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THERMAL STABILITY OF LITHIUM ALUMINIUM HYDROXY SALTS

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ABSTRACT

Lithium aluminium hydroxy salts, obtained by exchanging the interlayer OH^- groups of $[LiAl_2(OH)_6]$ $OH \cdot 2H_2O$ with solutions of the appropriate salt, were studied with respect to their thermal behaviour. These layered compounds of formula $[LiAl_2(OH)_6]$ $X \cdot mH_2O$, where $X = Cl^-$, OH^-, NO_3^-, $1/2CO_3^{2-}$ and $1/2SO_4^{2-}$, show, upon heating, several decomposition stages depending on the interleaved anion. The decomposition intermediates were also examined in order to study their thermal stability and the structure of the interlayer arrangement.

INTRODUCTION

Synthetic Li, Al double hydroxide of formula $[LiAl_2(OH)_6]$ $OH \cdot 2H_2O$ consists of positively-charged layers of $[LiAl_2(OH)_6]^+$ in which Li^+ cations occupy, in an ordered fashion, the free sites of $Al(OH)_3$ layers [1]. These positively charged brucite-type layers are balanced by an equivalent negative charge coming from an interlayer containing OH^- anions and water molecules.

Mixed hydroxy salts with analogous structures exist for a variety of divalent and trivalent metals with most anions [2]. Although the first synthesis of mixed hydroxy salts goes back more than fifty years [3], their importance is still relevant. Anionic exchange [4–7], ionic conduction [8,9] and antacid behaviour [10,11] are typical of the properties of such compounds. They are also interesting as precursors of oxyhydroxides obtained through controlled thermal decomposition. These oxyhydroxides also may be of interest because of their ionic conduction [12], since the presence of anions together with O^{2-}/OH^- pairs can enhance their ionic conductivity.

With the exception of Ca, Al hydroxy salts [13], the decomposition intermediates of these compounds are not well known, while thermal be-

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haviour has been studied only on salts of the following pairs of metals: Mg, Al [14–17] and Zn, Cr [12]. The thermal decomposition behaviour occurs in several stages to produce metal oxides at higher temperatures.

EXPERIMENTAL

Following the procedure previously published [11], the various anion-forms were prepared by exchanging the interlayer OH groups of $[LiAl_2(OH)_6]OH \cdot 2H_2O$ with solutions of the appropriate salt. These samples were equilibrated over silica gel at ambient temperature (21°C).

The heat-induced weight loss of the exchanged forms was determined through simultaneous TG and DTA utilizing a Stanton Redcroft instrument, mod. 781. The following conditions were used: weight of the sample, 20 mg; heating rate, 10°C min^{-1}; α-Al_2O_3 as reference material. All experiments were carried out under a dry nitrogen flow.

The samples were also thermally treated at selected temperatures in an electrical furnace for 24 h and subsequently cooled in air. The decomposition intermediates were characterized through X-ray powder diffraction analysis (XRD) using a Guinier de Wolff camera and CuKα radiation.

Some samples were also chemically analyzed: chloride analysis was carried out according to Mohr's method; the sulfate was gravimetrically determined as $BaSO_4$ and CO_2 content was determined by a calcimeter.

RESULTS AND DISCUSSION

Dehydration stage

Figure 1 shows the DTG curves for the hydroxy salts and α-$Al(OH)_3$ (bayerite) up to 1200°C.

The effects observed below 200°C are related to the dehydration stage. The water content was calculated from isothermal weight-change determinations at selected temperatures assuming the formula $[LiAl_2(OH)_6]X \cdot mH_2O$, where $X = Cl^-$, OH^-, NO_3^-, $1/2CO_3^{2-}$ and $1/2SO_4^{2-}$. This water loss corresponds to the removal of the interlayer water according to the following and reversible process:

$$[LiAl_2(OH)_6]X \cdot mH_2O \rightleftharpoons LiAl_2(OH)_6X + mH_2O$$

The accuracy of the evaluation of mH_2O is affected by three factors: absorbed water, due to the small size of the particles; overlap, in some cases, of the dehydration stage with that of the subsequent dehydroxylation (as will be discussed later); partial carbonatation of the samples during the thermal dehydration treatment when carried out in air. The absorbed water was almost completely eliminated by equilibrating the samples over silica gel

