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THERMAL STABILITY OF ALUMINIUM HYDROXYCARBONATES WITH MONOVALENT CATIONS

M.J. HERNÁNDEZ and M.A. ULIBARRI

Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Córdoba, Córdoba (Spain)

J. CORNEJO

Centro de Edafología y Biología Aplicada del Cuarto, C.S.I.C., Sevilla (Spain)

M.J. PEÑA and C.J. SERNA

Instituto de Fisico-Química Mineral, C.S.I.C., Madrid (Spain)

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ABSTRACT

Dawsonite-type compounds of formula $MAl(OH)_2CO_3$ ($M = Na, K, NH_4$) as well as a laminar hydrotalcite-type hydroxycarbonate of composition $[Al_2Li(OH)_6]_2CO_3 \cdot 4H_2O$, have been hydrothermally synthesized. The thermal decomposition of these compounds was monitored by DTA and TG, and the resulting products have been studied by X-ray and IR techniques. Sodium and potassium dawsonites are destroyed at 335°C, yielding a poorly crystalline compound in which part of the overall carbonate is present; the remaining carbonate is lost between 600 and 700°C, yielding $NaAlO_2$ and $KAlO_2$, respectively. Ammonium dawsonite and lithium hydrotalcite are less stable, their thermal decomposition occurring at about 240°C. The ammonium dawsonite heated at 680°C shows the presence of Al_2O_3 with a poorly ordered structure, while lithium hydrotalcite yields poorly crystalline γ-Al_2O_3 at 500°C and a mixture of γ-$LiAlO_2$ and $LiAl_5O_8$ when the compound is heated at higher temperatures (~ 1000°C).

INTRODUCTION

Dawsonite is a mineral of formula $NaAl(OH)_2CO_3$ first obtained synthetically by Bader [1] and, later, by Besson et al. [2]. Potassium and ammonium dawsonite have also been synthesized [3].

The crystal structure of dawsonite was determined by Frueh and Golightly [4] and subsequently refined by Corazza et al. [5]. Such a structure is orthorhombic (I_{mma}), and consists of an assembly of distorted $NaO_4(OH)_2$ and $AlO_2(OH)_4$ octahedra and carbonate groups [5].

The crystal structure of ammonium dawsonite has been determined as C_{mcm} [6]. Both crystal structures (dawsonite and ammonium dawsonite) are

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composed of the same $AlO_2(OH)_4$ chains of octahedra, but in ammonium dawsonite all the chains are in equivalent positions, whereas in dawsonite half of the chains differ in position by $1/2b$. No parallel studies have been carried out for potassium dawsonite, but it is supposed to have the same crystal structure as dawsonite [15].

Aluminium-lithium hydroxycarbonate, $[Al_2Li(OH)_6]_2CO_3 \cdot 4H_2O$, is, however, a laminar, hydrotalcite-type compound whose structure consists of layers in which Al ions are arranged as in gibbsite and the vacancies are filled with lithium cations [7]. Anions are present between the layers to balance the resulting charge. Interlayer water molecules are also present.

Both dawsonite- and hydrotalcite-type compounds are, thus, double hydroxycarbonates of aluminium and a monovalent cation, and all of them exhibit a well-known behaviour as antacids [8,9].

In order to contribute new data to the knowledge of the physico-chemical properties of this type of compounds, we have synthesized double hydroxycarbonates of aluminium with Na, K, NH_4 and Li, and studied their thermal stability in detail.

EXPERIMENTAL

Homoionic dawsonites were synthesized by two equivalent methods. Dawsonite was obtained from a freshly prepared aluminium hydroxide gel by adding a solution of sodium bicarbonate up to pH 8. Potassium and ammonium dawsonites were obtained by adding a solution of aluminium chloride to another of potassium and ammonium bicarbonates, respectively, until pH 8 was obtained.

