

An investigation on the calcination kinetics of zinc carbonate hydroxide and Calsimin zinc carbonate concentrate

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Abstract

In this study the thermal calcination of two materials, high purity zinc carbonate hydroxide and the Calsimin zinc carbonate concentrate have been investigated. Isothermal studies have been performed on samples at different temperatures and times. Non-isothermal analysis has been carried out by TGA and DSC. It has been found that the calcination behaviour of both materials corresponds to the shrinking core model. The activation energy for the calcination of zinc carbonate hydroxide is found to be 88.7 kJ/mol, and that for the Calsimin sample is 97.3 kJ/mol.

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1. Introduction

Situated in northwest Iran, near the city of Zanjan, the Angooran mine is the largest zinc and lead mine in the Middle East. Mineral processing and concentration operations result in the production of a high grade concentrate and a low grade residue. The concentrate has been the subject of this research. Table 1 shows the XRF analysis for the concentrate. In a recent study [1,2], the residue was initially calcined in a muffle furnace so that the zinc carbonate (hydrate–hydroxide) content together with all the other major carbonate compounds would convert to oxide (Eq. (1)):



The calcined ore was subsequently reduced in a fluidized bed furnace and in the next stage, the resulting zinc vapour was oxidized to form high purity zinc oxide. In the follow-up, the same treatment was applied to the high grade ore (the zinc concentrate), and a high purity zinc oxide was obtained. Zinc oxide has applications in many industries such as rubber, pigments and paint, paper, ceramics, etc. [3,4].

Since the ore is calcined prior to being fed into the fluidized bed furnace, it is necessary to have some information about the calcination kinetics of some compounds in the ore, and of the ore itself.

2. Theory and literature review

The unreacted shrinking core model was used to investigate calcination reactions for both materials in this study [5]. As a result of calcination, a solid, porous layer remained on the surfaces of all samples. For Calsimin concentrate, this layer consisted of a mixture of calcined oxides and other compounds such as silica. For zinc carbonate hydroxide, this layer consisted of zinc oxide.

In the general reaction $aA_{(s)} = bB_{(s)} + cC_{(g)}$, Coats and Redfern [6] have shown that the plot of $\log_{10}((1 - (1 - X)^{1-n}) / (T^2(1 - n)))$ versus $1/T$ should produce a straight line with a gradient of $-E_a/2.3R$. According to Doyle [7], it is not necessary to know the reaction mechanism to calculate the reaction activation energy.

The number of research articles on the calcination kinetics of zinc carbonate is very limited. There are, however, certain similarities between calcium carbonate and zinc carbonate. It is therefore appropriate to mention some of the studies carried out on calcium carbonate.

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Nomenclature

A	constant
C	constant
E_a	activation energy (J/mol)
k	surface reaction rate constant (mol/cm ² s)
M	molecular weight (g/mol)
n	order of reaction
R	ideal gas constant (J/mol K)
R_c	radius of unreacted core at any time (cm)
R_0	initial radius of particles (cm)
t	time (s)
T	temperature (K)
W_t	weight of the sample at any time (mg)
W_0	initial weight of the sample (mg)
X	fraction of the reacted at time t
X_c	conversion of calcination reaction at any time

Greek letters

$\gamma_{Zn_5(CO_3)_2(OH)_6}$	zinc carbonate hydroxide content in the sample
ρ	density (g/cm ³)

Three main rate controlling steps in the calcination of calcium carbonate have been identified as [8]:

1. heat transfer into the bulk of the particle [9–11];
2. the transfer of released CO₂ away from the reaction front [12];
3. a chemical reaction [13–15].

There have been many attempts to assign suitable models to the calcination of calcium carbonate [16–18]. Many investigators have also studied the effects of parameters such as particle size [17,19], temperature [18], and weight of the sample [8] on the reaction kinetics. The activation energy for the calcination of many calcium carbonate samples has been studied

Table 1
Typical analysis of the Calsimin concentrate

Material	Wt. %
MgO	1.02
Al ₂ O ₃	4.69
SiO ₂	15.58
SO ₃	0.66
K ₂ O	0.53
CaO	2.99
TiO ₂	0.10
MnO	0.07
Fe ₂ O ₃	4.13
NiO	0.16
ZnO	38.43
As ₂ O ₃	0.82
CdO	0.19
PbO	4.38
LOI	25.94

by several investigators. Values found fluctuate between 22 and 50 kcal/g mol [20,21].