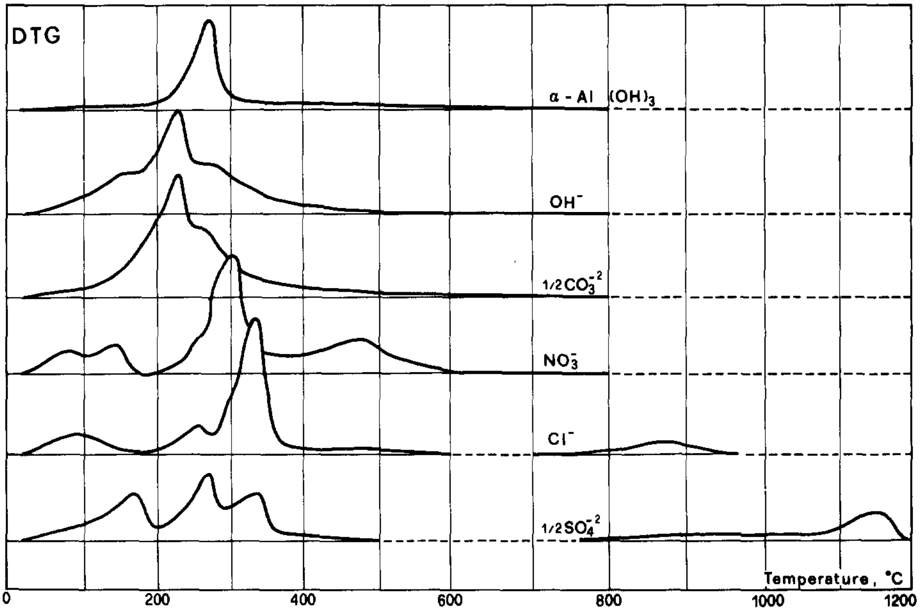

Fig. 1. DTG curves of α-$Al(OH)_3$ and $[LiAl_2(OH)_6]X \cdot mH_2O$, where X = OH^-, $1/2CO_3^{2-}$, NO_3^-, Cl^- and $1/2SO_4^{2-}$.

and submitting them as soon as possible to thermal investigation. The overlapping of the dehydration stage with dehydroxylation is very marked for the carbonate-form. The other anionic forms show both effects well separated (Fig. 1). This peculiar behaviour of the carbonate form, which is perfectly analogous to that previously found for Mg, Al hydroxides and related carbonate phases [15], may be related to the simultaneous presence of interleaved CO_3^{2-} and HCO_3^- species in chemical equilibrium, through a proton transfer [11], as follows

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$$

In this case the effect of the loss of the interlayer water overlaps with that of the dehydroxylation unlike the hydroxide form which shows the two effects more separated.

The evaluation of mH_2O interferes with the partial carbonatation of the samples during the anionic exchange reaction and/or the thermal treatment in air. The degree of carbonatation is related to the interleaved anion type; in particular it changes according to the selectivity sequence found in the anionic exchange reaction [11]. The sulfate form, in fact, characterized by a high selectivity value, shows no carbonatation unlike the other anionic forms. The degree of carbonatation of the samples changes from 15% for the synthetic hydroxide form to 4% for the chloride form obtained by anionic exchange. The small effect at about 250°C for the chloride and nitrate forms (Fig. 1) has been attributed to their partial carbonatation.

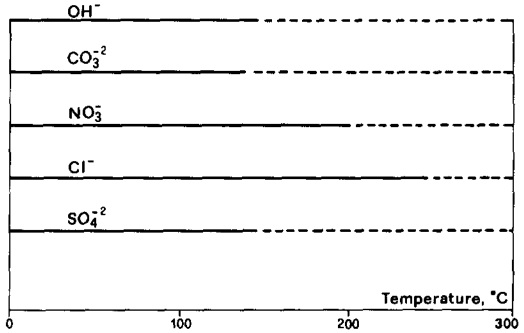

Fig. 2. Thermal stability range of samples in Fig. 1 towards the reversible dehydration process.

The dehydration temperature of the interlayer water for the various anionic forms is higher than 100°C. The lower value for the chloride form (< 100°C) can be explained by taking into account the "hydrogen" bond that occurs for the water molecules in the interlayer. A hydrogen bond of the type $Cl \cdots H{-}O$ can be expected for the chloride form, energetically weaker than the bond $O \cdots H{-}O$ that occurs for the other anionic forms characterized by anions with oxygen content. Consequently the loss of mH_2O for the chloride form takes place at a relatively low temperature.

