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KINETICS OF THE THERMAL DEHYDRATION OF SOME LAYERED HYDROXYCARBONATES

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ABSTRACT

The kinetics of thermal dehydration of hydrotalcite, $Mg_6Al_2(OH)_{16}CO_3.4H_2O$, and other related hydroxycarbonates has been studied by analysis of both dynamic and isothermal weight loss data. The results obtained seem to indicate that the water loss occurs through a diffusion mechanism. These results are according with the layered structure of the compounds.

INTRODUCTION

Hydrotalcite, which ideal unit cell formula is $Mg_6Al_2(OH)_{16}CO_3.4H_2O$, is a mineral of anionic clays group. The structure of these materials is very similar to that of brucite, $Mg(OH)_2$. Here, the magnesium cation is octahedrally surrounded by hydroxyl groups; the resulting octahedra share edges to form infinite sheets. When some of magnesium in this lattice is isomorphously replaced by a higher charged cation, e.g.,Al^{3+}, then this Mg^{2+}-Al^{3+}-OH layer gains positive charge. An appropiate number of interstitial anions, of almost any kind but most frequently carbonate, render this arrangement electrically neutral. Additionally, there are some water molecules located between each metal ion sheet. By synthesis, materials with Mg replaced by Zn, Ni, Co, etc. and Al replaced by Cr and Fe have been prepared (1-4).

The thermal decomposition of hydrotalcite and related compounds has been previously studied (5-7). Below 300ºC only interstitial water was lost reversibly and the structure does not change; between 250 and 550ºC both carbon dioxide and further water from the dehydroxylation were lost with destruction of layered structure and formation of a mixture of metallic oxides.

In this paper, the kinetics of thermal dehydration of various Mg,Al and Mg,Fe hydroxycarbonates, with molar ratios M^{2+}/M^{3+} 2/1 and 3/1, are studied through the analysis of isothermal and dynamic weight loss data.

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EXPERIMENTAL

Mg,Al and Mg,Fe hydroxycarbonates were prepared by slow addition of an NaOH solution to a mixed and diluted solution of Mg^{2+} and Al^{3+} or Mg^{2+} and Fe^{3+}, with molar ratios M^{2+}/M^{3+} 2/1 and 3/1 until a final pH about 10. The mixture was vigorously stirred during the reaction and the resulting gel was hydrothermally treated for several days at 130ºC to improve crystallinity.

The compounds were characterized by X-ray powder diffraction patterns recorded on a Siemens D500 diffractometer using Cu $K\alpha$ radiation. Mg, Fe and Al were determined by atomic absorption spectrometry on a Perkin-Elmer 380 spectrometer.

A Rigaku-Thermoflex TG-DTA instrument was used for the heating experiments. Both isothermal and continuous-heating TG curves were recorded under an air atmosphere using ≈30 mg of sample.

Kinetic analysis of the isothermal curves was carried out by means of the general kinetic equation:

$$g(\alpha) = kt \qquad (1)$$

where α is the reacted fraction at time t, k is the rate constant of the reaction and $g(\alpha)$ is a function depending on the mechanism assumed for the reaction. Various espressions taken from the literature and covering homogeneous (F_1), diffusion-controlled (D_1,D_2,D_3,D_4), phase-boundary-controlled (R_2,R_3) and random nucleation (A_2,A_3) reactions were applied. "Reduced time" master plots (8) and "lnln" (9) methods were also used.

Kinetic analysis of the TG data was carried out using the method described by Coats and Redfern (10) that employs the following expression:

$$\ln g(\alpha) - 2\ln T = \ln \frac{AR}{E\beta} - \frac{E}{RT} \qquad (2)$$

where T is the temperature, E the activation energy, A the pre-exponential Arrhenius factor, R the gas constant and β the heating rate.

RESULTS AND DISCUSSION

Several isotherms for the different Mg,Al and Mg,Fe hydroxycarbonates prepared were recorded in order to obtain information about the dehydration of these compounds. Figure 1 shows the isothermal traces for Mg_3Al-CO_3 and Mg_3Fe-CO_3 in the range 120-150ºC and 130-190ºC, respectively. These curves have similar shape that observed for analogous $Ni_4Al_2(OH)_{12}SO_4.nH_2O$ (11).

The plot of α vs. t according with the equation (1) permit obtain the rate constant values. These values, with the corresponding linear regression coefficients, for isotherms at 130 and 150ºC of Mg_3Fe-CO_3, obtained in the range $0.2 \leq \alpha \leq 0.6$ are included in Table I. Similar results were obtained for other temperatures and compounds.

