Research Article

Non-Isothermal Degradation Kinetics of CaCO_3 from Different Origin

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Thermogravimetric studies on two varieties of calcium carbonate, namely, analytical reagent-grade and in situ product from thermal degradation of calcium oxalate monohydrate, were carried out at four rates of linear increase of the temperature. The kinetics and mechanism of their solid-state thermal decomposition reaction were evaluated from the TG data using four calculation procedures and isoconversion method, as well as 27 mechanism functions. The comparison of the results obtained with these calculation procedures showed that they strongly depend on the selection of proper mechanism function for the process. Therefore, it is very important to determine the most probable mechanism function. In this respect the isoconversion calculation procedure turned out to be more appropriate. In the present work, the values of apparent activation energy E , preexponential factor A in Arrhenius equation, as well as the changes of entropy $\Delta S^\ddagger$, enthalpy $\Delta H^\ddagger$, and free Gibbs energy $\Delta G^\ddagger$ for the formation of the activated complex from the reagent are calculated. All calculations were performed using programs compiled by ourselves.

1. Introduction

The thermal decomposition of calcium carbonate has been intensively studied over the years [1–12]. It is explained by great technological importance due to his various industrial applications such as manufacturing of lime and additives or fillers in medicine, cosmetics, foods, plastics, printing ink and an apparent simplicity of the reaction. It is a high temperature reversible decomposition reaction involving a relatively large mass-loss associated with the evolution of carbon dioxide according to the reaction:

Admittedly the studying and measurements are complicated by the reversibility of this reaction and its strongly endothermic nature; however, these complications should only add interest to the resulting comparison.

Calcium carbonate mineral filler has been one of the most popular fillers used in the thermoplastic industry [13, 16]. CaCO_3 can be generally found in three distinct crystalline structures, that is, calcite, aragonite, and vaterite

[17, 18]. Calcite is the most stable and most commonly found in the nature. Aragonite, however, can only be found in precipitate CaCO_3 or seashells whereas vaterite is found from synthesized CaCO_3 and does not occur naturally [17, 18]. Generally, aragonite has higher density and hardness than calcite and vaterite which makes it a valuable inorganic material that can be used as a filler for armature plastic, rubber, paper, glass fiber, print ink, paint pigment, and composite [13, 16, 17]. From another side, very interesting is the comparative kinetics studying of the thermal degradation of in situ generated calcium carbonate, obtained from the calcium oxalate monohydrate thermal degradation [14, 15].

Apart from mechanical properties, thermal stability is also one of the most important factors for the processing of polymeric materials. Thermal decomposition kinetics of the polymeric materials depend from the thermal stability of the used fillers, which may be characterized with its kinetic parameters such as reaction order n , activation energy E , and preexponential or frequency factor A in the Arrhenius equation [19–21]. According to the results obtained from the different authors the apparent magnitudes of the Arrhenius

parameters range from 110 to 3800 kJ mol⁻¹ for the activation energy, and from 10² to 10¹⁷ s⁻¹ for the frequency factor [1–22]. The reason for widely varying values are different—the shape of the crystalline phase of used calcium carbonate, the mean size of the particles, sample mass, isothermal or nonisothermal heating, heating rate, static or dynamic atmosphere around the studied sample, furnace atmosphere, the partial pressure of carbon dioxide, and the used calculation procedure [2, 14, 21, 23, 24].

The aim of the present paper is to compare the parameters characterizing the kinetics of nonisothermal degradation of analytical reagent-grade commercial sample of CaCO₃ and insitu produced calcium carbonate from CaC₂C₄ · H₂O, obtained on the basis of thermogravimetric data using different kinetic equations and calculation procedures.

2. Experimental

2.1. Material and Measurement. The thermal decomposition on two calcium carbonate, namely, analytical reagent-grade commercial sample and in situ produced calcium carbonate from calcium oxalate monohydrate, were carried out. The samples of CaCO₃ (puriss, Fluka) and CaC₂C₄ · H₂O (puriss, Aldrich) were used after vigorously grounding in agate vibration mortar. The thermogravimetric measurements were carried out in a flow of nitrogen (99.999%) at a rate of 25 cm³ min⁻¹ under nonisothermal conditions on an instrument STA 449 F3 Jupiter (Nietzsch, Germany) with its high temperature furnace. Samples of about 5 ± 0.1 mg mass were used for the experiments varied out at heating rates of 3, 6, 9, and 12 K min⁻¹ up to 1000°C. The samples were loaded without pressing into an open 6 mm diameter and 3 mm high platinum crucible, without using of a standard reference material. The TG, DSC, and DTG curves were recorded simultaneously with 0.1 mg sensitivity.

The crystal structures of studied samples were determined by X-ray diffraction (XRD). The XRD intensity of the samples were collected from a JEOL/JDX 3530 diffractometer equipped with CuK_α generator (λ = 0.1540 nm) at voltage of 32 kV, Ni filter, and a filament current of 30 mA. The scans were taken in the range of the diffraction angle 2θ = 5–60°.

