

A COMPARATIVE STUDY OF THERMAL DECOMPOSITION BEHAVIOUR OF Zn–Cr, Zn–Cr–Al AND Zn–Al TYPE LAYERED DOUBLE HYDROXIDES

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Abstract

Hydrolysis of ZnO in acidic pH provides a facile route for synthesis of layered double hydroxides (LDH) bearing Zn²⁺ with Cr³⁺ and Al³⁺ without having carbonate ion in the inter-layer position. The thermal decomposition of the prepared LDH show that with the increase of Cr³⁺ content in the system there is an increase in the thermal stability of the compounds. In case of Zn–Cr LDH there is a non-mass loss transition around 420°C. Segregation of parent LDH structure to a bivalent oxide and a spinel takes place in both Zn–Cr and Zn–Al LDH only at temperatures above 550°C.

Keywords: anionic clays, hydrotalcites, layered double hydroxides, spinel, zinc oxide

Introduction

Layered materials are considered to be an important group of solids in the present day world, bearing enormous application prospects in various fields. Layered double hydroxides (LDH) are also known as anionic clay minerals or hydrotalcites. They are a group of important materials where elementary layers possess some positive charge due to substitution of bivalent metal ions in the parent brucite-like structure by trivalent metal ions [1]; the positive charge thus generated is neutralised by the interlayer anions like Cl⁻, SO₄²⁻, CO₃²⁻, etc. These are the only known class of ionic layered compounds where the layers are two dimensional crystalline solids [2]. Due to stereochemical factors, CO₃²⁻ ion is highly stable in the interlayer position of LDH [3]. Therefore, it is extremely difficult to synthesize LDH without having CO₃²⁻ ion in the interlayer positions, which is very easily available in alkaline pH from the atmospheric CO₂.

One of the easiest methods to have CO₃²⁻ free LDH is to hydrolyse the bivalent metal oxides in acidic pH [4, 5]. The method basically involves the reaction of a bivalent metal oxide with an aqueous salt solution of a trivalent metal ion at room temperature. This method is often used to prepare Zn–Cr, Zn–Al, Cu–Cr type LDH [6].

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The thermal properties of LDH draw special attention due to formation of immense number of phases like non-stoichiometric oxides, segregated spinels, bivalent oxides, metal nanoparticles, etc. at different temperatures [7]. The composition of metal ions, their ratios, the nature and type of interlayer species play very vital and significant roles in these transformations [8, 9].

It is a common practice to attempt to study the thermal decomposition behaviour of compounds having multiple decomposition steps using constant heating rate non-isothermal gravimetry, in that case the time required for a set of experiments is relatively short [10]. Therefore, the present work is done by constant heating rate experiments only.

Generally speaking, in the non-isothermal treatment starting from the room temperature to higher temperatures, the thermal decomposition of an LDH takes place at four different stages. These can be divided to evaporation of adsorbed water, loss of inter-layer water, dehydroxylation of brucite-like sheets and loss of inter-layer volatile anions like Cl^- , NO_3^- or CO_3^{2-} [11], etc. However, depending upon the various factors such as the dryness of the sample, the heating rate, chemical composition of the main layer, the nature of the inter-layer anion and its reactivity for possible guest-host interactions these four steps may vary their positions. Pinnavaia *et al.* [12] have observed that at a heating rate of 5°C min^{-1} the inter-particle pore water begins to disappear at a temperature of about 60°C and inter-layer water disappears at a temperature range of 240 to 280°C . After the disappearance of the inter-layer water structural dehydroxylation commences [13]. Sometimes even a specific decomposition is multi-stepped e.g. in structural dehydroxylation the decomposition of OH groups attached to trivalent metal ions may take place earlier than the same for OH groups attached to bivalent metal ions [14, 15]. Acro *et al.* [16] also have reported that apart from mass loss steps thermal decomposition pattern of an LDH may contain some non-mass loss DTA attributes owing to formation of certain new oxidic phases.

Experimental

In the present work mainly two types of LDH viz. Zn–Cr and Zn–Al type have been prepared by the reaction of ZnO with 1 M aqueous CrCl_3 and AlCl_3 solutions, respectively. The intermediate ternary system of Zn^{2+} with Cr^{3+} and Al^{3+} were prepared by reacting ZnO with mixtures of corresponding 1 M solutions of Cr^{3+} and Al^{3+} with different $\text{Cr}^{3+}:\text{Al}^{3+}$ ratios.

