$ and $[LiAl_2(OH)_6]OH$ are shown in Fig. 1, in which the basal spacing of $[LiAl_2(OH)_6]Cl$, 0.77 nm is a little bit bigger than that of $[LiAl_2(OH)_6]OH$, 0.76 nm as expected (peaks are shifted towards lower 2θ angles). Both are the same as reported [14,15].

3.2. Characterization of the products obtained from the abstraction of TP^{2-} by anion exchange reaction of $[LiAl_2(OH)_6]Cl$

The alkaline hydrolysis (reaction 6) at both 30 and 70 °C had completed as it was indicated by conductivity measurements. $[LiAl_2(OH)_6]Cl$ was then added to the resultant solution and stirred for 10 h. The resultant solid was filtered out, washed, dried and its XRD patterns measured, which is shown in Fig. 2. They are identical to each other as well as to the reported $[LiAl_2(OH)_6]_2TP$, and the basal spacing increases to 1.42 nm due to the replacement of Cl^- by terephthalate anion (the 0 0 *l* peaks move to much lower 2θ angles)[16]. This means that DMT can hydrolyze in 2:1 mixture solvent (v/v) of ethanol and water at 30 or 70 °C, and the anion exchange of $[LiAl_2(OH)_6]Cl$ and TP^{2-} can also take place under the conditions, that is, both reactions (6) and (8) can take place under the conditions.

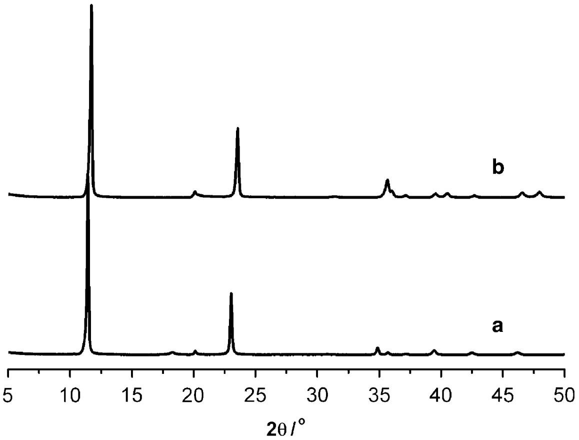

Fig. 1. XRD patterns of (a) $[LiAl_2(OH)_6]Cl$, and (b) $[LiAl_2(OH)_6]OH$.

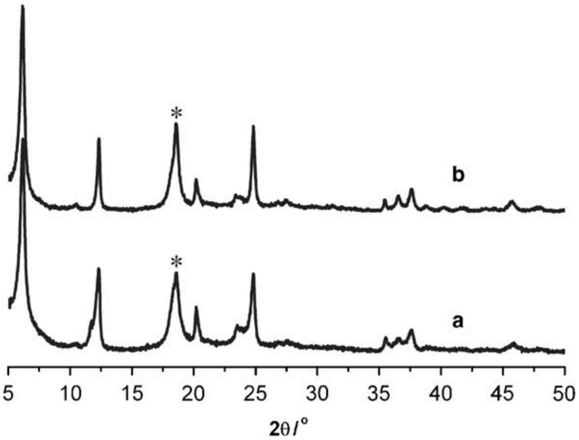

Fig. 2. XRD patterns of the anion-exchange products of $[LiAl_2(OH)_6]Cl$ and TP^{2-} formed in the alkaline hydrolysis at (a) 30 °C, and (b) 70 °C (the peak marked with *a** is the peak of $Al(OH)_3$).

3.3. Characterization of the products obtained from the alkaline hydrolysis of DMT in the presence of $[LiAl_2(OH)_6]Cl$

The alkaline hydrolysis of DMT in the presence of $[LiAl_2(OH)_6]Cl$ had been performed at 30 and 70 °C, respectively for 19 h, and XRD patterns of the products are shown in Fig. 3. It can be seen that no $[LiAl_2(OH)_6]_2TP$ is formed at 30 °C, and the product is $[LiAl_2(OH)_6]OH$; however, formation of $[LiAl_2(OH)_6]_2TP$ is obvious at 70 °C, although some $[LiAl_2(OH)_6]OH$ exists in the product. Consequently, reaction (6) in the presence of $[LiAl_2(OH)_6]Cl$ can take place at 70 °C, but it cannot occur or is too slow at 30 °C.