2.2. Mathematical Background. The kinetics of such solid-state reactions is described by various equations taking into account the special features of their mechanisms. The reaction rate can be expressed through the degree of conversion α according to the formula:

$$\alpha = \frac{m_i - m_\tau}{m_i - m_f}, \quad (1)$$

where m_i , m_f , and m_τ are the initial, final, and current sample mass at the moment τ, respectively. Generally, the kinetic equation of the process can be written as follows [1, 3, 13–15, 19–21, 23]

$$\frac{d\alpha}{dt} = k(T) f(\alpha). \quad (2)$$

The temperature dependence of the rate constant k for the process is described by the Arrhenius equation:

$$k = A \exp\left(-\frac{E}{RT}\right), \quad (3)$$

where A is the preexponential factor, E is the apparent activation energy, T is the absolute temperature, and R is the gas constant. Substitution of (3) in (2) gives

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) f(\alpha). \quad (4)$$

When the temperature increases at a constant rate,

$$\frac{dT}{dt} = q = \text{const}, \quad (5)$$

therefore:

$$\frac{d\alpha}{dT} = \frac{A}{q} \exp\left(-\frac{E}{RT}\right) f(\alpha). \quad (6)$$

The conversion function $f(\alpha)$ for a solid-state reaction depends on the reaction mechanism and can generally be considered to be as follows:

$$f(\alpha) = \alpha^m (1 - \alpha)^n [-\ln(1 - \alpha)]^p, \quad (7)$$

where m , n , and p are empirically obtained exponent factors, one of them always being zero [25].

The combinations of different values of m , n , and p make it possible to describe various probable mechanisms.

After substitution of (7) in (6), separation of variables and integration, the following general equation was obtained

$$\int_0^\alpha \frac{d\alpha}{\alpha^m (1 - \alpha)^n [-\ln(1 - \alpha)]^p} = \frac{A}{q} \int_0^T \exp\left(-\frac{E}{RT}\right) dT. \quad (8)$$

The solutions of the left hand side integral depend on the explicit expression of the function $f(\alpha)$ and are denoted as $g(\alpha)$. The formal expressions of the functions $g(\alpha)$ depend on the conversion mechanism and its mathematical model [13–15]. The latter usually represents the limiting stage of the reaction—the chemical reactions; random nucleation and nuclei growth; phase boundary reaction or diffusion. Algebraic expressions of functions of the most common reaction mechanisms operating in solid-state reactions are presented in Table 1 [13–15].

Several authors [1, 3, 14, 26, 27] suggested different ways to solve the right hand side integral. For the present study, one calculation procedure was based on Coats and Redfern equation [1]. Data from TG and DTG curves in the decomposition range 0.1 < α < 0.9 were used to determine the kinetic parameters of the process in all used calculation procedures. The integral method of Coats and Redfern has been mostly and successfully used for studying of the kinetics of dehydration and decomposition of different solid substances [1, 14]. The kinetic parameters can be derived using a linear form of modified Coats and Redfern equation:

$$\ln \frac{g(\alpha)}{T^2} = \ln \left[\frac{AR}{qE} \left(1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT} \cong \ln \frac{AR}{qE} - \frac{E}{RT}, \quad (9)$$

TABLE 1: Algebraic expressions of functions $g(\alpha)$ and $f(\alpha)$ and its corresponding mechanism [13–15].

No.	Symbol	Name of the function	$g(\alpha)$	$f(\alpha)$	Rate-determining mechanism
(1) Chemical process or mechanism noninvoking equations					
(1)	$F_{1/3}$	One-third order	$1 - (1 - \alpha)^{2/3}$	$(3/2)(1 - \alpha)^{1/3}$	Chemical reaction
(2)	$F_{3/4}$	Three-quarters order	$1 - (1 - \alpha)^{1/4}$	$4(1 - \alpha)^{3/4}$	Chemical reaction
(3)	$F_{3/2}$	One and a half order	$(1 - \alpha)^{-1/2} - 1$	$2(1 - \alpha)^{3/2}$	Chemical reaction
(4)	F_2	Second order	$(1 - \alpha)^{-1} - 1$	$(1 - \alpha)^2$	Chemical reaction
(5)	F_3	Third order	$(1 - \alpha)^{-2} - 1$	$(1/2)(1 - \alpha)^3$	Chemical reaction
(2) Acceleratory rate equations					
(6)	$P_{3/2}$	Mampel power law	$\alpha^{3/2}$	$(2/3)\alpha^{-1/2}$	Nucleation
(7)	$P_{1/2}$	Mampel power law	$\alpha^{1/2}$	$2\alpha^{1/2}$	Nucleation
(8)	$P_{1/3}$	Mampel power law	$\alpha^{1/3}$	$3\alpha^{2/3}$	Nucleation
(9)	$P_{1/4}$	Mampel power law	$\alpha^{1/4}$	$4\alpha^{3/4}$	Nucleation
(10)	E_1	Exponential law	$\ln \alpha$	α	Nucleation
(3) Sigmoidal rate equations or random nucleation and subsequent growth					
(11)	A_1, F_1	Avrami-Erofeev equation	$-\ln(1 - \alpha)$	$(1 - \alpha)$	Assumed random nucleation and its subsequent growth, $n = 1$
(12)	$A_{3/2}$	Avrami-Erofeev equation	$[-\ln(1 - \alpha)]^{2/3}$	$(3/2)(1 - \alpha)[- \ln(1 - \alpha)]^{1/3}$	Assumed random nucleation and its subsequent growth, $n = 1.5$
(13)	A_2	Avrami-Erofeev equation	$[-\ln(1 - \alpha)]^{1/2}$	$2(1 - \alpha)[- \ln(1 - \alpha)]^{1/2}$	Assumed random nucleation and its subsequent growth, $n = 2$
(14)	A_3	Avrami-Erofeev equation	$[-\ln(1 - \alpha)]^{1/3}$	$3(1 - \alpha)[- \ln(1 - \alpha)]^{2/3}$	Assumed random nucleation and its subsequent growth, $n = 3$
(15)	A_4	Avrami-Erofeev equation	$[-\ln(1 - \alpha)]^{1/4}$	$4(1 - \alpha)[- \ln(1 - \alpha)]^{3/4}$	Assumed random nucleation and its subsequent growth, $n = 4$
(16)	A_u	Prout-Tomkins equation	$\ln[\alpha / (1 - \alpha)]$	$\alpha(1 - \alpha)$	Branching nuclei
(4) Deceleratory rate equations					
(4.1) Phase boundary reaction					
(17)	R_1, F_0, P_1	Power law	α	$(1 - \alpha)^0$	Contracting disk
(18)	$R_2, F_{1/2}$	Power law	$1 - (1 - \alpha)^{1/2}$	$2(1 - \alpha)^{1/2}$	Contracting cylinder (cylindrical symmetry)
(19)	$R_3, F_{2/3}$	Power law	$1 - (1 - \alpha)^{1/3}$	$3(1 - \alpha)^{2/3}$	Contracting sphere (spherical symmetry)

