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ON THE THERMAL DECOMPOSITION MECHANISM FOR DEHYDROXYLATION OF ALKALINE-EARTH HYDROXIDES

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The activation energy for thermal dehydroxylation in vacuum of alkaline-earth hydroxides has been calculated from thermogravimetric data. The experimental results of $Mg(OH)_2$ $Ca(OH)_2$ and $Sr(OH)_2$ are in agreement with an unimolecular decay law and their activation energies are similar to the values of enthalpies of decomposition. In contrast, as the dehydroxylation process of $Ba(OH)_2$ takes place in liquid phase and the BaO does not dissolve into the molten $Ba(OH)_2$, a kinetic of zero order describes the reaction rate and the activation energy is lower than the enthalpy of decomposition.

The kinetic mechanism of thermal decomposition of both synthetic $Mg(OH)_2$ and natural brucite has received extensive attention [1—4]. However, though thermal decomposition of the other alkaline-earth hydroxides has been studied [5—8], these studies have been fundamentally guided to determine the stability and identification of the new phases formed during the dehydration processes, while nobody seems to have treated the kinetics aspects of these processes, performing calculations about the kinetic parameters.

The kinetic of thermal dehydroxylation of alkaline-earth hydroxides has been studied here, using thermogravimetric methods at programmed temperature. These methods have been widely used in literature [9—11] and have the advantage over the isothermal one that using a single TG curve the kinetic parameters of solid thermal decomposition can be determined.

Experimental

Materials. — The brucite sample came from a pencatite rock and its chemical analysis was: SiO_2 1.73%; Fe_2O_3 3.27%; CaO 16.70%; MgO 33.43%; loss on ignition 30.13%. From these data and taking into account that X-ray diagram showed that calcium and magnesium were found as calcite, dolomite and brucite, the percentage of these minerals in the brucite sample were calculated as: brucite 45.84%; dolomite 5.6%; calcite 26.20%.

Provided that the decomposition temperatures of calcite and dolomite are higher than that of brucite, its TG curve is not influenced by the decomposition of those species, being possible the kinetic study of the brucite diagram.

Sample of $Ca(OH)_2$, $Sr(OH)_2.8H_2O$ and $Ba(OH)_2.8H_2O$ were from Merck (Darmstadt). The latter two were heated at 300° for twenty-four hours to dehydrate them. Thermogravimetric studies were carried out using these dehydrated alkaline-earth hydroxides.

Method. – Experiments were performed at a vacuum of 10^{-4} torr, using a CAHN Electrobalance, model RG, and heating rate of 11°C/min.

Results and discussion

Kinetic studies of the thermal decomposition of $Mg(OH)_2$ from isothermal data have been performed using the general equation:

$$\frac{d\alpha}{dt} = k \cdot f(\alpha) = A \cdot e^{-E/RT} \cdot f(\alpha) \tag{1}$$

where α is the decomposed fraction of solid after a time t, $f(\alpha)$ a function depending on the mechanism of decomposition and A and E the preexponential factor and the activation energy, respectively. In these studies $f(\alpha)$ has been taken as $(1 - \alpha)^n$, where n is the reaction order, having only theoretical meaning for 0, 1/2, 2/3, and 1 [12]. The first three values are referred to as a phase-boundary controlled process and the latter as an unimolecular decay law.

On the other hand, the kinetic decomposition parameters in non-isothermal conditions can be calculated from the expression:

$$F(\alpha) = \int_0^{\alpha} \frac{d\alpha}{(1 - \alpha)^n} = \int_0^{T} \frac{A}{\beta} e^{-E/RT} dT \tag{2}$$

where β is the heating rate. An integration method of equation (2) has been developed by Coats and Redfern [13], using an approximate integration of the expo-

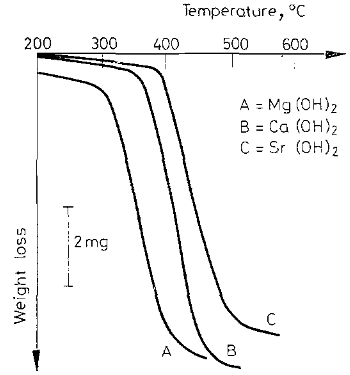

Fig. 1. TG curves of alkaline-earth hydroxides.

nential integral. Though other integral methods of Eq. (2) have been described in literature [9], in a recent paper [14] we have shown the Coats–Redfern's method to be more reliable than those so that we shall make use of it to analyse the thermogravimetric data of dehydroxylation of alkaline-earth hydroxides.

