TECHNICAL NOTE

EFFECT OF CO$_2$ PARTIAL PRESSURE ON THE THERMAL DECOMPOSITION KINETICS OF ZINC CARBONATE HYDROXIDE

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Abstract   In this work, the effect of carbon dioxide partial pressure on the calcination kinetics of high purity zinc carbonate hydroxide has been studied. Non-isothermal analysis has been performed on samples at different CO$_2$ partial pressures by TGA and DTA. It has been found that the calcination behaviour of this material corresponds to the shrinking core model and the reaction mechanism is phase boundary controlled. The calcination reaction of zinc carbonate hydroxide starts at 240 $^{\circ}$C. Increasing the carbon dioxide partial pressure can result in an increase in the reaction start temperature of up to 30°C. The activation energy for the reaction is calculated as 180 $\pm$ 5 kJ/mol at significant CO$_2$ partial pressures.

Key Words: Thermal Decomposition, Kinetics, Zinc Carbonate Hydroxide, CO$_2$ Partial Pressure

چکیده   در این پژوهش تاثیر فشار جزئی دی اکسید کربن بر سینتیک تکلیس هیدروکسید کربنات روی بررسی شده است. آنالیز غیر همدما توسط دستگاههای TGA و DTA در فشار جزئی های مختلف دی اکسید کربن روی نمونه ها صورت گرفته است. نتیجۀ آزمایشها نشان می دهد که تکلیس این ماده با مدل هستۀ کوچک شونده مطابقت دارد و واکنش توسط لایۀ مرزی کنترل می شود. واکنش تکلیس از دمای ۲۴۰°C آغاز می شود. افزایش فشار جزئی CO$_2$ باعث می شود دمای آغاز واکنش تکلیس حداقل ۳۰°C افزایش یابد. انرژی اکتیواسیون واکنش ۵ kJ/mol ± ۱۸۰ می باشد.

1. INTRODUCTION

Situated in North Western Iran, Angooran mining complex is the largest zinc and lead mine in the Middle East. Unlike the majority of zinc ores world wide, the Angooran mine ore is of carbonate nature. Angooran zinc carbonate concentrate may be used to produce zinc oxide with industrial purity [1-2]. The process involves the calcination and subsequent reduction of the concentrate in a fluidized bed furnace. Therefore, it is necessary and important to study the kinetics

of zinc carbonate calcination and effects of carbon dioxide partial pressure on the process.

Although the calcination kinetics of some carbonates such as limestone has been widely investigated, the number of research articles on the calcination kinetics of zinc carbonate is limited. However, some of the factors affecting the calcination kinetics of zinc carbonate have been studied by some researchers. Yamada et al. [3] investigated the effect of atmospheric CO_2 and H_2O on the thermal decomposition of zinc carbonate hydroxide. They reported no apparent effect by atmospheric CO_2. Li et al. [4] claimed that the thermal decomposition of zinc carbonate hydroxide is a two step reaction consisting of a reversible diffusion reaction in two dimensions and an irreversible reaction. Pysiak et al. [5] studied the thermal decomposition of zinc carbonate at different partial pressures of carbon dioxide at several temperatures in the range 300 – 380 °C. They have found activation energy values between 159.1 kJ/mol and 182.1 kJ/mol for different CO_2 partial pressures. They also showed that thermal decomposition of zinc carbonate obeyed the fundamental relationships for topochemical reactions occurring at constant pressure or constant supersaturation. Increasing the particle size, can increase the reaction temperature and decrease the activation energy as Liu et al. have reported [6]. Kanari et al. [7] have worked on pure and impure zinc carbonate hydroxide samples and have shown that pure samples are less temperature sensitive than impure samples. They proposed the value 113 kJ/mol for the activation energy of calcination of zinc carbonate in the temperature range 269 – 434 °C. Gotor et al. [8] have studied the calcination of zinc carbonate in the temperature range 330 – 452 °C. Based on TG results, they have proposed two different mechanisms for the nucleation and growth of products. Dollimore et al. [9] 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. Nobari and Halali [10] have studied the calcination kinetics of zinc carbonate hydroxide and Calsimin zinc carbonate concentrate and have reported the activation energies to be 88.7 kJ/mol and 97.3 kJ/mol, respectively.
Unlike zinc carbonate, the effect of CO_2 partial

pressure on the calcination reactions of calcium carbonate, cadmium carbonate, manganese carbonate and lead carbonate has been studied by many investigators [11-15]. Criado et al. [11] have applied a pressure correction term for obtaining reliable kinetic data in the thermal decomposition of limestone. It must, however, be noticed that in the calcination reaction of zinc carbonate hydroxide, CO_2 and H_2O are evolved simultaneously in the same temperature range [3, 10].

