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KINETIC STUDY OF THE THERMAL DEHYDRATION OF LAYERED $[Ni_2Al(OH)_6]_2SO_4 . nH_2O$

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The kinetics of thermal dehydration of $[Ni_2Al(OH)_6]_2SO_4 . nH_2O$ has been studied through the analysis of isothermal weight loss data. The results obtained seem to indicate that the process is governed by a diffusion mechanism up to an α value which is dependent on the temperature. An explanation is provided for this behaviour on the basis of the structural properties of the compound and the nature of the water loss.

Nickel aluminium hydroxysulphate, $[Ni_2Al(OH)_6]_2SO_4 . nH_2O$, is a hydrotalcite-type compound, the structure of which consists of positively-charged brucite-like layers resulting from the replacement of a divalent ion by a trivalent one, with the interlayer space filled by SO_4^{2-} ions and water molecules [1—4]. A schematic representation is shown in Fig. 1.

Water present in the interlayers of these compounds is removed reversibly up to about 573 K, and the structure does not change until this temperature is reached [5]. It is therefore expected that interstices in the interlayer, which result from the

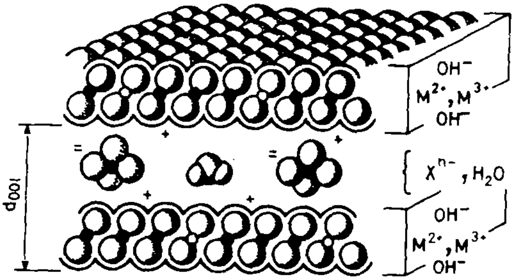

Fig. 1 Schematic representation of hydrotalcite-like compounds: $[M^{2+}_{1-x} M^{3+}_x (OH)_2]^{x+} X^{n-}_{x/n} . mH_2O$. (Taken from Serna *et al.* [5])

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removal of water, will become adsorbing sites for molecules by virtue of the polarity of the layer surface. In fact, the hydrotalcite-like compounds are utilized as acidic adsorbents and catalyst supports in industry.

The thermal decomposition of these compounds has been extensively studied [6—9]; however, the studies have been fundamentally devoted to determining their stability and to identifying the new phases formed in the processes. Little or no attention seems to have been paid to the study of the kinetic aspects of these processes, which could provide major additional information about the properties of these compounds.

The purpose of the present investigation is to elucidate the kinetics of thermal dehydration of $[Ni_2Al(OH)_6]_2SO_4 . nH_2O$ through the analysis of isothermal weight loss data.

Experimental

Sample preparation

A double nickel aluminium hydroxycarbonate, prepared by coprecipitation from Ni^{2+} and Al^{3+} salt solutions by slowly adding a NaOH solution until a suitable pH of 8–8.5 was reached, was used as starting material [4]. The resulting gel was treated hydrothermally at about 403 K for several days to improve the crystallinity. The hydroxy compound with SO_4^{2-} as interlayer anion was obtained by anion-exchange from the hydroxycarbonate, by dispersing 0.5 g of sample in 500 ml 0.01 M H_2SO_4 solution and allowing it to stand for 15 h at room temperature [9].

After dissolution of the solid in dilute HCl, NiO and Al_2O_3 were determined by atomic absorption on a Perkin-Elmer 380 instrument, and SO_4^{2-} was determined by precipitating it as $BaSO_4$. The layered double hydroxysulphate was characterized by means of X-ray diffraction patterns [9] recorded on a Philips PW 1130 instrument.

Thermal analysis

The isothermal weight loss under an air atmosphere was recorded with a Rigaku-Thermoflex TG-DTA instrument, using ~23 mg of sample and an accuracy of ±1 degree in temperature. The sample was inserted into the furnace preheated to the desired temperature and, after an interval of several minutes for thermal equilibrium to be reached, data collection was started.

The kinetic analysis of the isothermal curves was carried out on the basis of the general kinetic equation

$$g(\alpha) = kt \tag{1}$$

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 expressions 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. Plots of these $g(\alpha)$ functions against time, and the use of the least squares method, permits us to obtain the slopes (related to the constant rate of the process) and the regression coefficients.

Results and discussion

In order to obtain further information about the dehydration of the double hydroxysulphate, we recorded the X-ray powder diffraction patterns of the original compound and of the residues after heating at different temperatures (Fig. 2). A progressive decrease can be observed in the d_{002} spacing from 10.6 Å in the untreated compound to 7.09 Å in that heated at 623 K, a temperature at which the loss of interlayer water is complete [10].

Figure 3 shows the isothermal (α, t) data recorded in the temperature range 391–543 K.