The products formed were washed and dried at 40°C . Chemical compositions of the products and reactants were analysed by AAS and ICP-AES. The dried products were then tested in IR for the absence of 1400 cm^{-1} peak corresponding to ν_3 absorption band of CO_3^{2-} ion. Powder XRD were carried out in Philips single circle powder diffractometer at a step size of $0.01^\circ 2\theta\text{ s}^{-1}$ from CuK_α source under 35 kV and 20 mA current with Si as internal standard.

The TG/DTG patterns of the products were then carried out at different heating rates under air atmosphere in SDT-2960 DTA-TG equipment (M/S TA Corporation, USA), with approximately 20 mg sample in platinum crucibles. To orient the

layered materials on their basal planes tightly, samples in the crucible were slightly pressed over a hard base by a flat surface.

In order to make the Cl^- bearing samples harmless to DSC cell Cl^- ions from the interlayer positions have been exchanged with CO_3^{2-} ion by dipping the LDH in 30 mL 1 M Na_2CO_3 solution for 2 to 3 h. The products then washed to free from excess Na_2CO_3 and dried. DSC runs were then carried out in DSC 2010 (M/S TA Corporation, USA) at a heating rate of $20^\circ\text{C min}^{-1}$ with a sample size of about 5 mg.

In order to compare DTA-TG results, static thermal treatment viz. at 350, 450, 550, 650, 750, 950°C in electric muffle furnace for 30 min were carried out. The different crystalline phases formed during calcination were then characterized by powder X-ray diffractometry (XRD) in Jeol JDXIIP3A single circle goniometer at 20 kV and 10 mA current at a scan rate of $6^\circ 2\theta \text{ min}^{-1}$.

Results and discussion

It has been observed that an LDH type XRD pattern [15] i.e. one having characteristic basal ($00l$) peaks (Fig. 1) free from other recognizable crystalline phases like ZnO , $\text{Zn}(\text{OH})_2$, $\text{Zn}_5(\text{OH})_8\text{Cl}$ is obtained during hydrolysis of ZnO with aqueous CrCl_3 and AlCl_3 mixtures. As observed from the width of the peaks there is a gradual decrease of crystallinity with increase of Al^{3+} in the system. In case of Zn-Al-Cl

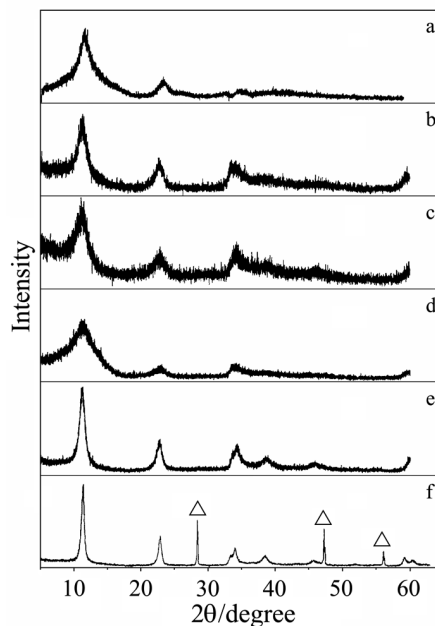


Fig. 1 XRD patterns of Zn–Cr–Al–Cl LDH at different Al:Cr ratios; a, b, c, d, e, f indicate different samples prepared from reactants with Al:Cr ratios; a – 1:0, b – 0.9:0.1, c – 0.7:0.3, d – 0.5:0.5, e – 0.3:0.7 and f – 0:1, respectively; (Δ =Si internal standard)