3.4. Characterization of the products obtained from the reaction of DMT and $[LiAl_2(OH)_6]OH$

Because the presence of $[LiAl_2(OH)_6]OH$ was identified in the last experiment, a mixture of LiAl$_2$_OH and DMT had been stirred at 30 and 70 °C for 48 h, respectively. Fig. 4 shows the XRD patterns of the products. It can be seen that no $[LiAl_2(OH)_6]_2TP$ forms at 30 °C; but it does form at 70 °C (please pay more attention to the peaks at 2θ angles between 11 and 12°, the peak close to 12° is from the second harmonic of $[LiAl_2(OH)_6]_2TP$). Compared with Fig. 3a, Fig. 4b has much smaller peak intensity of $[LiAl_2(OH)_6]_2TP$ relative to that of $[LiAl_2(OH)_6]OH$, even if the reaction took longer time; therefore, the reaction between $[LiAl_2(OH)_6]OH$ and DMT is slower than alkaline hydrolysis of DMT in the presence of $[LiAl_2(OH)_6]Cl$.

A reaction of DMT and $[LiAl_2(OH)_6]OH$ with NaCl added was also performed to imitate the composition of the alkaline hydrolysis in the presence of $[LiAl_2(OH)_6]Cl$, which showed that the addition of NaCl did not help with the hydrolysis; however, it did reduce the production of $Al(OH)_3$ (Fig. 5, when compared especially with Fig. 4b, has a very big peak at around 18°).

Both the reactions show that the reaction of DMT and $[LiAl_2(OH)_6]OH$ is slower than the alkaline hydrolysis in the presence of $[LiAl_2(OH)_6]Cl$. By analyzing the difference among the systems, it is believed that the system of the alkaline hydrolysis in the presence of $[LiAl_2(OH)_6]Cl$ has bigger OH^- concentration at the beginning, since anion exchange reaction (7) takes some time to finish (please notice that at the beginning of the reaction, the system has NaOH, DMT and $[LiAl_2(OH)_6]Cl$ only). The bigger OH^- concentration makes the hydrolysis quicker and more terephthalate anions are produced; and the bigger terephthalate anion concentration could make reaction (9) produce more OH^-, which makes the hydrolysis quicker. Therefore, in those reactions, once it was slower, it would be slower forever.

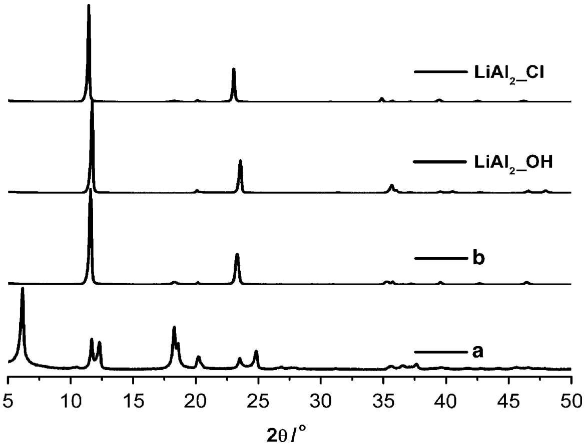

Fig. 3. Powder X-ray diffraction patterns of the products of the alkaline hydrolysis of DMT in the presence of $[LiAl_2(OH)_6]Cl$ at (a) 70 °C, and (b) 30 °C. XRD patterns of $[LiAl_2(OH)_6]Cl$ (noted as LiAl$_2$_Cl) and $[LiAl_2(OH)_6]OH$ (noted as LiAl$_2$_OH) are also shown for reference.

