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THERMAL STABILITY OF LI,AL HYDROXIDE MODIFIED BY ANIONIC EXCHANGE

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ABSTRACT

Lithium, aluminium double hydroxide of formula $[LiAl_2(OH)_6]$ $OH\cdot 2H_2O$ is a synthetic compound related to hydrotalcite mineral.

Various anionic forms were prepared by exchanging the interlayer OH^- groups of the hydroxide-form with solution of the corresponding salts. The thermal behaviour of the more extensively exchanged forms was examined in order to study the thermal stability and the nature 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 $[LiAl_2(OH)_6]^+$ in which the Li cations occupy, in an ordered fashion, the free sites of $Al(OH)_3$ layers (1). These brucite-type layers are interleaved by OH^- anions and water molecules (2,3).

An analogous compound of formula $[Zn_2Cr(OH)_6]$ $OH\cdot 2H_2O$ showed a high proton conductivity due to proton transfer between H_2O and OH^- species of the interlayer (4). As the Li,Al hydroxide shows exchange reaction of the interlayer OH^- anions (5), the aim of the present report has been to study the interlayer arrangement of the compound modified by anionic exchange; the presence in the interlayer of different anion types might, in fact, enhance the proton conductivity of the compounds. The thermal investigation of the compounds $[LiAl_2(OH)_6]$ $X\cdot mH_2O$, where X = Cl^-,NO_3^-, CH_3COO^-,HCO_3^- and $1/2SO_4^{2-}$, are here reported with particular reference to the interlayer content.

EXPERIMENTAL

Following the procedure previously published (6), the various anion-forms were prepared by echanging the interlayer OH groups of $[LiAl_2(OH)_6]$ $OH\cdot 2H_2O$ with solutions of the appropriate salts.

The heat-induced weight loss of the exchanged forms was determined through simultaneous TG and DTA adopting a Stanton Redcroft instrument Mod. 781. The

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following conditions were used: weight of the sample: 20mg; heating rate: $10^{o}C/min$; α-Al_2O_3 as reference material. All the experiments were carried out under a dry N_2 flow.

RESULTS AND DISCUSSION

The interlayer water content of the compounds was calculated from TG data assuming the formula $[LiAl_2(OH)_6]\,X\cdot mH_2O$, where X = Cl^-, NO_3^-, HCO_3^-, CH_3COO^-, $1/2SO_4^{2-}$. This stage corresponds to the following reversible reaction : $[LiAl_2(OH)_6]\,X\cdot mH_2O \rightleftarrows LiAl_2(OH)_6X + mH_2O$. A variation of the mH_2O with the water vapour pressure was observed; the samples showed in fact, upon heating, a loss of weight just above the starting room temperature. This makes difficult the distinction between the water absorbed by the sample and that coming from the interlayer. When the sample is dried over silica gel and submitted as soon as possible to thermal investigations, the absorbed water is almost completely eliminated.

In table I the value of mH_2O for the various anionic forms together the corresponding layer basal spacing are reported. It must be emphasized that in this case the variation of the c' value reflects mainly the interlayer content (anion + water molecules); in fact, the electrostatic attraction between the positively-charged and the negatively-charged interlayer, also influencing the c' value, remains constant as the various anionic forms are characterized by the same value of the a parameter (6).

The hydroxide-form, with an interlayer containing one OH anion and $2H_2O$ molecules per unit formula, shows a c' value slightly less than that of the carbonate-form (Table I). This last form containing only one HCO_3^-, in place of OH^-, determines a corresponding removal of $2H_2O$ that accompains the interlayer OH^- of the hydroxide-form. For the nitrate-form the value of mH_2O was not well defined because the loss of the interlayer water overlaps with the subsequent dehydroxylation stage. In this case the value of mH_2O appears higher than 2.5,

TABLE I

X	OH^-	CL^-	HCO_3^-	NO_3^-	CH_3COO^-	$1/2SO_4^{2-}$
c'(Å)	7.50	7.75	7.60	8.80	13.0	8.70
mH_2O	2	1	0	2.5 ÷ 3	2	1 ÷ 1.5

while the c' value equal to 8.80 Å suggests an additional packing of oxygens in the interlayer due to the interleaving of NO_3^- having a planar structure. Taking in account that the exchanged forms are characterized by the same area of the basic layer, the theoretical value of mH_2O for the nitrate-form might be equal to 3. In spite of the fact that the sulphate-form shows a value of mH_2O slightly than 1 (Table 1) the corresponding basal separation c' is relatively high. This may be related to the tetrahedral form of the sulphate anion in contrast with NO_3^- and HCO_3^- anions both characterized by a planar structure. For the chloride-form, both the mH_2O and the c' values, agree with the larger ionic radius of Cl^- compared to that of the OH anion. Very large basal separation has been observed for the acetate-form in agreement with the larger dimensions of this anion compared to the compounds with interleaving inorganic anions; in this case mH_2O was found equal to 2.

Figure 1 shows the c' parameters for the various anionic forms against the corresponding dehydration temperature due to the loss of the mH_2O. This temperature was determined from the peak temperature observed in DTA curves.

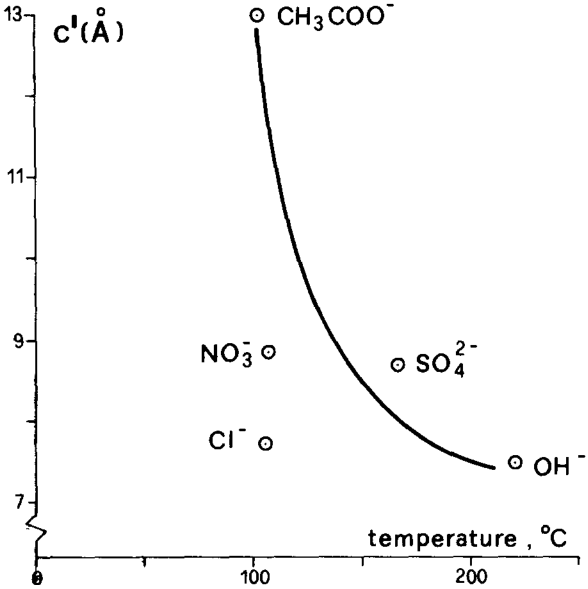

Fig. 1 Dehydration temperature of the interlayer water for the various anionic forms against the basal separation c'

With the exception of the chloride-form the loss of mH_2O takes place at decreasing temperature while increasing of the basal separation c'. This is in accordance with a more easy departure of H_2O from interlayers characterized by a weaker electrostatic field. The anomalous behaviour of the chloride-form might be explained taking into account the hydrogen bond that settles for the water molecules in the interlayer; this bond, in fact, takes place among the interlayer water, the interlayer anion and/or the OH groups of the positively-charged layer. A hydrogen bond of the type Cl...H_O can be expected for the chloride-form; this is a bond energetically weaker than O...H_O that take place for the other anionic forms characterized by anion with oxygen content. Consequently, in spite of the fact that the chloride-form has a low c' value, the loss of mH_2O takes place at relatively low temperature.

CONCLUSIONS

The study of the interlayer arrangement of the compounds $[LiAl_2(OH)_6]\ X \cdot mH_2O$ shows that the thermal stability of the various anionic forms toward the interlayer water is related to the basic layer separation and to the type of hydrogen bond that settles for the interlayer water. In order to obtain anionic forms characterized by a high proton conductivity it is essential that the water content of the interlayer is high and that the interleaved anions behave as acceptors and donors of protons.

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