The thermal stability of $[LiAl_2(OH)_6]\ X \cdot mH_2O$ towards the reversible dehydration process has been estimated from X-ray patterns of the samples thermally treated for 24 h at programmed temperatures. These results are summarized in Fig. 2 in which the thermal stability range is represented by a full line. It appears that the chloride and nitrate forms are characterized by the widest range of thermal stability.

In Table 1 the values of mH_2O for the various anionic forms together with the layer basal spacings of the corresponding hydrated samples are reported. X-ray measurements on the dehydrated samples cooled from selected temperatures, revealed no significant change in the basal spacing with respect to the corresponding hydrated samples. This behaviour is different from that of $[Ca_2Al(OH)_6]\ OH \cdot mH_2O$ whose basal spacing changes with the interlayer water content [18].

TABLE 1

Basal spacing c' and interlayer water molecules of $[LiAl_2(OH_6]X \cdot mH_2O$

	X				
	OH^-	Cl^-	$1/2CO_3^{2-}$	NO_3^-	$1/2SO_4^{2-}$
c' (Å)	7.50	7.70	7.60	8.80	8.70
mH_2O	2.0	1.0	1.5	1–1.5	1.5

It must be emphasized that the variation of c' values reflects mainly the interlayer content (anion + water molecules); the electrostatic attraction between the positively-charged and the negatively-charged interlayer, which also influences c' values, remains constant as the various anionic forms are characterized by the same positively-charged layer. These data suggest that c' values are only related to size and space arrangement of the interleaved anion while interlayer water molecules fill the remaining and available interlayer sites.

The hydroxide form, with an interlayer containing one OH anion and two water molecules per unit formula, shows a c' value slightly lower than that of the carbonate form (Table 1). This latter form, containing $1/2CO_3^{2-}$, in place of OH^{-1}, and 1.5 water molecules, shows the interlayer oxygen packing of the corresponding hydroxide form. In any case exchange of the OH groups with larger anions promotes the removal of some of the interlayer water molecules related to the hydroxide form. The value of mH_2O, in fact, ranges between 1 and 1.5 (Table 1).

As the NO_3^- and CO_3^{2-} anions are both characterized by a planar structure, the different observed c' values (8.80 and 7.60 Å, respectively) may be justified by two different space arrangements. Carbonate anion interleaves in parallel to the basic layers, while nitrate interposes orthogonally. A basal spacing equal to 8.70 Å for the sulfate form suggests the tetrahedral form of this anion.

Dehydroxylation stage

The effect associated with the dehydroxylation stage occurs at variable temperatures depending on the interleaved anion. Taking in account the thermal behaviour of Zn, Cr hydroxy salts [12] and of α-Al(OH)$_3$, from which derives the structure of Li, Al compounds [11], the dehydroxylation stage may be represented by the following thermal decomposition

$$LiAl_2(OH)_6X \rightarrow LiAl_2(OH)_{6-2x}O_xX + xH_2O$$

The dehydroxylation temperature of α-Al (OH)$_3$ lies between those of the Li, Al hydroxy salts as can be observed from DTG curves in Fig. 1. The hydroxide, sulfate and carbonate forms show the effect at lower temperatures unlike the chloride and nitrate ones. These last, when cooled from 200°C, showed the same X-ray patterns as the corresponding hydrated forms and with no significant variation up to 250°C for the chloride form in which all the initial chloride content was still present. The anionic forms with X equal to OH^-, CO_3^{2-} and SO_4^{2-}, cooled from 200°C, show a similar X-ray pattern with weak and very broad reflections. These unidentified patterns have been attributed, on the ground of TG data and anion content in the dehydroxylated solids, to oxyhydroxide formation. Oxyhydroxides with an extended range of thermal stability are those deriving from the hydroxide and carbonate forms. Their X-ray patterns remained unchanged, up to 400°C, while the chloride and nitrate forms have a narrow stability range.

Further decomposition stages

With the exception of the chloride and sulfate forms, there were no significant weight changes between 800 and 1200°C and the final products were $LiAl_5O_8$ and γ-$LiAlO_2$ according to the Li_2O–Al_2O_3 system [19].

Among the decomposition intermediates, Li_2SO_4 was identified in the sulfate form cooled from 250°C. Its formation may be represented by the following decomposition

$$LiAl_2(OH)_{6-2x}O_x0.5SO_4 \rightarrow Li_{1-2y}Al_2(OH)_{6-2x'}O_{x'}(0.5-y)SO_4 + yLi_2SO_4 + (x'-x)H_2O$$

The Li_2SO_4 content increases by treating the sulfate form at increasing temperatures and attains a maximum at 800°C. Li_2SO_4 disappears at 1200°C following its decomposition as can be deduced from the weight loss rate which, starting from 800°C, reaches a maximum at 1150°C (Fig. 1).