As mentioned before, there are only few publications on the calcination of zinc carbonate [22]. As with calcium carbonate, many factors such as heat transfer and diffusion are of importance in the calcination of zinc carbonate [23]. Liu et al. [22] have found out that with increasing the particle size, the reaction temperature increases and activation energy decreases. Kanari et al. [24] have worked on pure and impure zinc carbonate samples. They have shown that impure samples are more temperature sensitive than pure samples. Their TG results correspond to the values found in Ref. [23]. Gotor et al. [25] have studied the calcination of zinc carbonate in the temperature range of 330–452 °C. They have proposed two different mechanisms for the nucleation and growth of products based on TG results. Kanari et al. [24] have found a value of 113 kJ/mol for the activation energy of calcination of zinc carbonate in the temperature range of 269–434 °C. Dollimore et al. [26] have found an activation energy value of 94 ± 9 kJ/mol for the calcination reaction of zinc carbonate hydroxide in the temperature range of 200–260 °C. The main reasons for the variation of activation energy values found by different investigators could be different starting materials, different analysis methods used and so on.

3. Experimental procedure

In this study samples used were both in powder form and in pellets. Pellets of 4–6 mm diameter were prepared from high purity zinc carbonate hydroxide Zn₅(CO₃)₂(OH)₆, provided by Merck, and three different pellets of 1–2, 4–6, and 9.5–13 mm from the Calsimin concentrate. Pellets were subsequently dried in an oven by heating at 110 °C for 1.5 h.

3.1. Isothermal experiments

Zinc carbonate hydroxide powder samples (<50 μm) were heated at four different temperatures (210, 240, 270, and 300 °C) for different time intervals (15, 30, 60, 120, and 180 min). The weight change of the samples was subsequently measured using a digital balance with an accuracy of 10⁻⁴ g. Each experiment was repeated three times to increase accuracy. Pellets of 4–6 mm in diameter were heated at 240 °C for the same periods.

Calsimin concentrate powder (<0.5 mm) samples were heated at the temperatures of 270, 300, 330, 360, and 390 °C for the same durations as zinc carbonate hydroxide samples. Heating experiments were also performed on Calsimin pellets at 330 °C for the same periods to study the effect of sample size on calcination kinetics.

3.2. Non-isothermal experiments

In addition to isothermal tests, experiments were performed on both samples using TG and DSC. In TG, only a small sample is required to study the reaction progress and the temperature can be measured accurately [7,27,28].

DSC and TG analyses were performed on dried powder samples of both materials. DSC experiments were performed on

Polymer Laboratories (STA/625) thermal analyzer, and for TG experiments Perkin-Elmer (TG/Pyris1) thermo-gravimetric analyzer was used.

DSC analysis was carried out on samples weighing 7 mg at a heating rate of 10 °C/min in nitrogen with a flow rate of 40 ml/min. The two temperature limits were room temperature and 650 °C. For TG analysis similar samples were prepared. Zinc carbonate hydroxide samples were heated to 500 °C and Calsimin concentrate was heated to 800 °C.

In this study conversion was calculated using the following equations.

conversion (X_c) for zinc carbonate hydroxide

$$= \frac{M_{Zn_5(CO_3)_2(OH)_6}}{\gamma_{Zn_5(CO_3)_2(OH)_6} M_{CO_2}} \times \frac{W_0 - W_t}{W_0} \quad (2)$$

where for the pure sample, $\gamma_{Zn_5(CO_3)_2(OH)_6} = 1$.

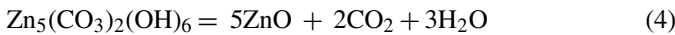
conversion (X_c) for Calsimin concentrate = $\frac{(wt.\%)_t}{(wt.\%)_{final}} \quad (3)$

4. Results and discussion

4.1. Isothermal experiments

4.1.1. Effect of time and temperature

Isothermal test results for pure zinc carbonate hydroxide and Calsimin concentrate are shown in Figs. 1 and 2. The maximum amount of weight loss for zinc carbonate hydroxide is 25.9% according to the calcination reaction, shown in Eq. (4):



It is also observed that while the calcination reaction proceeds at both 210 and 240 °C, the reaction rate at these temperatures is slow. The wt.% diagrams at 270 and 300 °C are very close and it can also be assumed that the reaction is completed in less than 2 h at both these temperatures.