TABLE 1: Continued.

No.	Symbol	Name of the function	$g(\alpha)$	$f(\alpha)$	Rate-determining mechanism
(4.2) Based on the diffusion mechanism					
(20)	D ₁	Parabola low	α^2	$1/2\alpha$	One-dimensional diffusion
(21)	D ₂	Valensi equation	$\alpha + (1-\alpha)\ln(1-\alpha)$	$[-\ln(1-\alpha)]^{-1}$	Two-dimension diffusion
(22)	D ₃	Jander equation	$[1 - (1-\alpha)^{1/3}]^2$	$(3/2)(1-\alpha)^{2/3}[1 - (1-\alpha)^{1/3}]^{-1}$	Three-dimensional diffusion, spherical symmetry
(23)	D ₄	Ginstling-Brounstein equation	$1 - 2\alpha/3 - (1-\alpha)^{2/3}$	$(3/2)[(1-\alpha)^{-1/3} - 1]^{-1}$	Three-dimensional diffusion, cylindrical symmetry
(24)	D ₅	Zhuravlev, Lesokhin, Tempelman equation	$[(1-\alpha)^{-1/3} - 1]^2$	$(3/2)(1-\alpha)^{4/3}[(1-\alpha)^{-1/3} - 1]^{-1}$	Three-dimensional diffusion
(25)	D ₆	anti-Jander equation	$[(1+\alpha)^{1/3} - 1]^2$	$(3/2)(1+\alpha)^{2/3}[(1+\alpha)^{1/3} - 1]^{-1}$	Three-dimensional diffusion,
(26)	D ₇	anti-Ginstling-Brounstein equation	$1 + 2\alpha/3 - (1+\alpha)^{2/3}$	$(3/2)[(1+\alpha)^{-1/3} - 1]^{-1}$	Three-dimensional diffusion,
(27)	D ₈	anti-Zhuravlev, Lesokhin, Tempelman equation	$[(1+\alpha)^{-1/3} - 1]^2$	$(3/2)(1+\alpha)^4/3[(1+\alpha)^{-1/3} - 1]^{-1}$	Three-dimensional diffusion

where $g(\alpha)$ is an integral form of the conversion function, the expression of which depends on the kinetic model of the occurring reaction. If the correct $g(\alpha)$ function is used, a plot of $\ln[g(\alpha)/T^2]$ against $1/T$ should give a straight line from which the values of the activation energy E and the preexponential factor A in Arrhenius equation can be calculated.

Later, several authors [14, 28–31] suggested different solutions of the temperature integral in (8), sustaining the opinion that this increases the precision of the kinetic parameters being calculated. For instance, Madhysudanan-Krishnan-Ninan [28, 29] suggested the following equation:

$$\ln \left[\frac{g(\alpha)}{T^{1.921503}} \right] = \left[\ln \frac{AE}{qR} + 3.772050 - 1.921503 \ln E \right] - 0.120394 \frac{E}{T}. \quad (10)$$

Tang et al. [30] suggested another kinetic equation:

$$\ln \left[\frac{g(\alpha)}{T^{1.894661}} \right] = \left[\ln \frac{AE}{qR} + 3.63504095 - 1.894661 \ln E \right] - 1.00145033 \frac{E}{RT}, \quad (11)$$

and Wanjun et al. [31] suggested the equation:

$$\ln \left[\frac{g(\alpha)}{T^2} \right] = \ln \left[\frac{AR}{q(1.00198882E + 1.87391198RT_p)} \right] - \frac{E}{RT}. \quad (12)$$

Equations (9)–(12) imply that there would be differences in the calculated values of the activation energy and pre-exponential factor A even when the same $g(\alpha)$ function is used. To find which calculation procedure would turn out to be the most suitable for the calculations, they were estimated by the criterion “the best” correlation coefficient of the linear regression R^2 for (9)–(12). The advantage of these equations is that the values of E and A can be calculated on the basis of single rate thermogravimetric curves and the type of the most probable mechanism function of the studied reaction can be determined. For the calculations of the kinetic parameters a computer program was developed for all the data manipulations.

The second approach used for the calculations was based on multiple rates thermogravimetric curves and so-called isoconversion calculation procedures [13, 15, 21, 23, 24, 32–35].