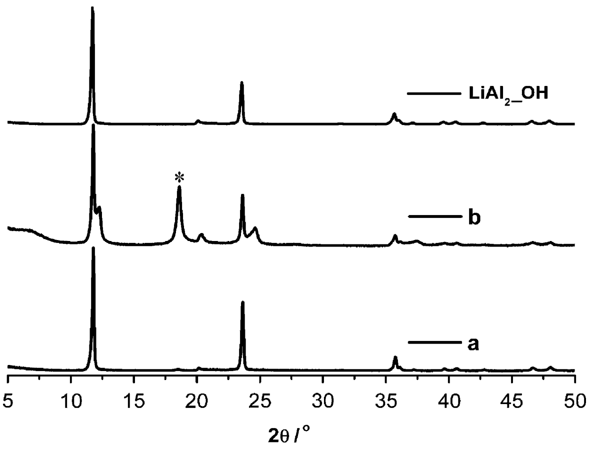

Fig. 4. Powder X-ray diffraction patterns of the products of the reaction of $[LiAl_2(OH)_6]OH$ with DMT at (a) 30 °C, and (b) 70 °C (the peak marked with a * contains peak of $Al(OH)_3$). XRD pattern of $[LiAl_2(OH)_6]OH$ (noted as LiAl$_2$_OH) is also shown for reference.

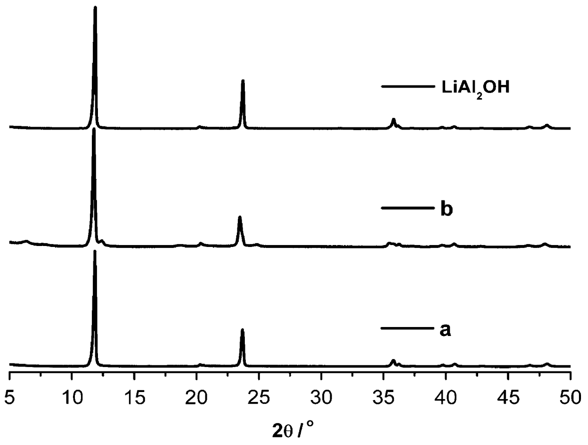

Fig. 5. Powder X-ray diffraction patterns of the products of the reaction of $[LiAl_2(OH)_6]OH$, DMT and NaCl at (a) 30 °C, and (b) 70 °C. XRD pattern of $[LiAl_2(OH)_6]OH$ (noted as LiAl$_2$_OH) is also shown for reference.

3.5. The kinetic studies of the alkaline hydrolysis of DMT without the presence of $[LiAl_2(OH)_6]Cl$

The alkaline hydrolysis of DMT with NaOH was monitored by measuring the conductivity of solution at different times. The conductivity data was converted to the extent of reaction and showed in Fig. 6 as a function of time. It can be read on the curve that the reaction goes to 95% completion in 455 min at 30 °C and 135 min at 70 °C, respectively.

3.6. *The kinetic studies of the alkaline hydrolysis of DMT in the presence of [LiAl$_2$(OH)$_6$]Cl*

Due to the alkaline hydrolysis of DMT in the presence of [LiAl$_2$(OH)$_6$]Cl has little change in conductivity through the reaction course, the kinetic studies of the reaction at 70 °C was investigated by halting it at different times. The XRD patterns of the products are shown in Fig. 7.

It can be seen in Fig. 7 that the peaks assigned to [LiAl$_2$(OH)$_6$]Cl shifts to higher angles, the final angles are the same as those of [LiAl$_2$(OH)$_6$]OH, and at the same time, peaks of [LiAl$_2$(OH)$_6$]$_2$TP grow up. This indicates that reactions (6)–(8) take place simultaneously at the reaction conditions.

Fig. 8 shows the chart of integrated intensity of the first XRD peak of [LiAl$_2$(OH)$_6$]$_2$TP versus time, which shows that the reaction goes to 95% completion in about 15 h. Since the alkaline hydrolysis of DMT without [LiAl$_2$(OH)$_6$]Cl finishes in a bit more than 2 h, it is very much slower.

It has been known that the anion exchanges of LDH is very fast, and can finish in minutes [1,11]. Since the alkaline hydrolysis of DMT takes 135 min to reach 95% completion, much of the unreacted OH$^-$ can certainly be exchanged with chloride anion in [LiAl$_2$(OH)$_6$]Cl and produces [LiAl$_2$(OH)$_6$]OH quickly (reaction 7). This reaction lowered OH$^-$ concentration, and makes the alkaline hydrolysis (reaction 6) much slower. It is well known that OH$^-$ is one of the reactant as well as a catalyst in the alkaline hydrolysis of esters. This accounts for why the alkaline hydrolysis in the presence of [LiAl$_2$(OH)$_6$]Cl proceeds much slower than that without the presence of the LDH.