The synthesis of the lithium hydrotalcite was conducted by slowly adding a 0.1 M solution of aluminium nitrate to an LiOH-saturated solution up to pH 12.5 [7].

In every case, the resulting gel was treated hydrothermally at about 130°C for several days in order to improve particle size, and the product was subsequently washed to remove excess substances.

The chemical analysis of the cations was carried out by atomic absorption on a Perkin-Elmer 380 instrument, after disolving the solids in dilute HCl.

XRD patterns were obtained by means of a Philips PW 1362 diffractometer, using CuK_α radiation and a scanning speed of $1° \ 2\theta \ \text{min}^{-1}$. IR spectra were recorded on a Perkin-Elmer 580 B apparatus, applying the KBr pellet technique.

The electron micrographs of dawsonites were obtained by scanning electron microscopy on a JEOL JSM-50A instrument, whereas those of the hydrotalcite-type compound were obtained with a Siemens 102 Elmiskop apparatus.

Specific surface areas were calculated by the BET method [10]. Absorption isotherms for N_2 at 77 K were determined on a Pyrex high-vacuum apparatus and dead spaces were measured with He gas.

DTA and TG diagrams were recorded with a Rigaku-thermoflex TG–DTA instrument, the heating rate being 8°C min^{-1}.

RESULTS AND DISCUSSION

Characteristics of the samples

Sodium, potassium and ammonium dawsonites were identified from the XRD patterns (Table 1), which agree with those previously published by Corazza et al. [5] and Serna et al. [11]. The table also includes the spacings corresponding to the lithium hydrotalcite, whose d_{hkl} spacings were analysed in an earlier paper [7], and interpreted by an ordered cation arrangement in the octahedral layer, on the basis of a hexagonal superlattice with dimensions: $a = 5.32$ and $c = 15.24$ Å.

TABLE 1

X-ray diffraction data of synthetic aluminium hydroxycarbonates

Dawsonite						Hydrotalcite	
Na		K		NH_4		Al-Li	
d (Å)	I/I_0	d (Å)	I/I_0	d (Å)	I/I_0	d (Å)	I/I_0
5.69	100	5.60	80	5.81	100	7.6	100
3.39	20	4.10	40	4.06	30	4.40	10
3.32	20	3.37	60	3.41	20	4.27	< 5
3.09	10	3.14	100	3.31	50	4.12	< 5
2.78	70	2.89	10	3.17	20	3.96	< 5
2.61	20	2.81	35	2.92	20	3.78	55
2.50	25	2.78	35	2.89	15	2.52	20
2.16	20	2.64	20	2.87	20	2.50	15
1.99	25	2.51	70	2.56	40	2.27	5
1.95	10	2.22	20	2.35	15	2.25	
1.74	15	2.16	40	2.24	10	2.22	10
1.73	10	1.99	50	2.18	10	2.11	< 5
1.69	15	1.66	20	2.16	10	1.95	< 5
1.68	15	1.57	10	2.03	30	1.93	
1.66	15			1.99	15	1.897	15
				1.86	20	1.826	< 5
				1.85	15	1.793	< 5
				1.72	20	1.721	< 5
				1.65	10	1.600	< 5
				1.43	10	1.517	< 5
				1.40	10	1.475	12
						1.445	11

TABLE 2

Characteristics of the samples

Sample	Morphology	Particle size (μm)	Specific surface ($m^2 g^{-1}$)	Ideal formula
D-Na	Spherical	0.15	64	$AlNa(OH)_2CO_3$
D-K	Fibrous	0.75 × 0.15	36	$AlK(OH)_2CO_3$
D-NH_4	Spherical	0.10	161	$AlNH_4(OH)_2CO_3$
H-Li	Hexagonal plates	1 – 2	7	$[Al_2Li(OH)_6]_2CO_3 \cdot 4H_2O$