2.3. Isoconversional Methods. Isoconversion methods employ multiple temperature programs (e.g., different heating rates) in order to obtain data on varying rates at a

constant extent of conversion. Thus, isoconversion methods allow complex (i.e., multistep) processes to be detected via a variation of E with α . As has results from some critical analyses [15, 23, 24, 32–35], the correct determination of nonisothermal kinetic parameters involves the use of experimental data recorded at several heating rates. These data have allowed applying the isoconversion (model-free) methods in accessing the activation energy on the conversion degree that can be correlated with the investigated process mechanism. These methods are recommended from ICTAC kinetics committee for performing kinetic computations on thermal analytical data [24].

2.3.1. Calculation of Activation Energy by Iterative Procedure. Thermal decomposition kinetic of Ozawa-Flynn-Wall (OFW) is an isoconversion or model-free method, which can calculate the values of the activation energy E and frequency factor A in Arrhenius equation through following equation [13, 27, 32, 33, 35]:

$$\ln q = \ln \frac{0.0048AE}{g(\alpha)R} - 1.0516 \frac{E}{RT}, \quad (13)$$

and Kissinger-Akahira-Sunose (KAS) equation [32–35]:

$$\ln \frac{q_i}{T_{\alpha,i}^2} = \ln \frac{A_{\alpha}R}{g(\alpha)E_{\alpha}} - \frac{E_{\alpha}}{RT_{\alpha,i}}. \quad (14)$$

These two methods of plotting a linear regressive curve were used at fraction conversion $0.1 < \alpha < 0.9$, different heating rates q , and sample masses. The plots of $\ln q$ versus $1/T$ (Equation (13)) and $\ln(q_i/T_{\alpha,i}^2)$ versus $1/T_{\alpha,i}$ (see (14)) have been proved to give the values of the apparent activation energies for the different stages of decomposition of $\text{CaC}_2\text{C}_4 \cdot \text{H}_2\text{O}$ and CaCO_3 at different values of α . According these equations, the reaction mechanism and the shape of $g(\alpha)$ function cannot affect the calculation of the activation energies of the different stages. Iterative procedure was used to calculate the values of E approximating the exact value, according to the next equations [32, 35]:

$$\begin{aligned} \ln \frac{q}{H(x)} &= \ln \frac{0.0048AE}{g(\alpha)R} - 1.0516 \frac{E}{RT}, \\ \ln \frac{q}{h(x)T^2} &= \ln \frac{AR}{g(\alpha)E} - \frac{E}{RT}. \end{aligned} \quad (15)$$

Because

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} \approx \frac{A}{q} \int_0^T e^{-E/RT} dT = \frac{AEe^{-x}}{qRx^2} h(x), \quad (16)$$

and where $h(x)$ is expressed by the fourth Senum and Yang approximation formulae [32, 34, 35]:

$$h(x) = \frac{x^4 + 18x^3 + 86x^2 + 96x}{x^4 + 20x^3 + 120x^2 + 240x + 120}, \quad (17)$$

where $x = E/RT$ and $H(x)$ is equal to [32, 35]

$$H(x) = \frac{\exp(-x) h(x) / x^2}{0.0048 \exp(-1.0516x)}. \quad (18)$$

The iterative procedure performed involved the following steps. (i) Assume $h(x) = 1$ or $H(x) = 1$ to estimate the initial value of the activation energy E_1 . The conventional isoconversional methods stop the calculation at this step. (ii) Using E_1 , calculate a new value of E_2 for the activation energy from the plot of $\ln[q/H(x)]$ versus $1/T$ or $\ln[q/h(x)T^2]$ versus $1/T$. (iii) Repeat step (ii), replacing E_1 with E_2 . When $E_i - E_{i-1} < 0.1 \text{ kJ mol}^{-1}$, the last value of E_i was considered to be the exact value of the activation energy of the reaction. These plots are model independent since the estimation of the apparent activation energy does not require the selection of particular kinetic model (type of $g(\alpha)$ function). Therefore, the activation energy values obtained by this method are usually regarded as more reliable than these obtained by a single TG curve.

2.3.2. Determination of the Most Probably Mechanism Function. The following equation was used to estimate the most correct reaction mechanism, that is, $g(\alpha)$ function, [32, 34]:

$$\ln g(\alpha) = \left[\ln \frac{AE}{R} + \ln \frac{e^{-x}}{x^2} + \ln h(x) \right] - \ln q. \quad (19)$$

Plotting $\ln g(\alpha)$ versus $\ln q$ and using a linear regressive of least square method, if the mechanism studied conforms to certain $g(\alpha)$ function, the slope of the straight line should be equal to -1.0000 and the linear correlation coefficient R^2 should be equal to unity. The values of E and A do not influence the shape of the most correct reaction mechanism function determined. For determination of the most probable mechanism function, the values of the conversion α corresponding to multiple rates taken at the same temperature were put into the left side of (19) and all the thirty-five types of mechanism functions presented in Table 1 were tested. The slope and correlation coefficient were obtained from the plot of $\ln g(\alpha)$ versus $\ln q$. The most probable mechanism function was assumed to be the one for which the value of the slope of the straight line was closest to -1.0000 and the correlation coefficient was highest. If several $g(\alpha)$ functions comply with this requirement, the values of conversion α corresponding to multiple rates at the same temperature were applied to calculate the probable mechanism by the same method. Thus, the most probable mechanism function was considered to be the one for which the slope of the straight line was closest to -1.0000 and the linear correlation coefficient R^2 was near to unity.