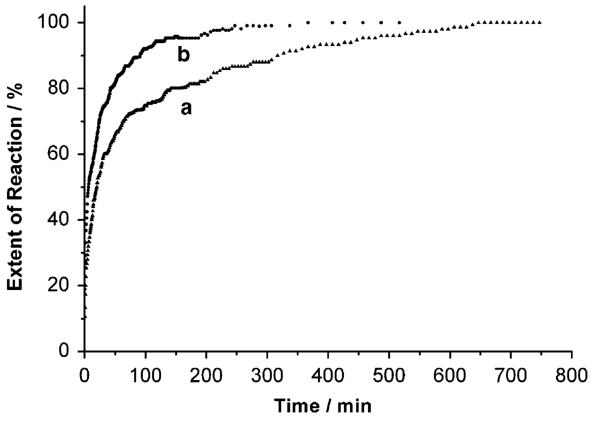

Fig. 6. Curves for extent of reaction versus time of the alkaline hydrolysis of DMT in a solution of NaOH at (a) 30 °C and (b) 70 °C.

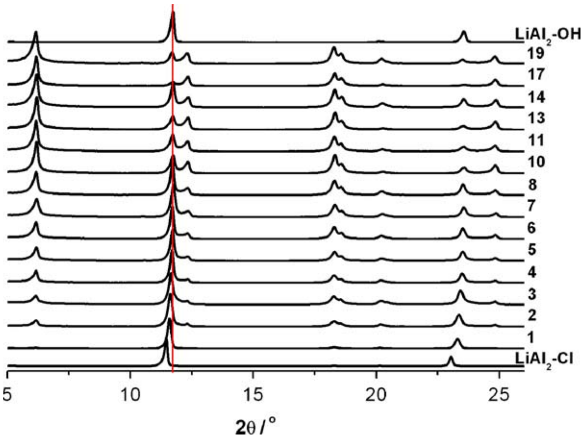

Fig. 7. XRD patterns of the solid products of the alkaline hydrolysis of DMT in the presence of [LiAl$_2$(OH)$_6$]Cl at 70 °C halted at 1, 2, 3, 4, 5, 6, 7, 8, 10, 11, 13, 14, 17, and 19 h.

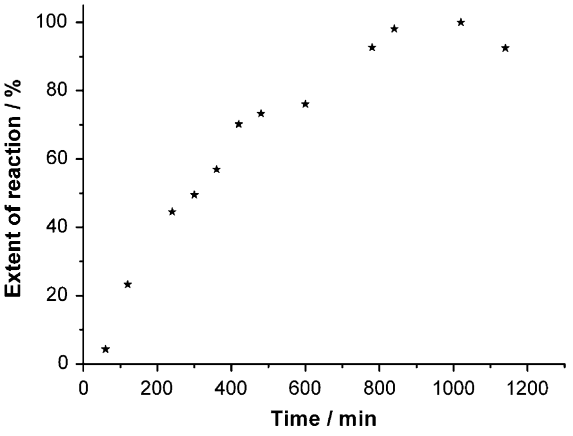

Fig. 8. Extent–time curve of the alkaline hydrolysis of DMT in the presence of [LiAl$_2$(OH)$_6$]Cl at 70 °C.

However, the alkaline hydrolysis of DMT in the presence of [LiAl$_2$(OH)$_6$]Cl is faster than the reaction between DMT and [LiAl$_2$(OH)$_6$]OH, as the reaction is far from completion in 48 h (Fig. 4b). Compared with both the reactions, the only differences are that the alkaline hydrolysis of DMT in the presence of [LiAl$_2$(OH)$_6$]Cl (1) has chlorine anions, while the reaction between DMT and [LiAl$_2$(OH)$_6$]OH has not; (2) [LiAl$_2$(OH)$_6$]OH is formed during the reaction course, therefore there are many free OH$^-$ anions at first, while there are no free OH$^-$ anions in the reaction between [LiAl$_2$(OH)$_6$]OH and DMT.