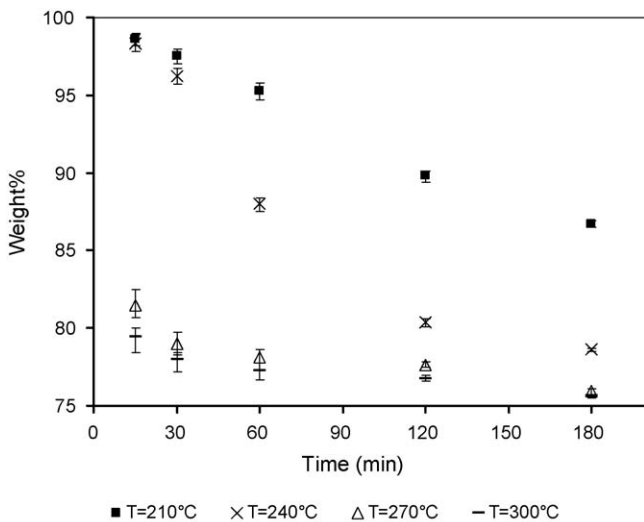


Fig. 1. Effect of time and temperature on the wt.% of pure zinc carbonate hydroxide.

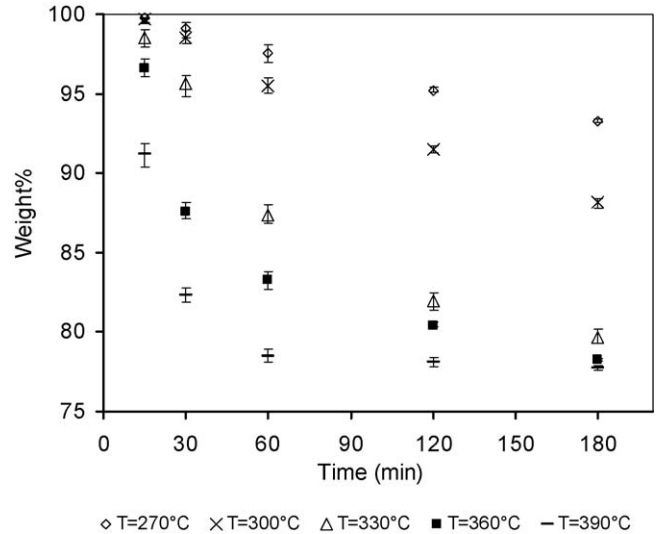


Fig. 2. Effect of time and temperature on the wt.% of Calsimin zinc carbonate.

In Fig. 2 it is seen that the calcination rate of the Calsimin concentrate increases sharply as temperature is raised above 300 °C. For example, after 120 min, the weight loss at 330 °C is roughly twice that at 300 °C.

In Fig. 3 weight loss has been plotted versus temperature for the two types of materials. It is observed that calcination of zinc carbonate hydroxide proceeds at a higher rate compared to Calsimin sample. Both samples exhibit the typical sigmoid curve associated with many other calcination reactions. While the curvatures of the two plots in the reaction section are similar, it is observed that weight loss of Calsimin sample occurs in a broader temperature range than that of pure carbonate hydroxide. This difference in behaviour may be attributed to the impurity content in Calsimin concentrate.

4.1.2. Effect of sample size

Figs. 4 and 5 show the effect of sample size on the wt.% of samples. It is observed that for both types of samples, the conversion decreases slightly with increasing size. This increase is only significant for larger samples (9.5–13 mm for Calsimin concentrate). For smaller samples, size does not affect reaction rate. This observation is consistent with the assumption that the

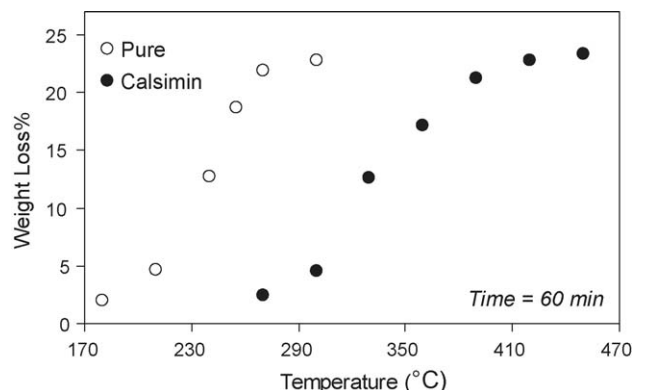


Fig. 3. Comparison of the effect of time and temperature on the two materials.