2.3.3. Calculation of Preexponential Factor in Arrhenius Equation. The preexponential factor A can be estimated from the intercept of the plots of (15), inserting the most probable $g(\alpha)$ function determined. All calculations were performed using a programs compiled by ourselves.

The values of the preexponential factor A in Arrhenius equation for solid phase reactions are expected to be in a wide range (six or seven orders of magnitude), even after the effect of surface area is taken into account [15, 36–40]. For first order reactions, the preexponential factor may vary from 10^5 to 10^{18} s^{-1} . The low factors will often indicate a

surface reaction, but if the reactions are not dependent on surface area, the low factor may indicate a “tight” complex. The high factors will usually indicate a “loose” complex [15, 36]. Even higher factors (after correction for surface area) can be obtained for complexes having free translation on the surface. Since the concentrations in solids are not controllable in many cases, it would have been convenient if the magnitude of the preexponential factor indicated for reaction molecularity. However, this appears to be true only for nonsurface-controlled reactions having low ($<10^9 \text{ s}^{-1}$) preexponential factors. Such reactions (if elementary) can only be bimolecular [36, 37].

From the theory of the activated complex (transition state) of Eyring [15, 36–40], the following general equation may be written

$$A = \frac{e\chi k_B T_p}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right), \quad (20)$$

where $e = 2,7183$ is the Neper number; χ : transition factor, which is unity for monomolecular reactions; k_B : Boltzmann constant; h : Planck constant, and T_p is the peak temperature of DTG curve. The change of the entropy may be calculated according to the formula

$$\Delta S^\ddagger = R \ln \frac{Ah}{e\chi k_B T_p}. \quad (21)$$

Since

$$\Delta H^\ddagger = E - RT_p, \quad (22)$$

the changes of the enthalpy $\Delta H^\ddagger$ and Gibbs free energy $\Delta G^\ddagger$ for the activated complex formation from the reagent can be calculated using the well-known thermodynamical equation:

$$\Delta G^\ddagger = \Delta H^\ddagger - T_p \Delta S^\ddagger. \quad (23)$$

The values of $\Delta S^\ddagger$, $\Delta H^\ddagger$, and $\Delta G^\ddagger$ were calculated at $T = T_p$ (T_p is the DTG peak temperature at the corresponding stage), since this temperature characterizes the highest rate of the process, and therefore, is its important parameter.

3. Results and Discussion

Figure 1 shows the X-ray diffraction patterns of CaCO_3 reagent-grade and CaCO_3 produced in situ as a result from the thermal degradation of calcium oxalate monohydrate.

The X-ray diffraction pattern of CaCO_3 obtained in situ from calcium oxalate monohydrate corresponds to calcite which has hexagonal crystal lattice with the following parameters of the unit cell: $a=4.99013(8) \text{ \AA}$, $b=4.99013(8) \text{ \AA}$, $c=17.0690(3) \text{ \AA}$, $\alpha=90^\circ$, $\beta=90^\circ$, $\gamma=120^\circ$, and volume $=368.09(1) \text{ \AA}^3$. Beside the reflexes for calcite observed in the X-ray diffraction pattern of the initial CaCO_3 reagent-grade (Fluka) used, two other reflexes characteristic for aragonite were registered which have orthorhombic crystal lattice with the following parameters of the unit cell: $a=4.9632(5) \text{ \AA}$, $b=7.9673(7) \text{ \AA}$, $c=5.7442(4) \text{ \AA}$, $\alpha=90^\circ$,

FIGURE 1: X-ray diffraction patterns of in situ generated CaCO_3 from calcium oxalate monohydrate—1 and CaCO_3 reagent-grade—2.

$\beta=90^\circ$, $\gamma=90^\circ$, and volume $=227.15(2) \text{ \AA}^3$. The mean crystalline size $L_{2\theta}$ of the samples studied was calculated according to the Debye-Scherrer formula:

$$L_{2\theta} = \frac{k\lambda}{\beta \cos \theta}, \quad (24)$$

where k is a dimensionless constant or shape factor that may range from 0.89 to 1.39 depending on the specific geometry of the scattering objects (in our case equal to 0.9), λ is the X-ray wavelength (0.154 nm) for Cu anode, β is the peak width at half the maximum intensity reflex in radians, and θ is the Bragg angle. For the first sample, the mean size of the crystallites was 920 $\text{\AA}$ and for the second one 2310 $\text{\AA}$, respectively.

The TG and DTG curves of thermal degradation of CaCO_3 reagent-grade and CaCO_3 generated in situ from calcium oxalate monohydrate are presented in Figure 2.

In the DTG curve of CaCO_3 , there is only one peak at 742.8°C corresponding to the process of substance decarbonation. The thermal decomposition of $\text{CaC}_2\text{C}_4 \cdot \text{H}_2\text{O}$ proceeded in three reaction steps observed at increased temperature, corresponding to the splitting of H_2O , CO , and CO_2 , respectively [15]:

The stages of dehydration, decarbonylation, and decarbonation of $\text{CaC}_2\text{C}_4 \cdot \text{H}_2\text{O}$ are all well separated, though

FIGURE 2: TG (1,3) and DTG (2,4) curves of thermal degradation of CaCO_3 (1,2) and $\text{CaC}_2\text{C}_4 \cdot \text{H}_2\text{O}$ (3,4) obtained at heating rate of 12 K min^{-1} .