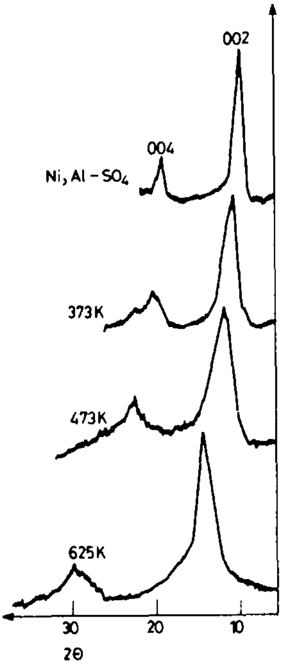

Fig. 2 X-ray powder diffraction patterns corresponding to d_{002} and d_{004} spacings for Ni,Al hydroxysulphate, both untreated and after calcination at the indicated temperatures

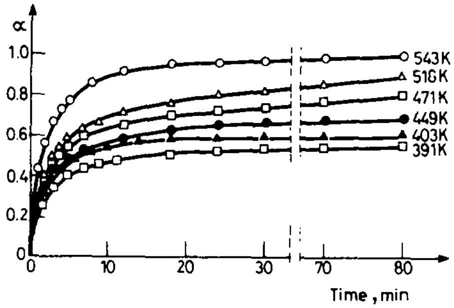

Fig. 3 Isothermal curves for dehydration of Ni,Al hydroxysulphate hydrate

These curves are observed to have a special shape, with a plateau from some α value which is different for every isotherm onwards and above which the reaction can be said not to progress with time.

The rate constants and linear regression coefficients of the plots of the above functions *vs.* time for the isotherm at 471 K, in the ranges $0.2 \leq \alpha \leq 0.8$ and $0.3 \leq \alpha \leq 0.6$, are given in Table 1; similar results were obtained for other temperatures. The regression coefficients obtained for the second α range are better than those for the first. It can be observed in Fig. 3 that α values lower than 0.3 are attained in a span of less than 3 min, which is probably too short for the sample to have reached the steady-state.

Typical plots of $g(\alpha)$ *vs.* t for two representative temperatures (391 and 543 K) in the whole α range are shown in Fig. 4. It is seen that Eq. (1) is not satisfied by any of

Table 1 Rate constants and regression coefficients values obtained from $g(\alpha)$ *vs.* time plots for the isotherm at 471 K in the ranges 0.2–0.8 and 0.3–0.6

	$0.2 \leq \alpha \leq 0.8$		$0.3 \leq \alpha \leq 0.6$	
Mechanism	k	r	k	r
F_1	0.01492	0.8226	0.03500	0.9492
A_2	0.00771	0.7626	0.01870	0.9269
A_3	0.00524	0.7400	0.01278	0.9184
R_2	0.00451	0.7728	0.01115	0.9310
R_3	0.00354	0.7897	0.00863	0.9374
D_1	0.00652	0.7949	0.01645	0.9410
D_2	0.00518	0.8317	0.01250	0.9549
D_3	0.00197	0.8733	0.00443	0.9689
D_4	0.00137	0.8465	0.00325	0.9601

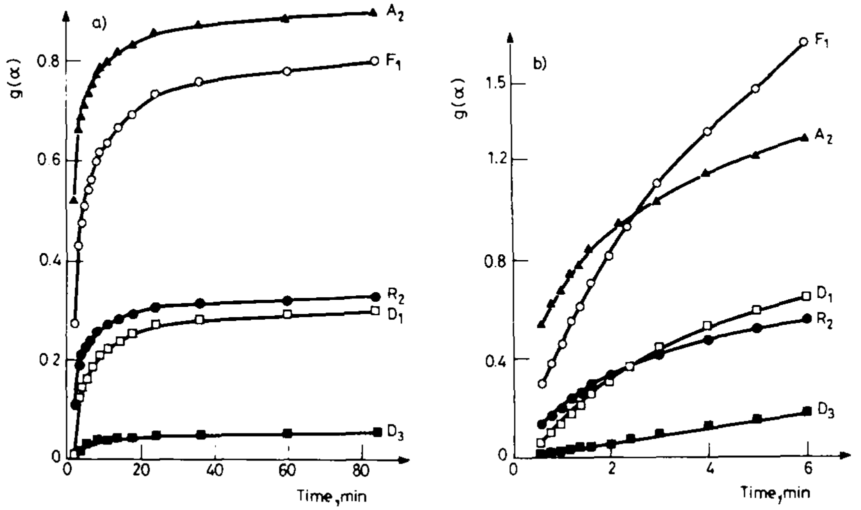

Fig. 4 Plots of $g(\alpha)$ vs. time for two representative temperatures: (a) 391 K, (b) 543 K

the kinetic laws considered, although the linear correlations increase when the reaction temperature does. The results in Table 1 and Fig. 4 seem to indicate that the data in Fig. 3 conform better to first-order or diffusion kinetics.