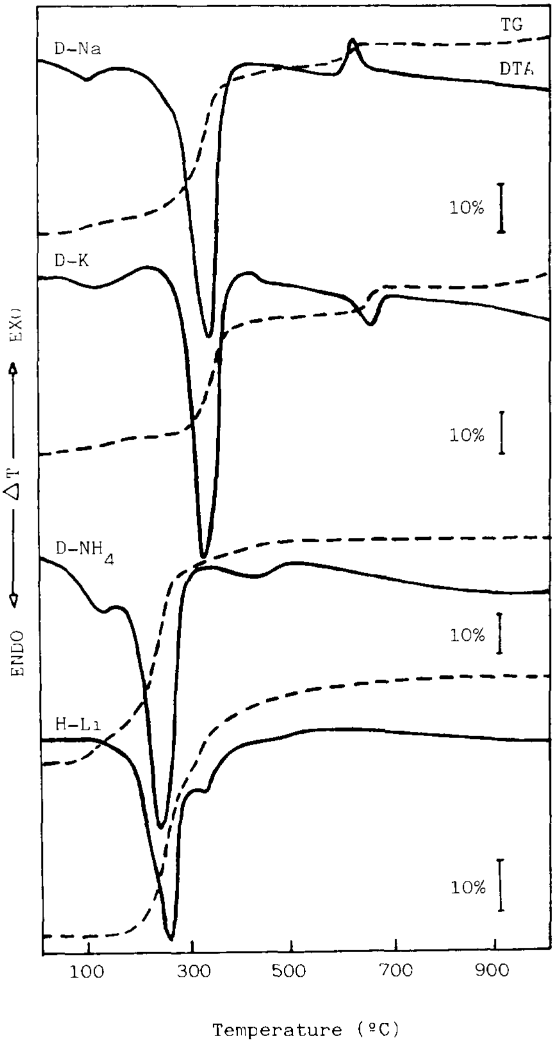

Fig. 1. DTA and TG curves for samples D-Na, D-K, D-NH_4 and H-Li.

On the other hand, the electron micrographs obtained clearly show the different morphology of potassium dawsonite (fibrous) from that of sodium and ammonium dawsonites (spherical). Moreover, an X-ray comparison between the different dawsonite samples indicates that crystallinity increases in the order ammonium < sodium < potassium, which is consistent with a decrease in the specific surface for these compounds (Table 2). It should also be pointed out that the particle size of ammonium dawsonite is probably smaller than the stated value as result of the poor dispersion of the sample (particulate aggregates are observed rather than individual particles). These data are listed in Table 2, together with the characteristics corresponding to lithium hydrotalcite, whose electron micrographs show a plate morphology with a distinct hexagonal contour in analogy to that observed for hydrotalcite-like compounds [12]. It shows a much smaller specific surface than homoionic dawsonites as a result of its much larger particle size (~ 1 μm).

Thermal analysis

Figure 1 shows the DTA and TG curves for the four aluminium hydroxycarbonates synthesized. All homoionic dawsonites exhibit a first endo-