Figure 1 and 2 show the TG curve of the alkaline-earth hydroxides under vacuum.

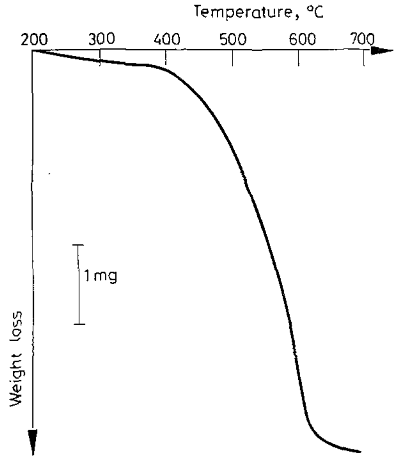

Fig. 2. TG curves for $Ba(OH)_2$

While the maximum reaction rate of $Mg(OH)_2$, $Ca(OH)_2$ and $Sr(OH)_2$ is reached when the decomposed fraction of the reactant, α_{max}, has a value between 0.5–0.6, the reaction rate of thermal dehydroxylation of $Ba(OH)_2$ does not reach a maximum, but increases continually till the decomposed fraction is near unity. The value of α_{max} has been used to predict the decomposition mechanism of the solid and several equations have been deduced to relate such a parameter with the reaction order [15]. Then, as this analysis procedure of the shape characteristics of the TG curves leads to analogous results applying to $Mg(OH)_2$, $Ca(OH)_2$ and $Sr(OH)_2$, their thermogravimetric data might be fitted to the same equation, but a different mechanism could describe the thermal dehydroxylation of $Ba(OH)_2$. It is known both $Sr(OH)_2$, and $Ba(OH)_2$ have low melting points, and an extensive range of values has been reported in literature [16]. From simultaneous DTA and TG curves, we have obtained about 480 and 360° for the melting point of $Sr(OH)_2$ and $Ba(OH)_2$ respectively [17]. Thus, thermal dehydroxylation of $Sr(OH)_2$ and, certainly, $Mg(OH)_2$ and $Ca(OH)_2$ would take place in solid phase while $Ba(OH)_2$ decomposition should occur in liquid phase. This different behaviour might be suitable to explain the change of the shape characteristics that the TG curve of $Ba(OH)_2$, included in Fig. 2, seems to show as regards the curves included in Fig. 1.

As mentioned above, the isothermal dehydroxylation of $Mg(OH)_2$ has been shown to proceed according to the Eq. (1), and values of n equal to 1/2, 2/3, and 1 have been used [1–3]. Sharp and Brindley [18] have concluded that the same experimental data can be described assuming different mechanisms which lead to a little change in the activation energy. However, this conclusion should be taken with a great caution because the range of α used by these authors in the determination of k (constant rate) was only 0.0–0.4 for $n = 1/2$ and 2/3, and 0.1–0.5 for $n = 1$. In Fig. 3 the functions $F(\alpha)$, obtained by integrating the left hand side of the Eq. (2), are plotted against $F(\alpha)$ for $n = 1$, also proceeding in the same way. It has been taken values of α at interval of 0.05 from $\alpha = 0.1$ to $\alpha = 0.9$. As shown in this Figure, an excellent linearity is obtained from $\alpha = 0.1$ to $\alpha = 0.5$, suggesting that the three reaction orders could describe the reaction mechanism. Therefore, it is necessary to analyse the complete reaction to ensure which mechanism governs the process.

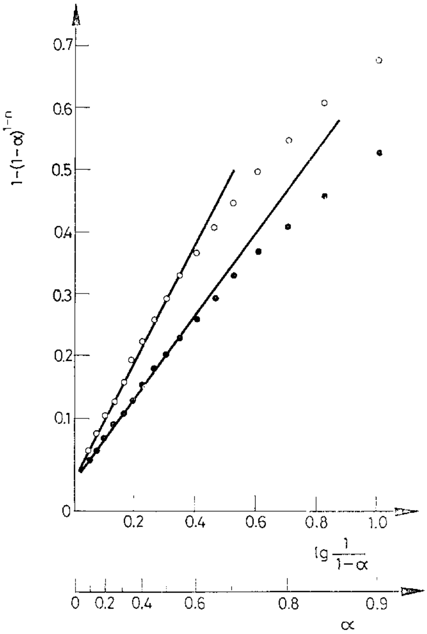

Fig. 3. Plot of $1-(1-\alpha)^{1-n}$ *vs.* Log $1/(1-\alpha)$. ○ $n = 1/2$ ● $n = 2/3$