In the chloride and nitrate forms, cooled from 300°C, microcrystalline $LiAl_5O_8$ [20] was identified. This justifies the narrow stability range of the corresponding intermediate oxyhydroxides. The broad effect with a maximum at 880°C for the chloride form is indicative of the sublimation of LiCl [21]. This sample, unlike the other anionic forms, does not generate γ-$LiAlO_2$ [22] when cooled from 1200°C.

The nitrate-form also shows a broad effect, with a maximum at about 480°C, due to the evolution of nitrogen oxides [23]. Microcrystalline $LiAl_5O_8$ was observed in all cooled samples from 500°C. At 800°C, with the exception of the sulfate form, a metastable form, α-$LiAlO_2$ [24] was identified together with γ-$LiAlO_2$ and γ-$LiAl_5O_8$. This metastable phase disappears in cooled samples from 1200°C.

CONCLUSIONS

From this study the following conclusions can be drawn.

The basal spacing c' of the various anionic forms depends mainly upon the size and space arrangement of the interleaved anion between the basic layers with the interlayer water molecules that fill the remaining and available sites.

The temperature for the dehydration stage of the interlayer water is affected by the interleaved anion and by the "hydrogen" bond type that occurs for the water molecules in the interlayer.

The samples are characterized by loosely-held interlayer water molecules which allow reversible dehydration, especially in the case of high selectivity anions.

The thermal stability of the samples towards the reversible dehydration process changes with the interleaved anion type.

Oxyhydroxides can be obtained through appropriate thermal decomposition of the hydroxy salts at selected temperatures.

A metastable α-$LiAlO_2$, which disappears at high temperature, has been identified among the decomposition intermediates.

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REFERENCES

1 C.J. Serna, J.L. Rendon and J.E. Iglesias, Clays and Clay Minerals, 30 (1982) 180.
2 R. Allmann, Chimia, 24 (1970) 99.
3 W. Feitknecht, Z. Angew. Chem., 49 (1936) 24.
4 H.P. Boehm, J. Steinle and C. Vieweger, Angew. Chem., 89 (1977) 259.
5 S. Miyata, Clays and Clay Minerals, 23 (1975) 369.
6 V.P. Danilov, I.N. Lepeshkov, Yu.Ya. Kharitonov, T.O. Ashchyan, L.V. Goeva and O.F. Kosyleva, Russ. J. Inorg. Chem., 22 (1977) 1137.
7 O. Marino and G. Mascolo, Thermochim. Acta, 55 (1982) 337.
8 M. Lal and A.T. Howe, J. Chem. Soc. Chem. Commun., (1980) 739.
9 M. Lal and A.T. Howe, J. Solid State Chem., 39 (1981) 377.
10 C.J. Serna, J.L. White and S.L. Hem, Clays and Clay Minerals, 25 (1977) 384.
11 G. Mascolo, Mineral. Petrogr. Acta, (1985) in press.
12 M. Lal and A.T. Howe, J. Solid State Chem., 39 (1981) 368.
13 F.G. Butler, L.S. Dent Glasser and H.F.W. Taylor, J. Am. Ceram. Soc., 42 (1959) 121.
14 G. Brown and M.G. Gastuche, Clay Minerals, 7 (1967) 193.
15 G. Mascolo and O. Marino, Thermochim. Acta, 35 (1980) 93.
16 G.J. Ross and H. Kodama, Am. Mineralog., 52 (1967) 1036.
17 G. Mascolo and O. Marino, Mineralog. Mag., 43 (1980) 619.
18 M.H. Roberts, J. Appl. Chem., 7 (1957) 543.
19 H.K. Kim and F.A. Hummel, J. Am. Ceram. Soc., 43 (1960) 613.
20 J.C.P.D.S. Inorganic Phases, Comp. file 17-573.
21 T. Duval and C. Duval, Anal. Chim. Acta, 2 (1948) 57.
22 J.C.P.D.S. Inorganic Phases, Comp. file 18–714.
23 C. Duval, Inorganic Thermogravimetric Analysis, Elsevier (1963) p. 166.
24 J.C.P.D.S. Inorganic Phases, Comp. file 19–713.