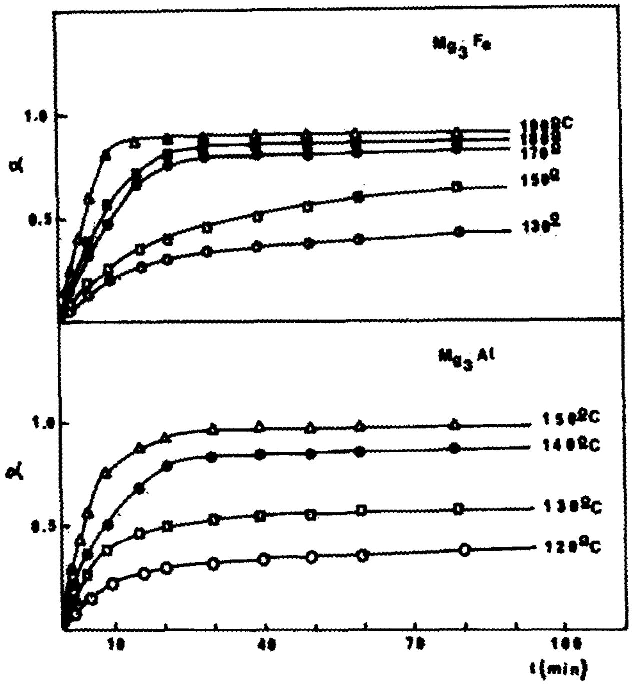

Fig. 1. Isothermal curves for dehydration of $Mg_6Al_2(OH)_{16}CO_3.4H_2O$ and $Mg_6Fe_2(OH)_{16}CO_3.4H_2O$.

TABLE I

Rate constants and regression coefficients values obtained from g(α) vs. time plots for the isotherms at 130 and 150ºC of Mg_3Fe–CO_3 in the α-range 0.2–0.6.

	130ºC		150ºC	
Mechanism	k	r	k	r
F_1	0.0038	0.949	0.0692	0.981
A_2	0.0029	0.925	0.0467	0.961
A_3	0.0023	0.916	0.0346	0.952
R_2	0.0012	0.941	0.0258	0.969
R_3	0.0011	0.944	0.0189	0.973
D_1	0.0016	0.966	0.0327	0.983
D_2	0.0011	0.971	0.0218	0.990
D_3	0.0003	0.977	0.0064	0.996
D_4	0.0002	0.973	0.0054	0.992

These results seems to indicate that the data in Fig. 1 conform better to first-order or diffusion kinetics.

The values of the rate constant, k, calculated from different kinetic models were plotted as a function of 1/T, according to Arrhenius law, and the activation energy values calculated (see Table II).

TABLE II

Activation energy (KJ.mol^{-1}) calculated from the application of the Arrhenius equation to the kinetic data for selected kinetic models in Table I

Mechanism	Mg_3Fe-CO_3	Mg_2Fe-CO_3	Mg_3Al-CO_3	Mg_2Al-CO_3
F_1	9.8	10.9	9.2	18.0
D_1	10.2	11.3	9.5	18.5
D_2	9.9	11.7	9.8	19.2
D_3	10.4	12.0	10.1	19.9
D_4	10.4	11.8	9.9	19.4

It should be noted that the activation energy is practically independent of the kinetic mechanism. This is in agreement with that found in other kinetic analysis (11,12) and a theoretical explanation for this fact has been proposed(13).

The activation energy increase as the compound molar ratio M^{2+}/M^{3+} decrease. This result suggest that the greater the extent of substitution of M^{2+} by M^{3+} and hence the positive charge density in the basic layer, the stronger the attraction between layers which could account for the fact that the loss of molecular water take places at higher temperatures (6) and is accompanied by higher activation energy.

Non-isothermal method of the kinetic analysis was applied to dynamic TG traces (Fig. 2), which was converted into α-T plots and analyzed by means of the Coats and Redfern method (10). The values of activation energy for F_1, D_1, D_2, D_3 and D_4 are similar that obtained for isothermal method but the corresponding regression coefficients allowed cannot be used to discern the true mechanism governing the dehydration.

On the other hand, the "reduced time" master plots method which involves plotting α vs. $t/t_{0.5}$ ($t_{0.5}$ is time for $\alpha = 0.5$ has been suggested by several authors in order to discern the mechanism describing a solid-state reaction. The reduced time plots calculated from the data in Fig. 1 are compared in Fig. 3 with the series of master plots. The results indicate that the dehydration in the temperature range 130-150ºC exhibits a behaviour intermediate between those the first order (F_1) and diffusion-controlled model(D_1, D_2, D_3, D_4).