The best linearity for the thermogravimetric data of $Mg(OH)_2$, from Fig. 1, and applying the Coats and Redfern's equations, was obtained for $n = 1$ (see Fig. 4), while other significant values of n 0, 1/2 and 2/3 gave pronounced curves. This result is in agreement with the value of α_{max} 0.54 from the TG curves [15] and suggests that the decomposition of $Mg(OH)_2$ is reasonably represented as a random nucleation process with one nucleus on the individual particles and the rate of reaction proportional to the amount of the undecomposed substance. The activation energy calculated from the slope of the best straight line was 21 Kcal/mole. This value lies near the one of 20 Kcal/mole proposed by Sharp [19] for the dehydroxylation of pure $Mg(OH)_2$ in vacuum and suggests that the impurities

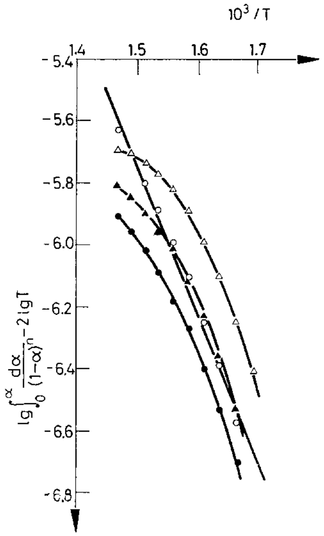

Fig. 4. Data of decomposition of $Mg(OH)_2$ analysed using different reaction mechanism ○ $n = 1$; ● $n = 2/3$; ▲ $n = 1/2$; △ $n = 0$

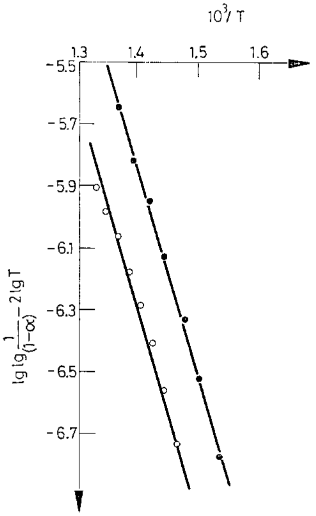

Fig. 5. Kinetic study of decomposition of $Ca(OH)_2$ and $Sr(OH)_2$ after the unimolecular decay law. ○ $Sr(OH)_2$; ● $Ca(OH)_2$

of the brucite studied here have no influence on its decomposition activation energy.

The thermogravimetric data of $Ca(OH)_2$ and $Sr(OH)_2$ were also analysed with the Coats and Redfern's equations, using different values of n; in both cases the best straight line was obtained for $n = 1$. The calculated activation energies were 28 and 30 Kcal/mole for $Ca(OH)_2$ and $Sr(OH)_2$ respectively (see Fig. 5).

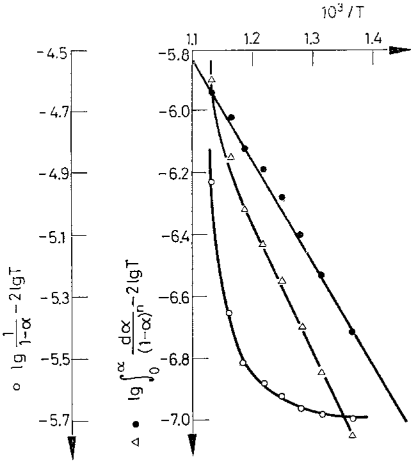

Fig. 6. Data of decomposition of $Ba(OH)_2$ analysed using different reaction mechanisms. ● $n = 0$; △ $n = 1$; ○ $n = 2$

Table 1

Calculated activation energies and enthalpies of dehydroxylation of alkaline-earth hydroxides

Compound	Range of α	E, Kcal/mole	$\Delta H°$, Kcal/mole (+)
$Mg(OH)_2$	0.2–0.9	21	19.4
$Ca(OH)_2$	0.1–0.9	28	26.8
$Sr(OH)_2$	0.2–0.9	30	30.4
$Ba(OH)_2$ (*)	0.1–0.9	15	30.5

(+) Ref. (25).
(*) $\Delta H°$ for the reaction $Ba(OH)_2\ (l) \rightarrow BaO\ (s) + H_2O\ (g)$.