LDH in order to obtain sharper XRD peaks comparable to that of Zn–Cr–Cl LDH one has to carry out the reaction under continuous stirring for several weeks at room temperature. Which indicates a slower reaction rate of aqueous solution of salt of Al^{3+} than Cr^{3+} with ZnO. Both Al^{3+} and Cr^{3+} form different soluble hydrolytic polycations in acidic pH [17]. Roussel *et al.* [18] have shown that in case of Cr^{3+} there is the formation of some hydrolytic complex which is responsible for the formation of Zn–OH–Cr bridges and that forms the initial nuclei for Zn–Cr–Cl LDH. It has been described that in case of Cr^{3+} the oligomerisation of this hydrolytic complex is slow and that helps in the formation of Zn–OH–Cr bridges. Although, similar study on the detail mechanism of the reaction of Al^{3+} salt with ZnO has not been reported so far, yet the fate of Al^{3+} ion in aqueous medium at acidic pH is well documented. Various workers have reported the formation of a tridecameric polycation [19, 20] which is further stabilized if solution has Cl^- ion in it [21]. Thus, it is possible that slower rate of formation of Zn–Al–Cl LDH is due to this stable polycation. The slower reactivity of Al^{3+} in comparison to Cr^{3+} is further evidenced by decreased Al^{3+} content in the products than in the reactants with respect to their Cr^{3+} contents, e.g. the reactants with Al:Cr ratios 0.3:0.7, 0.5:0.5, 0.7:0.3, 0.9:0.1 give products with Al:Cr ratios 0.28:0.72, 0.41:0.59, 0.63:0.37, 0.85:0.15, respectively.

The TG patterns of Zn–Cr–Cl LDH, Zn–Cr–Al–Cl LDH (at Cr:Al ratio 0.5:0.5) and Zn–Al–Cl LDH carried out at an air atmosphere at a heating rate of 8°C min^{-1} show (Fig. 2) mainly the various mass loss transitions characteristic of different LDH described earlier. The total mass loss in two extreme end members of the series i.e. in Zn–Cr–Cl is 31.52% while the same in Zn–Al–Cl is 33.16% w/w.

When compared from the point of position of DTG peaks of the two decomposition regions viz. the interlayer dehydration and structural dehydroxylation, an idea of relative thermal stability of different compositions is obtained. The different DTG peak temperatures of Zn–Cr–Cl, Zn–Cr–Al–Cl (Cr:Al ratio 0.5:0.5) and Zn–Al–Cl type LDHs are given in Table 1. It is observed that in Al bearing LDH the decompositions are gradually taking place at lower temperatures than their Cr bearing counterparts.

Table 1 The DTG peak positions of two structurally important decompositions

LDH species	Interlayer dehydration	Structural dehydroxylation
	DTG peak/ $^\circ\text{C}$	
Zn–Cr–Cl	323.00	453.00
Zn–Cr–Al–Cl	278.81	420.70
Zn–Al–Cl	187.00	248.21

There is observed a higher amount of mass loss (12.7%) in interlayer dehydration stage of Zn–Cr–Cl LDH than Zn–Al–Cl LDH (7.75%). Which can be described as due to improved crystallinity of the former, which causes larger interlayer surface for accommodation of a larger amount of water.