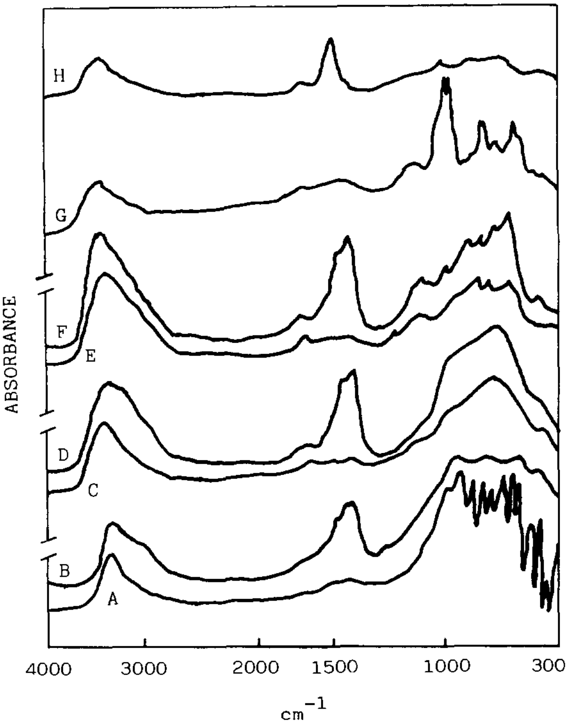

Fig. 2. Infrared spectra of dawsonites and lithium hydrotalcite treated at different temperatures: (A) H-Li, 1000°C; (B) H-Li, 500°C; (C) D-NH_4, 680°C; (D) D-NH_4, 250°C; (E) D-K, 680°C; (F) D-K, 450°C; (G) D-Na, 700°C; (H) D-Na, 450°C.

thermic effect at a temperature of about 100°C which should be attributed to surface effects since neither the X-ray nor the IR analyses show effects on the solid structure at such low temperatures.

In the case of sodium and potassium dawsonites, heating at the temperature corresponding to the second endothermic peak (~ 335°C) gives rise to the formation of aluminium double oxides with the alkaline metal in which a part of the original carbonate is still present [13,14]. This is shown by the absorptions in the IR spectrum at around 1400 cm^{-1} [15], although the

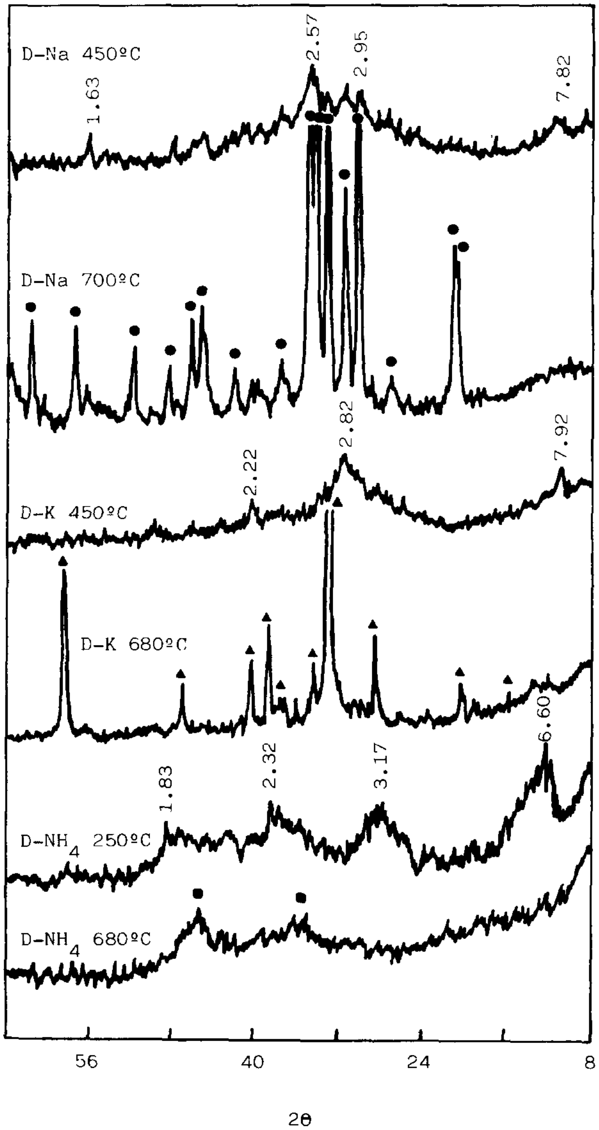

Fig. 3. X-ray powder diffraction patterns for compounds D-Na, D-K and D-NH_4 calcined at different temperatures: (●) $NaAlO_2$, (▲) $KAlO_2$, (■) γ-Al_2O_3.

nature of this carbonate is very different from the starting dawsonites (Fig. 2F and H). On the other hand, the XRD patterns of the compounds heated at 450°C (immediately after the endothermic peak) show, in both cases, the disappearance of the original dawsonite and the formation of a poorly crystalline compound (Fig. 3).