Kinetic analysis of $Ba(OH)_2$, making use of the values of α taken from the TG curves included in Fig. 2, is shown in Fig. 6. As a melting process takes place before the thermal decomposition, the interface boundary disappears and two or three mechanisms can be expected, namely: zero, first and second order [20].

The best linearity is obtained for a mechanism of zero order, Fig. 6, being the rate of the reaction independent of the amount of $Ba(OH)_2$ undecomposed. These experimental results are best explained as follows. The oxide formed during the decomposition does not dissolve in the residual liquid phase, and the "concentration" of the reactant holds constant during the decomposition process. The calculated activation energy for the dehydroxylation of $Ba(OH)_2$ was only 15 Kcal/mole, notably lower than the activation energy of the other alkaline-earth hydroxides.

Many authors [21–23] have found an approximate agreement comparing experimental values of activation energy and enthalpy for the decomposition of many solids. Table 1 contains the activation energy calculated in this paper for the dehydroxylation of alkaline-earth hydroxides and the values of the enthalpy of the same reaction.

This table shows that, in the case of $Mg(OH)_2$, $Ca(OH)_2$ and $Sr(OH)_2$, there is a good agreement between these energetic parameters, taking into account both experimental error and the enthalpy of reaction is referred to the standard conditions. In a recent study of the decomposition mechanism of $CaCO_3$, Hills [24] has concluded that the activation energy is equal to the enthalpy of decomposition as the reaction rate is controlled by the rate of heat transfer towards the reaction interface. Then, these ideas could also be applied to the mechanism of dehydroxylation of $Mg(OH)_2$, $Ca(OH)_2$ and $Sr(OH)_2$. Nevertheless, the dehydroxylation of $Ba(OH)_2$, as it takes place in liquid phase, this has an effect on the kinetic of decomposition, leading to an important decrease in the activation energy with regards to the enthalpy of decomposition.

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RÉSUMÉ — L'énergie d'activation de la déshydroxylation sous vide des hydroxydes des métaux alcalins est calculée à partir des données thermogravimétriques. Les résultats expérimentaux obtenus avec $Mg(OH)_2$, $Ca(OH)_2$ et $Sr(OH)_2$ sont en accord avec une loi de décomposition unimoléculaire et les énergies d'activation correspondantes sont du même ordre de grandeur que les enthalpies de décomposition. Par contre, du fait que la déshydroxylation de $Ba(OH)_2$ a lieu en phase liquide et que BaO ne se dissout pas dans $Ba(OH)_2$ fondu, la vitesse de la réaction est décrite par une cinétique d'ordre zéro et l'énergie d'activation est plus faible que l'enthalpie de décomposition.

ZUSAMMENFASSUNG — Die Aktivierungsenergie zur thermischen Dehydroxilierung von Erdalkali-Hydroxiden im Vakuum wurde aus thermogravimetrischen Daten errechnet. Die Versuchsergebnisse bezüglich $Mg(OH)_2$, $Ca(OH)_2$ und $Sr(OH)_2$ sind mit einem unimolekularen Zersetzungsgesetz in Übereinstimmung und die entsprechenden Aktivierungsenergien sind den Werten der Zersetzungsenthalpien ähnlich. Im Gegensatz hierzu wird im Falle von $Ba(OH)_2$, da der Dehydroxylierungsvorgang in der flüssigen Phase stattfindet und das BaO sich nicht im geschmolzenen $Ba(OH)_2$ löst, die Reaktionsgeschwindigkeit durch eine Kinetik nullter Ordnung beschrieben und die Aktivierungsenergie liegt hierbei niedriger als die Zersetzungsenthalpie.

Резюме — Из термогравиметрических данных вычислена активационная энергия термического дегидроксилирования в вакууме гидроокисей щелочноземельных металлов. Экспериментальные результаты для $Mg(OH)_2$, $Ca(OH)_2$ и $Sr(OH)_2$ находятся в согласии с мономолекулярным законом разложения и их энергии активции подобны значениям энтальпии разложения. В противоположность этому, поскольку процесс дегидроксилирования $Ba(OH)_2$ протекает в жидкой фазе и BaO не растворяется в расплавленной гидроокиси бария, скорость реакции описывается нулевым порядком и энергия активации ниже, чем энтальпия разложения.