The values of the rate constant, k, calculated from different kinetic models are plotted in Fig. 5 as a function of $1/T$, according to the Arrhenius law. In calculating the activation energy, we have used the isotherms obtained between 391 and 518 K, since at 543 K the reaction develops so rapidly (80% of the reactant has decomposed within 5 min) that the reaction is probably controlled by heat-transfer processes. An activation energy of 11 ± 1 kJ mol^{-1} was obtained from these plots whatever the kinetic model previously assumed. This is in agreement with previous

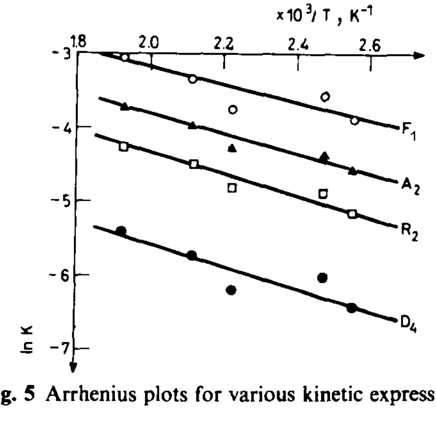

Fig. 5 Arrhenius plots for various kinetic expressions

findings which demonstrate that the kinetic data in solid-state reactions show a good fit to Eq. (1), regardless of the nature of the $g(\alpha)$ function assumed, leading to the same value of the activation energy [11, 12]. A theoretical explanation for this fact, based on the linear correlations between the $g(\alpha)$ functions for a wide range of decomposed fraction, α, has recently been proposed by Criado *et al.* [11].

Use of the "reduced time" master plots method, which involves plotting α *vs.* $t/t_{0.5}$ ($t_{0.5}$ is the time for $\alpha = 0.5$), has been suggested by several authors [13, 14] in order to discern the mechanism describing a solid-state reaction. The reduced time plots calculated from the data in Fig. 3 are compared in Fig. 6 with the series of

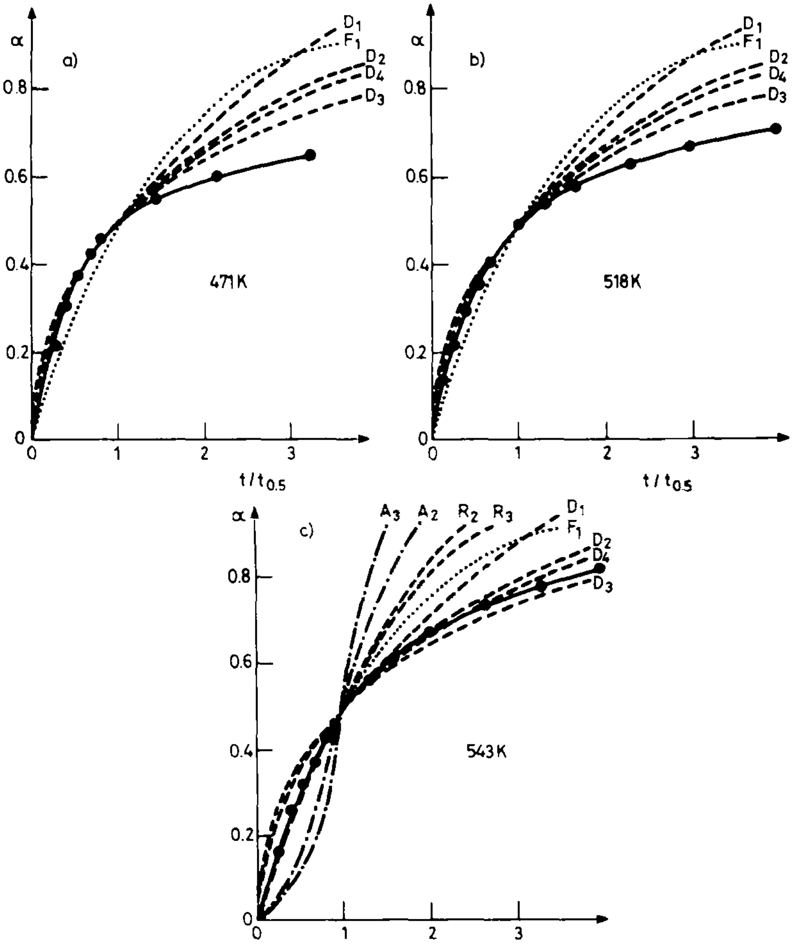

Fig. 6 Comparison of experimental isothermal data at various temperatures with a series of reduced-time master curves: (a) 471 K; (b) 518 K; (c) 543 K