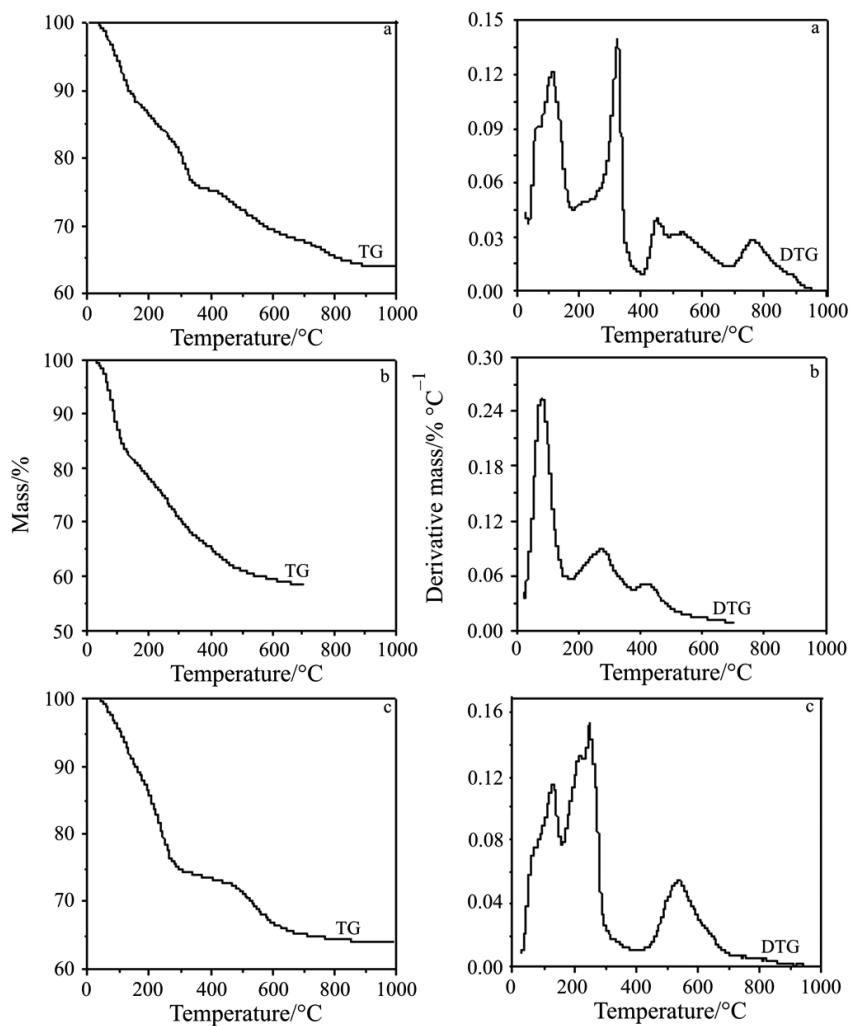


Fig. 2 TG-DTG patterns of Zn–Cr–Cl, Zn–Cr–Al–Cl and Zn–Al–Cl LDH; a, b, c indicate different samples prepared from reactants with Cr:Al ratios; a – 1:0, b – 0.5:0.5 and c – 0:1, respectively

There is an exothermic non-mass loss DTA peak at 416°C immediately preceding the structural dehydroxylation peak at 453°C (Fig. 3). While the exact nature of this DTA conversion is not known, but Acro *et al.* [16] have reported that at this stage some of the Cr(III) species gets partially oxidized to Cr(VI), giving rise to formation of an amorphous zinc hydroxychromate and at higher calcination temperatures it get converted to ZnO and ZnCr₂O₄. Similar explanation of oxidation of trivalent species is not applicable in Al³⁺, because of that DTA peak similar to Zn–Cr–Cl is not observed in Zn–Al–Cl system.

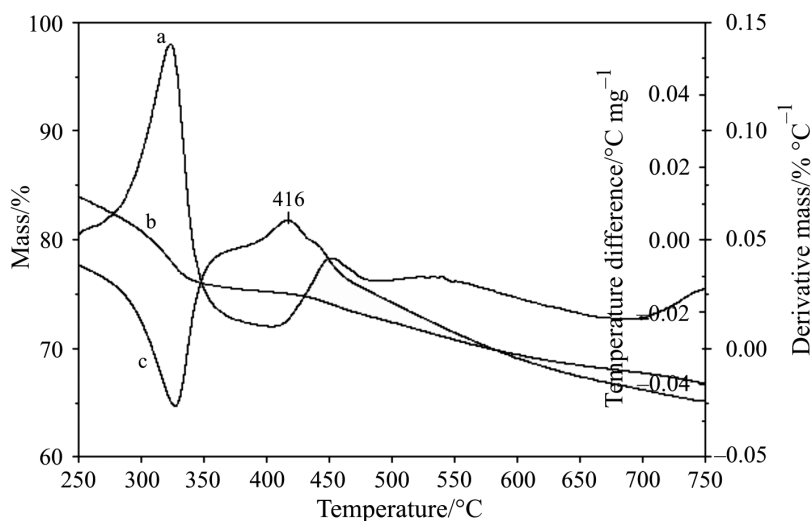


Fig. 3 TG-DTG-DTA patterns of Zn–Cr–Cl LDH magnifying the non-mass loss and structural dehydroxylation stage; a, b, c indicates; a – DTA, b – TG and c – DTG curves, respectively

It has been observed that apart from trivalent ion present in the system the appearance of this DTA peak is dependent upon the interlayer species present in the system e.g. in CO_3^{2-} , NO_3^- form of Zn–Cr LDH the same is not observed. This is probably due to the formation of certain ‘green-house like’ gas produced from the decomposition of CO_3^{2-} and NO_3^- ion in the inter-layer region, which absorbs the heat produced in the exothermic transition. This is the reason for the absence of the said exothermic peak in DSC patterns of Zn–Cr type LDH (Fig. 4) at around 416°C, as due to the instrumental limitations the Cl^- bearing Zn–Cr–Cl type LDH is initially converted to its CO_3^{2-} form to avoid any damage to the sample cell from the Cl^- species.