The existence of Cl$^-$ has been proved to make little difference as it was shown in Section 3.4. This can actually be expected as Cl$^-$ is a much worse competitor than OH$^-$. The second difference is certainly when more DMT molecules get hydrolyzed in the first few hours, thus making more terephthalate anions exist in the solution. Since anion exchange reactions of LDHs (reactions (7)–(9)) are reversible reactions, more terephthalate anions and chloride anions make more OH$^-$ anions to be exchanged out of the LDH host (in spite of terephthalate anion being a worse competitor than OH$^-$, it has a bigger amount and still gets more and more), and the more OH$^-$ anions make

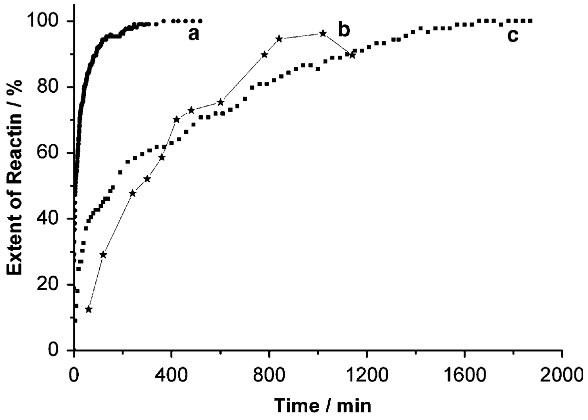

Fig. 9. Extent of reaction versus time curves of (a) the alkaline hydrolysis of DMT, (b) the alkaline hydrolysis of DMT in the presence of $[LiAl_2(OH)_6]Cl$, and (c) the alkaline hydrolysis of DMT in the slightly alkaline buffer solution. All the reactions were carried out at 70 °C.

the alkaline hydrolysis of DMT in the presence of $[LiAl_2(OH)_6]Cl$ faster than the reaction of DMT and $[LiAl_2(OH)_6]OH$.

3.7. The kinetic studies of the alkaline hydrolysis of DMT in a slightly alkaline buffer solution

To verify the role that the concentration of OH^- plays, we carried out a hydrolysis of DMT in a buffer solution which has a pH of about 8. The buffer solution was chosen because we noticed that the pH of the solution of the alkaline hydrolysis of DMT in the presence of $[LiAl_2(OH)_6]Cl$ decreased rapidly and gradually stabilized at about 8. The buffer solution was made from mixed KH_2PO_4 and K_2HPO_4 in a 2:1 mixture solvent (v/v) of ethanol and water. The hydrolysis of DMT in this slightly alkaline buffer solution was monitored by measuring the conductivity of solution, and the result is shown in Fig. 9c. The data in Fig. 6b and 8 are also shown to get a better comparison.

From Fig. 9, it can be seen that the reaction time of the alkaline hydrolysis of DMT in the presence of $[LiAl_2(OH)_6]Cl$ is longer than that of the alkaline hydrolysis of DMT, but shorter than that of the hydrolysis of DMT in the slightly alkaline buffer solution. Compared with the hydrolysis of DMT in the slightly alkaline buffer solution, the hydrolysis of DMT in the presence of $[LiAl_2(OH)_6]Cl$ is different principally in that TP^{2-} formed in the latter reaction can be intercalated into the interlayer of the LDH, which should definitely lower the concentration of TP^{2-}. This might be a reason (but we are not sure) why the latter goes a little bit faster. At least, this last investigation could tell us why the hydrolysis of DMT in the presence $[LiAl_2(OH)_6]Cl$ is so slow compared to that without the presence of $[LiAl_2(OH)_6]Cl$.

4. Summary

This study reveals that the anion exchange property of LDH can be used to control chemical reaction that has the anionic reactant or product. In this particular reaction, the alkaline hydrolysis of DMT (reaction 6) is controlled by the selective anion exchange of OH^- in between the LDH layers, which reduces the concentration of OH^-. The interlayer OH^- is then control released by anion exchange equilibriums (both reactions 8 and 9 is possible, but reaction 9 should be dominant because TP^{2-} is a better competitor than Cl^-), which makes the hydrolysis go about continuously.

Acknowledgments

We would like to thank The Jiangsu Province Fundamental Research Project (Natural Science Fund) BK2004071, The Chinese Ministry of Education and The Royal Society for financial support. LL also wishes to thank The China Association of Science and Technology for support.

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