master plots. The results indicate that the dehydration of the hydroxysulphate in the temperature range 391–518 K exhibits a behaviour intermediate between those of a first-order (F_1) and a diffusion-controlled model for $\alpha \leq 0.5$. Therefore, this method does not allow distinction between models F_1, D_1, D_2, D_3 and D_4. The isotherm corresponding to 543 K better fits an F_1 mechanism for α values lower than 0.5, but, as we stated above, it is necessary to interpret the data obtained at this temperature cautiously.

The "ln ln" method, which requires determination of the slope, m, of the plot of $\ln(-\ln(1-\alpha))$ *vs.* $\ln t$, has also been applied. The m values reported by Hancock and Sharp [15] for the different kinetic models are as follows: for F_1 1.00, for R_2 1.11, for R_3 1.07, for A_2 2.00, for A_3 3.00, for D_1 0.62, for D_2 0.57, for D_3 0.54 and for D_4 0.57. The plots obtained from the data in Fig. 3 in the range $0.3 \leq \alpha \leq 0.65$ are shown in Fig. 7. The analysis of these data leads to the m values and linear regression coefficients shown in Table 2. It can be seen that the m values increase when the reaction temperature does. At temperatures between 391 and 518 K, these values are consistent with those corresponding to a diffusion mechanism, in agreement with the results obtained for the "reduced time" plots.

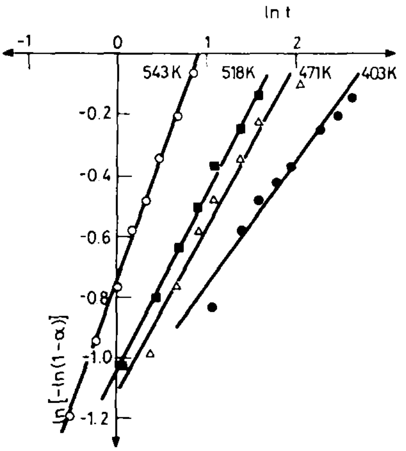

Fig. 7 Plots of $\ln[-\ln(1-\alpha)]$ *vs.* $\ln t$

The above results could be interpreted by taking into account the lamellar structure of $[Ni_2Al(OH)_6]_2SO_4 . nH_2O$ (Fig. 1). The loss of interlayer water results in a gradual decrease in the interlayer spacing (Fig. 2). This accounts for the fact that the dehydration proceeds rapidly up to an α value dependent on the temperature, above which a plateau is reached in the isotherms in Fig. 3. A significant decrease in the interlayer space will hinder the further loss of water, thereby calling for very high temperatures to accomplish complete dehydration.

Table 2 Results of the "ln ln" analysis for the isothermal data in Fig. 1

Temperature, K	*m*	*r*
391	0.40	0.9211
403	0.41	0.9748
449	0.45	0.9731
471	0.54	0.9812
518	0.62	0.9940
543	0.83	0.9986

This interpretation is analogous with that formulated recently by Criado *et al.* [16] for the dehydroxylation of kaolinite. Likewise, Martin *et al.* have observed a change from a D_3 to a D_4 mechanism as the dehydration of various cerium sulphates develops, which has been attributed to the decrease in the interfacial area and the consequent reduction in the free space of the system after the first dehydration step has taken place [17].

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Zusammenfassung — Die Kinetik der thermischen Dehydratisierung von $[Ni_2Al(OH)_6]_2SO_4.nH_2O$ wurde mittels isothermer TG untersucht. Die Ergebnisse scheinen darauf hinzudeuten, daß der Prozeß bis zu einem von der Temperatur abhängigen α-Wert von einem Diffusionsmechanismus bestimmt wird. Für dieses Verhalten wird basierend auf den strukturellen Eigenschaften der Verbindung und der Natur der Wasserabgabe eine Erklärung gegeben.

Резюме — Посредством анализа данных изотермической потери веса, изучена кинетика термической дегидратации $[Ni_2Al(OH)_6]_2SO_4.nH_2O$. Полученные результаты показали, что процесс протекает по диффузионному механизму до степени, зависящей от температуры. Исходя из структуры соединения и типа потери воды, приведено объяснение такому поведению.