According to the above statements, the TG analysis (Table 3) is consistent with the loss of all the hydroxyl groups, in the form of H_2O, and 2/3 of the carbonate, as CO_2. At higher temperatures (612°C for sodium and 668°C for potassium dawsonites) the remainder of the carbonate is lost (Fig. 2E and G), giving rise to the formation of sodium and potassium aluminates, respectively (Fig. 3).

In the light of the above-mentioned data, the decomposition of sodium and potassium dawsonites could be expressed by the following scheme

$$3MAl(OH)_2CO_3 \xrightarrow{\sim 335^\circ C} 2CO_2 + 3H_2O$$

$$+ [Al_3M_3O_5CO_3] \xrightarrow{650^\circ C} \rightarrow 3MAlO_2 + CO_2$$

Regarding ammonium dawsonite, its decomposition occurs at lower temperatures, probably due to the presence of the NH_4 ion. As can be observed from Fig. 1, the most important endothermic effect appears at 234°C and coincides with the destruction of the compound according to the XRD pattern of the sample heated at 250°C (Fig. 3), which corresponds to an ill-defined compound but does not show the spacings of the original ammonium dawsonite. According to the TG data (Table 3), a weight loss corresponding to hydroxyl and ammonium ions as well as 2/3 of the carbonate takes place between 50 and 250°C, which is in agreement, as a whole, with the presence of a broad band at around 1400 cm^{-1} in the IR spectrum (Fig. 2). This indicates that part of the carbonate is still present at that temperature, although the characteristic bands of carbonate in ammonium dawsonite have disappeared [15].

The IR spectrum recorded after heating ammonium dawsonite at temperatures above 600°C (Fig. 2D) shows that all the carbonate has been eliminated. As expected, the weight loss detected from the TG curve between 350 and 600°C (Fig. 1), corresponds to the elimination of 1/3 of the overall carbonate in the original dawsonite (Table 3). The XRD pattern of the sample heated at 680°C is indicative of the presence of Al_2O_3 in a poorly ordered structure (Fig. 3).

According to the above data, the decomposition of ammonium dawsonite can be expressed with the aid of the following scheme

$$6NH_4Al(OH)_2CO_3 \xrightarrow{\sim 230^\circ C} 4CO_2 + 9H_2O + 6NH_3$$

$$+ [Al_6O_7(CO_3)_2] \xrightarrow{435^\circ C} 3Al_2O_3 + 2CO_2$$

TABLE 3

Weight loss (%) with temperature

Dawsonite-Na			Dawsonite-K			Dawsonite-NH_4			Hydrotalcite-Li		
Temp. (°C)	Exp.	Theor.	Temp. (°C)	Exp.	Theor.	Temp. (°C)	Exp.	Theor.	Temp. (°C)	Exp.	Theor.
50–150	2.5	–	50–200	5	–	50–150	12.5	–	150–290	30	–
150–450	33	33	200–450	27	29.5	150–350	39	52.5	290–500	16	–
450–700	7	10	450–750	7	9.1	350–600	10.9	10.5	500–1000	3.4	–
	42.5	43		39	38.1		62.4	63		49.4	48.9

It should be noted that the thermal stability of lithium hydrotalcite (Fig. 1) is quite different from that observed for other compounds with the same structure, whose thermal decomposition has been previously studied [16–20]; lithium hydrotalcite exhibits a thermal behaviour rather different from that of its Ni or Mg analogues with an M^{2+}/Al^{3+} ratio of 2 and an octahedral cation arrangement similar to that of hydrotalcite [7]. In these compounds, interlayer water is lost in every case between 200 and 300°C. The X-ray diffraction patterns show a slight reduction of the interlayer space, but the hydrotalcite-type structure is preserved (it is only destroyed at temperatures of 350–500°C [16,19,20]). Conversely, the DTA curves of lithium hydrotalcite show a sole endothermic peak appearing at 150°C and extending up to approximately 500°C (with two peaks at 240 and 340°C) which is accompanied by a weight loss (TG curve) corresponding to the elimination of interlayer H_2O and carbonates, as well as hydroxyl groups of the octahedral layer (Table 3). The XRD patterns of the compound heated above 240°C show the decomposition of the laminar compound to have taken place and they correspond to a poorly crystalline compound of ill-defined structure. On the other hand, the IR spectra of the compounds heated at different temperatures (up to 500°C) allow the assumption that