FIGURE 3: Thermal degradation curves of reagent-grade CaCO_3 at 1–3, 2–6, 3–9, and 4–12 K min^{-1} heating rate

the kinetic characteristics are affected by the presence of H_2O , O_2 , and CO_2 , as well as by the reaction conditions, including heating rate, sample mass, sample size, and type of sample container [13, 15]. In the DTG curve of $\text{CaC}_2\text{C}_4 \cdot \text{H}_2\text{O}$ decomposition, there are three peaks at 180.3, 488.7, and 749.5°C corresponding to the dehydration, decarbonylation and decarbonation processes, respectively. In both cases, the mass-loss values measured were all in good agreement with the value of 44% calculated according Stage III.

The TG curves of thermal decomposition of the initial reagent-grade CaCO_3 obtained at different heating rates are presented in Figure 3

Using Coats-Redfern calculation procedure and F_n -functions with different values of n , the values of the activation energy E , and frequency factor A were calculated at four heating rates of thermal decomposition of the reagent-grade CaCO_3 . The dependencies of the coefficient of linear regression R^2 on the values of n at the used heating rates are presented in Figure 4.

As can be seen from Figure 4, each curve had a local maximum. The curves presented can be successfully described by empirical polynomials of second power and different coefficients. Differentiating and nullifying these polynomials,

FIGURE 4: Dependence of the coefficient of linear regression R^2 on the values of n in F_n type functions.

the value of n at which R^2 has maximum value can be calculated. Despite the heating rate, it turned out that the maximal value of R^2 was obtained at $n = 0.66 \pm 0.02$. It means that, in all cases, the most appropriate mechanism function describing the kinetics of decomposition of CaCO_3 in integral form is $g(\alpha) = 1 - (1 - \alpha)^{1/3}$ and in differential form $f(\alpha) = 3(1 - \alpha)^{2/3}$ which belongs to the mechanism of phase boundary reaction (contracting sphere). The same tendency was established for the other calculation procedures. The values of E , A , and R^2 for the thermal decomposition of reagent-grade CaCO_3 obtained at different heating rates by different calculation procedures are presented in Table 2 for comparison.

As can be seen from Table 2, regardless of the calculation procedure used, the values of E and A regularly increased with the heating rate while these of R^2 decreased. In our opinion, the tendency of increase of the activation energy values with the increase of the heating rate observed was due to the process sensibility to the heat transfer to the reaction interface. The average values of the activation energy obtained from the calculation procedures used was $326.4 \pm 2.5 \text{ kJ/mol}$.

The same approach was used for the studies on the kinetics of the thermal decomposition of in situ produced CaCO_3 . It was established that the most appropriate mechanism function is the same— $g(\alpha) = 1 - (1 - \alpha)^{1/3}$ and in differential form $f(\alpha) = 3(1 - \alpha)^{2/3}$ which belongs to the mechanism of phase boundary reaction or contracting sphere. The values of E , A , and R^2 for the thermal decomposition of in situ produced CaCO_3 obtained at different heating rates and by different calculation procedures are shown for comparison in Table 3.

At the thermal decomposition of in situ produced CaCO_3 is observed the same tendency of increasing of the values of

FIGURE 5: Plots of Ozawa-Flynn-Wall equation for the thermal degradation of reagent-grade CaCO_3 .

the activation energy and frequency factor with the increasing of the heating rate, as well as at the thermal decomposition of reagent-grade CaCO_3 . In this case, however, the values of E and A are considerably lower at the same heating rate. According to us, the reason for this is the fact that the reagent had higher reactivity at the in situ generated CaCO_3 because it was in “status nascendi” and the mean size of the crystallites according to the X-ray diffraction data was smaller.

Figure 5 presents the linear relationships between $\ln q$ and $1/T$ for the thermal degradation of reagent-grade CaCO_3 according to OFW calculation procedure.

At constant heating rate, the kinetic parameters can be calculated by using the slope and cut-off from the ordinate axis. The results obtained are presented in Table 4.

The linear relationships between $\ln q$ and $1/T$ for the thermal degradation of reagent-grade CaCO_3 drawn according to KAS calculation procedure are presented in Figure 6.

The activation energy E was directly evaluated from the slopes of these plots and frequency factor A —from the cut-off from the ordinate axis. The results obtained are summarized in Table 4.

As can be seen from Table 4 for all the cases shown, the values of the calculated activation energy regularly increase with the increase of the degree of conversion α . According to some authors [20], three rate controlling processes are possible: heat transfer to the reaction interface, chemical reaction, and CO_2 diffusion through the product layer. In our case, diffusion control of the reaction seems to be plausible; therefore, as the thickness of the products layer increases, the resistance against CO_2 diffusion increases, and, as a consequence, the activation energy also increases. In corroboration of the suggestion that CO_2 diffusion through the product layer is the rate controlling process comes the fact that the

FIGURE 6: Plots of Kissinger-Akahira-Sunose equation for the thermal degradation of reagent-grade CaCO_3 .

value of the activation energy of the thermal decomposition of CaCO_3 in vacuum is smaller than that obtained in dry argon atmosphere [22]. The values for the activation energy of the thermal decomposition of the reagent-grade CaCO_3 obtained were close to these reported in [20, 22].

Comparing the values of the kinetic parameters calculated on the base of single curve methods and the isoconversion procedures, it can be seen that the latter were twice smaller. Obviously, the type of the calculation procedure used had significant effect on the values of the kinetic parameters of certain reaction which can explain the great difference between the values of the calculated activation energy E (from 110 to 3800 kJ mol^{-1}) and from 10^2 to 10^{157} s^{-1} for the frequency factor A [1–22]. According to ICTAC kinetics committee recommendations for performing kinetic computations on thermal analysis data, more appropriate calculation procedures are these based on the isoconversion procedure [24].