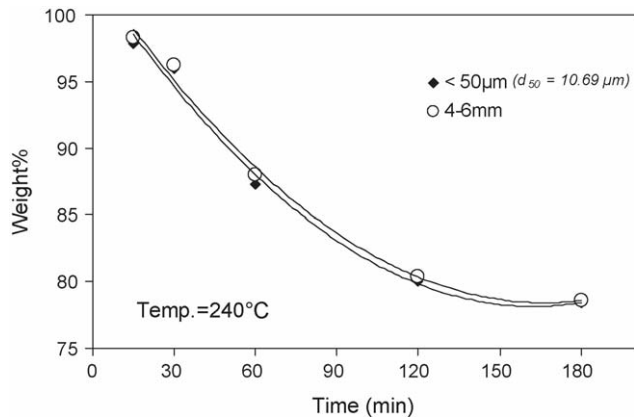


Fig. 4. Effect of particle size with wt.% on pure zinc carbonate hydroxide (temperature = 240 °C).

rate controlling step is a chemical reaction. This assumption has been proven correct by the values of activation energy calculated for calcination of these samples. For larger samples, the conversion extent is lowered. This observation may be justified by considering the slower rate of heating up in larger samples, and slower rate of CO_2 effusion out through the product layers in larger samples. In this case, the rate controlling step might no longer be the chemical reaction at the surface.

4.2. Non-isothermal experiments

4.2.1. TG experiments

Fig. 6 shows the results of TG analysis for both samples. The results are fairly consistent with those obtained in isothermal tests. For the carbonate hydroxide sample, a rapid weight loss is observed to start at 250 °C. At 340 °C there is a sharp change in the curvature and the wt.% value gently approaches the theoretical value of 72.11%. For Calsimin concentrate the bulk of the reaction occurs in the temperature range of 390–520 °C.

4.2.1.1. Kinetic model. Based on the similarities between the calcination reaction of calcium carbonate and the samples considered in this study, the shrinking core model was adopted for

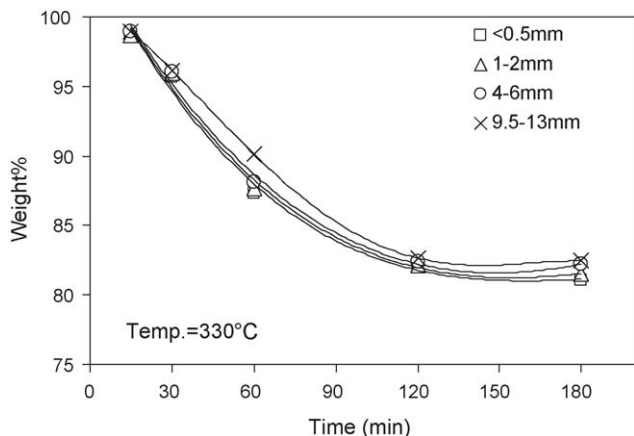


Fig. 5. Effect of particle size with wt.% on Calsimin zinc carbonate (temperature = 330 °C).

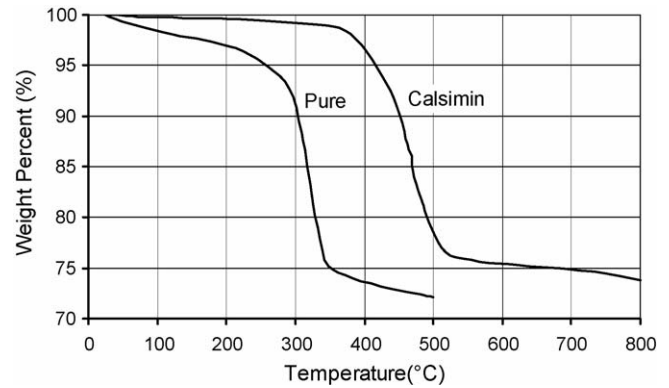


Fig. 6. TG non-isothermal treatment of pure zinc carbonate hydroxide and Calsimin concentrate.