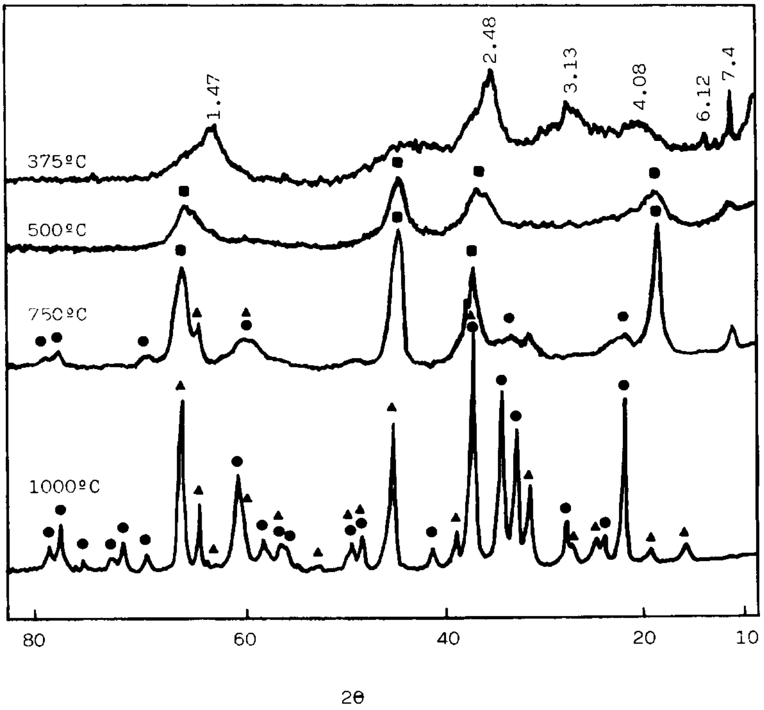

Fig. 4. X-ray powder diffraction patterns for compound H-Li calcined at 375–1000°C: (■) γ-Al_2O_3, (●) γ-$LiAlO_2$, (▲) $LiAl_5O_8$.

CO_2 is eliminated in successive stages. As can be observed from Fig. 2, a broad band still appears at around 1400 cm^{-1} after heating the compound at 500°C, which is indicative of the presence of the CO_3^{2-} ion [21], whereas the corresponding XRD pattern (Fig. 4) only shows the spacings attributable to poorly crystalline γ-Al_2O_3 whose crystallinity, as expected, increases with increasing temperature; this can be seen in the XRD pattern of the sample heated at 750°C, in which the spacings corresponding to a much more crystalline γ-Al_2O_3 can be identified. Such a pattern also shows the beginning of the interaction between aluminium and lithium oxides to yield the corresponding aluminates (γ-$LiAlO_2$ and $LiAl_5O_8$) which are readily identifiable in the XRD pattern of the compound heated at 1000°C [22]. The weight loss data (Table 3), together with the XRD patterns corresponding to the heated samples, allow the following scheme to be proposed for the decomposition of lithium hydrotalcite

$$[Al_4Li_2(OH)_{12}]CO_3 \cdot 4H_2O \xrightarrow{200-1000^\circ C} 10H_2O$$

$$+ CO_2 + \tfrac{3}{2}\gamma\text{-}LiAlO_2 + \tfrac{1}{2}LiAl_5O_8$$

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