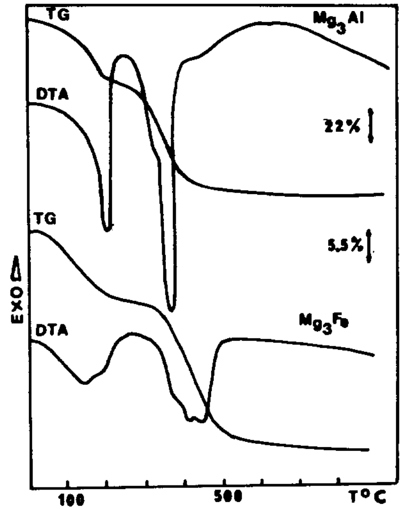

Fig. 2. DTA and TG curves for samples $Mg_6Fe_2(OH)_{16}CO_3.4H_2O$ and $Mg_6Al_2(OH)_{16}CO_3.4H_2O$

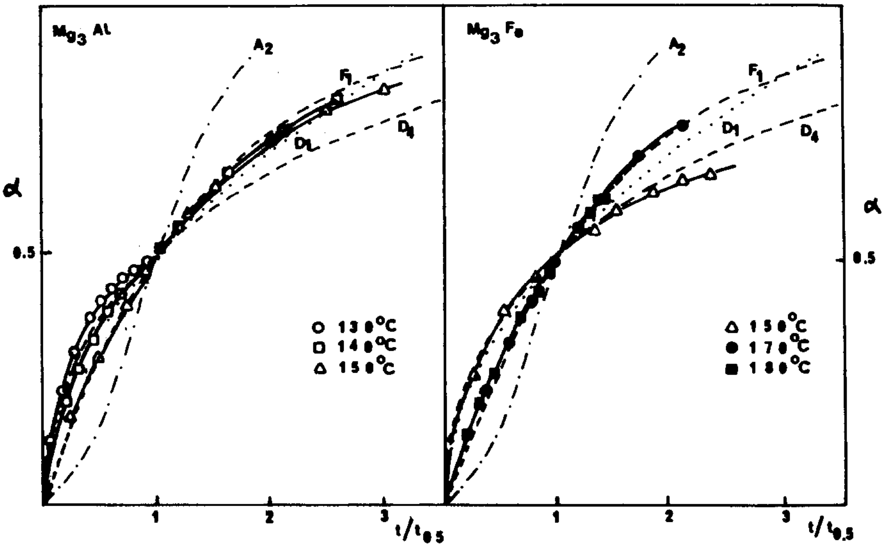

Fig. 3. Comparison of isothermal data at various temperatures with a series of reduced- time master curves.

Additionally, the"lnln"method which requires determination of the slope m of the plot of $\ln[-\ln(1-\alpha)]$ vs. lnt has been applied. The analysis of these data leads to m values as shown in Table III. It can be seen that the m values increase when the reaction temperature does. At temperatures between 120-150ºC these values are consistent with those corresponding to a diffusion mechanism in agreement with the results obtained for the "reduced time" plots.

TABLE III

Values of m resulting of the "lnln" analysis for the isothermal data in Fig.1.

Temperature (ºC)	Mg_3Fe-CO_3	Mg_2Fe-CO_3	Mg_3Al-CO_3	Mg_2Al-CO_3
120	—	—	0.41	—
130	0.54	0.43	0.48	0.40
140	—	—	0.80	0.56
150	0.60	0.62	0.90	0.79
170	1.01	0.65	—	0.60
180	1.00	0.90	—	0.80
190	0.95	0.80	—	—

m values reported (9): F_1(1.00);R_2(1.11); R_3(1.07); A_2(2.0); A_3(3.0); D_1(0.62); D_2(0.57; D_3(0.54); D_4(0.57).

At higher temperatures the m values deviate from a diffusion mechanism. This effect is most accusated for the Mg_3Fe-CO_3 where an overlap of two endothermic peaks occurs (Fig.2). Therefore, the m values calculated on the basis of isotherms obtained at high temperatures must be interpreted with precaution.

The above results are similar that obtained for $Ni_4Al_2(OH)_{12}SO_4.nH_2O$ (11) and the interpretation is analogous. The loss of the interlayer water results in a gradual decrease in the interlayer spacing (14). This accounts for the fact that the dehydration proceeds rapidly up to an α value dependent on the temperature above which the water escapes only with difficulty. This assumption explains the fact that a plateau is reached in the isotherms in Fig. 1, and higher temperatures are required to accomplish complete dehydration.

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