this investigation. In the shrinking core model with the surface reaction rate controlling mechanism, the reaction takes place at the surface of the unreacted core and proceeds towards the centre. The surface and outer layers of the sample consist of a porous product (and other unreacted materials for Calsimin sample). If mass balance for the solid reactant is written and the simplifications depending on the above assumptions are made, governing equations are as follows:

$$k = A \exp\left(-\frac{E_a}{RT}\right) = -\frac{\rho_{\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6}}{M_{\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6}} \left(\frac{dR_c}{dt}\right) \quad (5)$$

Based on Eq. (5), if the plot of $\ln k$ versus $1/T$ is a straight line, the mechanism chosen will be correct. Furthermore, activation energy of the reaction and rate constant may be calculated. For the calculation of k the following steps may be taken:

$$X_c = 1 - \left(\frac{R_c}{R_0}\right)^3 \quad (6)$$

$$\frac{dX_c}{dt} = 3(1 - X_c)^{2/3} k \frac{M_{\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6}}{\rho_{\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6} R_0} \quad (7)$$

$$\frac{dX_c}{dt} = 3(1 - X_c)^{2/3} k C \quad (8)$$

$$k = \frac{\frac{dX_c}{dt}}{3(1 - X_c)^{2/3} C} \quad (9)$$

In Fig. 7 values of $-\ln k$ versus $1/T$ have been plotted for the carbonate hydroxide and for Calsimin sample, respectively. Both plots exhibit a linear behaviour in the temperature ranges concerned. Therefore, the shrinking core model may be applied to both samples satisfactorily.

4.2.1.2. Calculation of activation energy. Two methods were used for the calculation of activation energy in the temperature range of 300–350 and 420–500 °C for zinc carbonate hydroxide and Calsimin, respectively. In the first method the slope of the $-\ln k$ versus $1/T$ curve (Fig. 7) was found for each sample. As the slope for this curve is E_a/R , the value of activation energy may be calculated. The calculated values for the activation energy of calcination of pure zinc carbonate hydroxide and Calsimin sample are thus 86.7 and 98.5 kJ/mol, respectively.

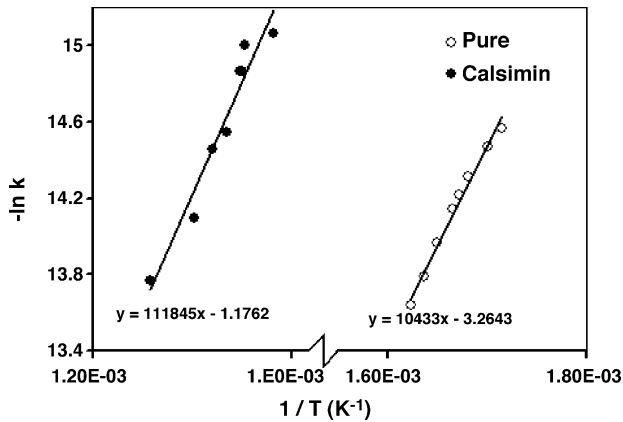


Fig. 7. Application of shrinking core model with surface reaction rate controlling mechanism to the calcination reaction data of pure zinc carbonate hydroxide and Calsimin zinc carbonate.

Activation energy of the calcination reactions may also be calculated using the approach that has been mentioned in Section 2. In Fig. 8 values of $\log_{10}((1 - (1 - X)^{1-n})/(T^2(1 - n)))$ have been plotted against the reciprocal of absolute temperature ($1/T$) for the two samples. The slope of this linear diagram is equal to $-E_a/2.3R$. For the carbonate hydroxide sample, the activation energy for calcination is therefore calculated as 90.7 kJ/mol. This value is quite close to the one found using data from the first method. The degree of the reaction is calculated as 0.95. The reaction may be assumed first order with a good approximation.

For Calsimin concentrate, the activation energy is calculated as 96.0 kJ/mol. This value too, corresponds closely to the one found later. The degree of the reaction is found to be 0.92; therefore, the calcination of Calsimin concentrate is first degree to a good approximation.