Other than that, the CO_3^{2-} form of Zn–Cr LDH prepared by exchanging interlayer Cl^- ion with CO_3^{2-} ion shows similar TG pattern to Zn–Cr–Cl LDH. However, there is a slight shift in peak positions e.g. first mass loss DTG peak appears at 95.5°C corresponding to 3.3% mass loss in the range, second mass loss DTG peak appears at 160.10°C with corresponding mass loss of 9.83%, the third mass loss DTG peak appears at 291.31°C with corresponding mass loss in the range as 13.99%, the fourth DTG peak appears at 480°C with corresponding mass loss being 1.88%. Thus the total mass loss in four different transitions is 29.0% which is smaller than total mass loss of 31.52% in Zn–Cr–Cl LDH. Considering the fact that bivalent carbonate ion is charge wise equivalent to two monovalent chloride ions and molecular mass of CO_3^{2-} being smaller than two chloride ions such a lower mass loss in Zn–Cr– CO_3 form of LDH appears reasonable.

The crystalline phases identified from the XRD patterns of different calcined products show that Zn–Al or Zn–Cr type LDH maintains ZnO type poorly crystalline structure at least upto 550°C.

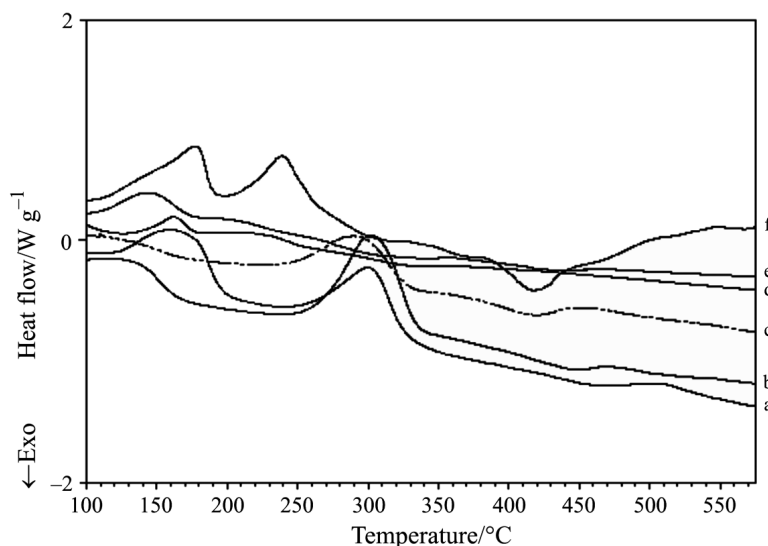


Fig. 4 Comparative DSC patterns of Zn–Cr–Al–CO₃ LDH at different Cr:Al ratios; a, b, c, d, e, f indicate different samples prepared from reactants with Cr:Al ratios a – 1:0, b – 0.9:0.1, c – 0.7:0.3, d – 0.5:0.5, e – 0.1:0.9 and f – 0:1, respectively

Conclusions

Layered double hydroxide prepared from hydrolysis of ZnO with aqueous chromium chloride is more crystalline than the same prepared by reaction of aqueous aluminium chloride. Zn–Cr–Cl LDH is thermally more stable than Zn–Al–Cl LDH. Zn–Cr–Cl LDH at around 420°C undergoes a non-mass loss DTA transition. The appearance of the DTA peak is dependent upon the nature of interlayer species. The oxide formed on decomposition of these two LDH initially maintains a ZnO type structure which later on segregates to ZnO and their corresponding spinel. The DSC pattern is complementary to their DTA-TG patterns.

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