2. THEORY

Under non-isothermal conditions, the rate of the thermal decomposition Equation is described by the following relation [11]:

$$\frac{d\alpha}{dt} = K(T) f(\alpha) \qquad (1)$$

where, α is the conversion or transformation degree at time t, K(T) the rate constant as a function of temperature, and f(α) the conversion function dependent on the mechanism of the reaction. For the reversible decomposition the rate constant may be calculated from Arrhenius Equation [11]:

$$K(T) = A \exp\left(\frac{-E}{RT}\right)\left(1 - \frac{p}{p^*}\right) \qquad (2)$$

where, A is the pre-exponential factor, E the activation energy, R the gas constant, p the partial pressure of CO_2, and p* is the equilibrium pressure of CO_2. In Equation (2), the $1 - p/p*$ term is known as the pressure correction term. The CO_2 equilibrium pressure dependence on temperature can be expressed by the following Equation [16]:

$$p^* = 1.64427 \times 10^{20} \exp\left(\frac{-22921.4}{T}\right) \qquad (3)$$

Integrating equation (1) gives:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \int_0^t K(T)dt \qquad (4)$$

The unreacted shrinking core model with phase boundary controlled reaction is used to investigate

the calcination reaction in this study, therefore, $f(\alpha)$ and $g(\alpha)$ are assumed to be $(1-\alpha)^{2/3}$, and $3[1-(1-\alpha)^{1/3}]$, respectively [8]. In this model, it is assumed that 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.
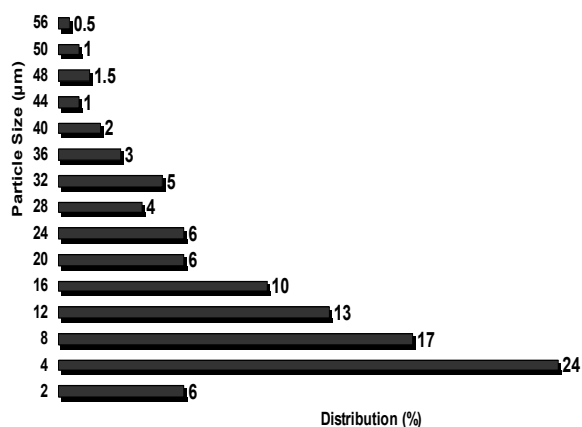
3. EXPERIMENTAL PROCEDURE

The sample used in this study was high purity zinc carbonate hydroxide $Zn_5(CO_3)_2(OH)_6$ powder with the average size of 12 μm provided by Merck. Figure 1 exhibits the size distribution of the used zinc carbonate hydroxide powder. The powder was dried in an oven by heating at 110 ºC for 1.5 hours. CO_2 and N_2 used in the experiments both had a purity of 99.9%. On heating, zinc carbonate hydroxide decomposes to solid and gaseous products.

$$Zn_5(CO_3)_2(OH)_6 \rightarrow 5ZnO + 2CO_2 + 3H_2O \quad (5)$$
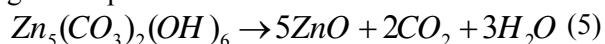
A Polymer Laboratories (STA/625) thermal analyzer was utilized for conducting experiments. This instrument permits the simultaneous recording of both TG and DTA curves. The operational characteristics are as follows:

- o heating rate: 10 K/min
- o sample size: 7 ± 0.5 mg
- o atmosphere: $N_2 + CO_2$
- o temperature range: $30 - 450\ ^{\circ}C$

- o gas flow: 40 ml/min

In thermal analysis, mixtures of CO_2 and N_2 with CO_2 partial pressure of 4.7 kPa, 16.6 kPa, 48.6 kPa and 101.3 kPa were used. The total pressure was 111.4 kPa in all the runs.