Figure 7 shows the straight lines drawn according to (19) using different $g(\alpha)$ functions.

As can be seen from Figure 7, the lines have different slopes. Line 1 corresponds to D_4 , line 2 to $F_{2/3}$ (R_3), and line 3 to D_3 mechanism function, respectively. The values of the slope and R^2 obtained for different mechanism functions are presented in Table 5 for comparison.

As can be seen from Table 5 for all the cases studied, the values of R^2 were very high but the slope of the line was closest to -1.0000 only for $F_{2/3}$ mechanism (-1.0086 and -1.0102). For the D_3 mechanism, it was higher and for D_4 smaller than -1.0000 . This was the reason to be concluded that the most appropriate mechanism describing

TABLE 2: Effect of the heating rate on the kinetic data for the thermal decomposition of reagent-grade CaCO_3 .

Heating rate	Calculation procedure					
	Coats-Redfern			Madhysudanan-Krishnan-Ninan		
K min^{-1}	$E, \text{kJ mol}^{-1}$	A, min^{-1}	R^2	$E, \text{kJ mol}^{-1}$	A, min^{-1}	R^2
3	290.4	2.42×10^{14}	0.9981	290.4	1.610×10^{14}	0.9980
6	329.0	1.96×10^{16}	0.9978	329.3	2.14×10^{16}	0.9978
9	329.2	1.66×10^{14}	0.9973	329.5	1.81×10^{16}	0.9973
12	353.3	2.60×10^{17}	0.9973	353.6	2.81×10^{17}	0.9971
Average	325.1 ± 35	7.41×10^{16}	0.9976	325.7 ± 35	8.02×10^{16}	0.9976
Tang et al.			Wanjun et al.			
3	290.5	1.64×10^{14}	0.9980	290.1	1.56×10^{14}	0.9980
6	329.4	2.16×10^{16}	0.9978	329.0	1.96×10^{16}	0.9978
9	329.5	1.82×10^{16}	0.9973	329.2	1.68×10^{16}	0.9973
12	353.6	2.83×10^{17}	0.9971	367.7	2.63×10^{17}	0.9973
Average	325.7 ± 30	8.07×10^{16}	0.9976	329.0 ± 39	7.50×10^{16}	0.9976

TABLE 3: Effect of heating rate on kinetic data for the thermal decomposition of in situ produced CaCO_3 .

Heating rate, K min^{-1}	Calculation procedure					
	Coats-Redfern			Madhysudanan-Krishnan-Ninan		
	$E, \text{kJ mol}^{-1}$	A, min^{-1}	R^2	$E, \text{kJ mol}^{-1}$	A, min^{-1}	R^2
3	221.2	4.32×10^{10}	0.9986	225.3	4.58×10^{10}	0.9988
6	227.1	8.78×10^{10}	0.9981	231.6	1.21×10^{11}	0.9983
9	238.8	3.01×10^{11}	0.9975	243.1	4.94×10^{11}	0.9974
12	249.6	8.32×10^{11}	0.9968	250.0	9.24×10^{11}	0.9968
Average	234.2 ± 15	3.16×10^{11}	0.9977	237.5 ± 12	3.96×10^{11}	0.9978
Tang et al.			Wanjun et al.			
3	225.2	5.52×10^{10}	0.9988	223.3	4.38×10^{10}	0.9982
6	231.4	1.18×10^{11}	0.9983	229.1	8.89×10^{10}	0.9973
9	243.1	4.94×10^{11}	0.9974	239.4	3.14×10^{11}	0.9968
12	250.1	9.39×10^{11}	0.9968	246.9	8.84×10^{11}	0.9964
Average	237.4 ± 13	4.02×10^{11}	0.9978	234.7 ± 12	3.33×10^{11}	0.9972

the thermal degradation of CaCO_3 is the phase boundary reaction R_3 —contracting sphere or spherical symmetry. The values of the parameters characterizing the kinetic of thermal decomposition of CaCO_3 from different origins are presented in Table 6.

The change of entropy for the formation of the activated complex from the reagent $\Delta S^\ddagger$ reflects how near the system is to its thermodynamic equilibrium. Lower activation entropy means that the material has just passed through some kind of physical or chemical rearrangement of the initial structure, bringing it to a state near its own thermodynamic equilibrium. In this situation, the material shows little reactivity, increasing the time necessary to form the activated complex. On the other hand, when high-activation entropy values are observed, the material is far from its own thermodynamic equilibrium. In this case, the reactivity is higher and the system can react faster to produce the activated complex and, consequently, short reaction times are observed. In particular, for example, the negative values of $\Delta S^\ddagger$ would indicate that the formation of activated complex is connected with the decrease of entropy, that is, the activated complex is

“more organized” structure compared to the initial substance and such reactions are classified as “slow” [41]. The more negative values of $\Delta S^\ddagger$ for the in situ produced CaCO_3 showed that its structure is far from its own thermodynamic equilibrium compared to reagent-grade CaCO_3 .

Using (22) and (23), the values of the change of enthalpy $\Delta H^\ddagger$ and the Gibbs free energy $\Delta G^\ddagger$ for the formation of the activated complex from the reagent can be calculated. The change of the activation enthalpy $H^\ddagger$ shows the energy difference between the reagent and activated complex. If this difference is small, the formation of the activated complex is favored because the potential energy barrier is low. The change of the Gibbs free energy $\Delta G^\ddagger$ reveals the total energy increase of the system at the approach of the reagents and the formation of the activated complex. As can be seen from Table 6, they are practically equal for both studied compounds, but there are significant differences between the values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$.