The values of reaction activation energy calculated for both reactions indicate that the rate controlling step is a chemical reaction in both samples. This reaction is the chemical reaction at the surface of the unreacted core.

4.2.2. DSC experiments

Fig. 9 shows the DSC analysis results for both carbonate hydroxide and Calsimin samples. The results obtained are con-

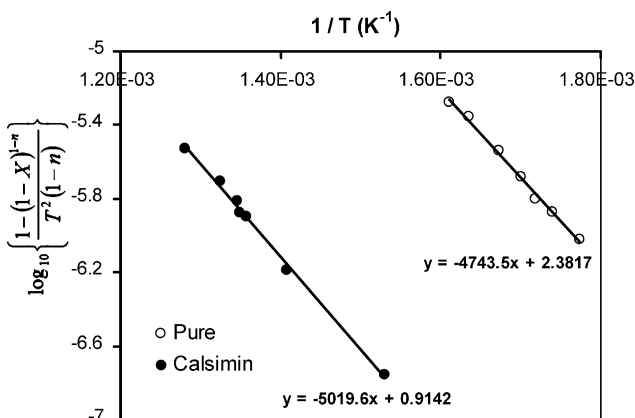


Fig. 8. $\log_{10}((1 - (1 - X)^{1-n})/(T^2(1 - n)))$ vs. $1/T$ for pure zinc carbonate hydroxide ($n=0.95$) and Calsimin zinc carbonate ($n=0.92$).

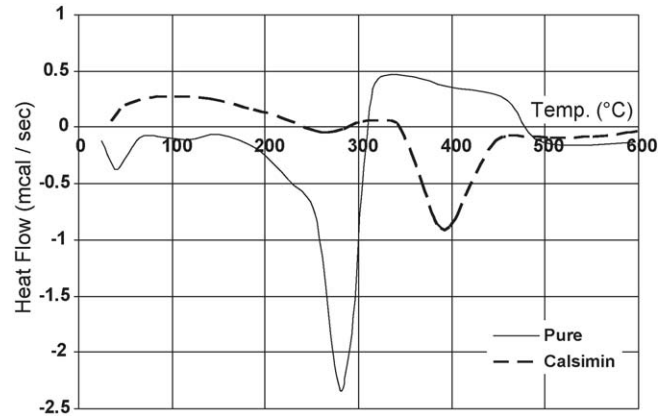


Fig. 9. DSC results for the pure zinc carbonate hydroxide and Calsimin zinc carbonate samples.

sistent with those of the isothermal experiments. For the carbonate hydroxide, the temperature range over which the reaction occurs is 240–310 °C. A sharp peak is observed at 280 °C, therefore it may be deduced that the de-hydroxylation and decarboxylation of the carbonate hydroxide occur simultaneously.

For Calsimin concentrate the temperature range is 340–440 °C. The peak occurs at 390 °C and is not as sharp as that of the pure carbonate hydroxide sample. This observation can be attributed to the high impurity content of Calsimin concentrate.

DSC results may be used to calculate the heat released (or absorbed) during a reaction. The area under the peak for each reaction was thus found, and heat absorbed for each endothermic reaction was calculated as 860 mcal for pure zinc carbonate hydroxide and 320 mcal for Calsimin concentrate. The heat of calcination for pure zinc carbonate hydroxide at 280 °C is thus calculated as 67.17 kcal/mol.

5. Conclusions

1. For pure zinc carbonate hydroxide, weight loss due to calcinations occurs in the temperature range of 250–350 °C. For Calsimin concentrate, this temperature range is 390–520 °C.
2. The de-carboxylation and de-hydroxylation reaction of zinc carbonate hydroxide occur simultaneously.
3. The reaction enthalpy for the calcinations of zinc carbonate hydroxide is 67.17 kcal/mol.
4. The shrinking core model is suitable for the calcination of both zinc carbonate hydroxide and Calsimin concentrate. The rate controlling step is the chemical reaction at the surface.
5. The activation energy for the calcinations of zinc carbonate hydroxide is 86.7–90.7 kJ/mol (average 88.7 kJ/mol). For the Calsimin sample, this value is 96.0–98.5 kJ/mol (average 97.3 kJ/mol).
6. For both samples, an increase in the size up to 6 mm does not have a significant effect on the reaction rate.

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