The linear relationship between $\ln A$ and E for all values of E and corresponding values of A obtained for both samples with different calculation procedures is presented in Figure 8.

TABLE 4: Dependence of activation energy E (kJ mol^{-1}) on the degree of conversion α using Ozawa-Flynn-Wall and Kissinger-Akahira-Sunose calculation procedures.

Degree of conversion, α	Reagent-grade CaCO_3		In situ produced CaCO_3	
	OFW	KAS	OFW	KAS
0.1	145.8	145.8	121.6	121.4
0.2	155.8	148.2	126.3	124.9
0.3	161.7	153.8	131.0	127.7
0.4	166.3	158.2	135.1	131.1
0.5	169.3	161.0	138.9	133.5
0.6	172.2	163.8	141.8	135.9
0.7	175.5	166.9	145.2	138.8
0.8	176.9	166.7	149.6	142.7
0.9	178.2	169.5	151.3	145.5
Average	166.9 ± 11	159.3 ± 10	137.8 ± 13	133.5 ± 12

TABLE 5: The shape of the most probable mechanism function $g(\alpha)$, slope and the correlation coefficient of linear regression R^2 for both the samples studied.

Mechanism	Shape of $g(\alpha)$ function	Reagent-grade CaCO_3		In situ produced CaCO_3	
		Slope	R^2	Slope	R^2
$F_{2/3}, R_3$	$1 - (1 - \alpha)^{1/3}$	-1.0086	0.9998	-1.0102	0.9993
D_3	$[1 - (1 - \alpha)^{1/3}]^2$	-2.0172	0.9995	-1.8986	0.9989
D_4	$1 - 2\alpha/3 - (1 - \alpha)^{2/3}$	-0.7639	0.9991	-0.7263	0.9992

FIGURE 7: Plots of $\ln g(\alpha)$ versus $\ln q$ for the thermal degradation of reagent-grade CaCO_3 : 1- D_4 , 2- $F_{2/3}$, and 3- D_3 mechanism.

The kinetic compensation effect was developed in order to determine the effect from the different specimens or experimental conditions when calculating the change of the activation energy. Under these circumstances, the kinetic parameter of preexponential factor A would vary with the

FIGURE 8: Compensation plot for the thermal decomposition of the studied samples

activation energy E . A good linear dependence between $\ln A$ and E was observed for these parameters, obtained from all the calculation procedures used. The straight line presented in Figure 8 is described with the following empirical equation:

$$\ln A = -2.8301 + 0.1224E. \quad (25)$$

TABLE 6: Kinetics parameters obtained with the most probable mechanism function $g(\alpha)$ using Ozawa-Flynn-Wall and Kissinger-Akahira-Sunose calculation procedures.

Parameters	Reagent-grade CaCO_3		In situ produced CaCO_3	
	OFW	KAS	OFW	KAS
E , kJ mol^{-1}	166.9	159.3	137.8	133.5
A , min^{-1}	5.69×10^7	5.46×10^7	2.25×10^6	1.11×10^6
$-\Delta S^\ddagger$, $\text{J mol}^{-1} \text{K}^{-1}$	148.7	149.1	175.6	181.5
$\Delta H^\ddagger$, kJ mol^{-1}	158.7	151.3	129.6	125.3
$\Delta G^\ddagger$, kJ mol^{-1}	304.9	297.9	302.2	303.7

According to the some authors [39, 41–44] the so-called kinetic compensation effect, isokinetic effect, or θ -rule may be described with the equation:

$$\ln A = \ln k_{\text{iso}} + \frac{E}{RT_{\text{iso}}}. \quad (26)$$

On the basis of (25) and (26) the values of k_{iso} and T_{iso} may be calculated. In our case they are 0.059 min^{-1} and 983 K , respectively. This temperature belongs in the temperature interval of the beginning and the end of the thermal decomposition of the both studied samples of CaCO_3 .

4. Conclusion

Thermogravimetric studies on two varieties of calcium carbonate namely, analytical reagent-grade and in situ produced from thermal degradation of calcium oxalate monohydrate, were carried out at four rates of linear increase of the temperature. The kinetics and mechanism of their solid-state thermal decomposition reaction were evaluated from the TG data using four calculation procedures and isoconversion method, as well as 27 mechanism functions. For all the sets of results, the E and A values of in situ generated CaCO_3 were marginally lower. On this basis, we can infer that the sample history has a definite effect on the computed values of E and A , even though the magnitude of the effect is very small. The observation can be explained as follows. In the phase boundary reaction the surface nucleation is instantaneous and hence the rate controlling process is the movement of the interface towards the interior. Thus, even though the numbers of nucleation sites for the both types of samples are likely to be largely different, it will have no effect on the reaction rate. However, marginal decrease of the values of the kinetics parameters for their in situ produced CaCO_3 can be attributed to the smaller average crystallite size and because this sample is in “status nascendi” and for this reason more reactive.

Independently from the high values of the correlation coefficient of linear regression R^2 obtained on the basis of single kinetic TG-curves, the values of E , calculated according to isoconversion methods are two times less and strongly depends on the heating rate and degree of conversion. For this reason it may be concluded that will be more correct if the values of E obtained on isoconversion calculation procedures are more representative.

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