4. RESULTS AND DISCUSSION

4.1. TGA and DTA Experiments   Figure 2 represents the temperature dependence of the pressure correction term at CO_2 partial pressures used in this study. It is obvious that the reaction goes to completion irrespective of the CO_2 partial pressure. The partial pressure of CO_2 has nevertheless a direct relationship with the reaction start temperature.

The results of TGA and DTA analysis for samples with different gas mixtures have been shown in figures 3 and 4. As in fig. 2, these curves show that increasing the carbon dioxide partial pressure result in an increase in thermal decomposition mean temperature.
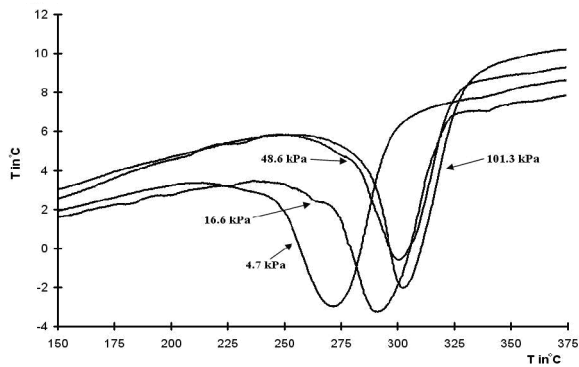
The maximum weight loss for zinc carbonate hydroxide is 25.9% according to Equation (5). This value is independent from the gas mixture. In Figures 5 and 6, the values of α and $d\alpha/dT$ versus T have been plotted for the zinc carbonate hydroxide in various gas mixtures. A method adopted by Caballero et al. [17] is employed to reduce the deviation of $d\alpha/dT$ curves. Equation (6) may be derived from Equations (1) and (2):

Figure 1. Size distribution of the used zinc carbonate hydroxide powder
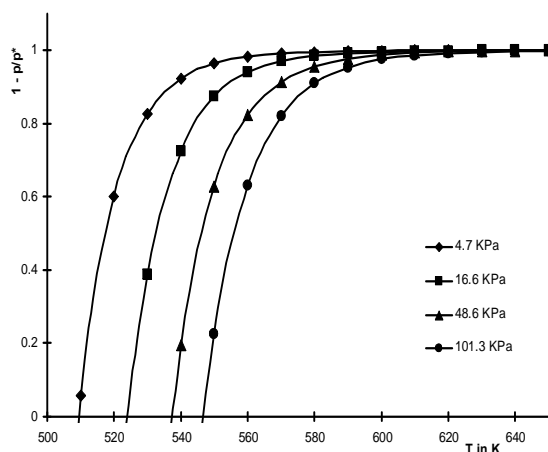
Figure 2. Temperature dependence of the pressure correction term at used CO_2 partial pressures
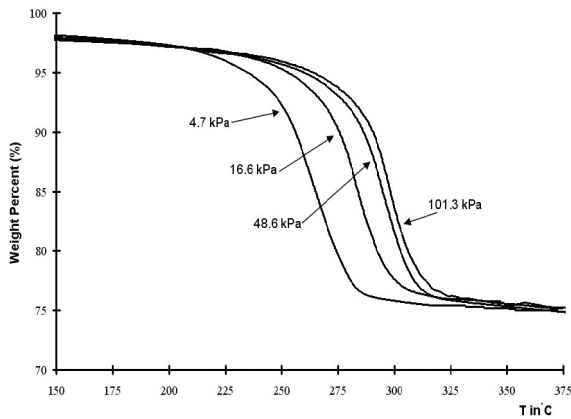
Figure 3. TGA analysis of sample with different gas mixtures

Figure 4. DTA analysis of sample with different gas mixtures

Figure 5. The α values versus T

Figure 6. The dα/dT values versus T

$$\frac{d\alpha}{dt} = A\exp\left(\frac{-E}{RT}\right)f(\alpha)\left(1 - \frac{p}{p^*}\right) \qquad (6)$$
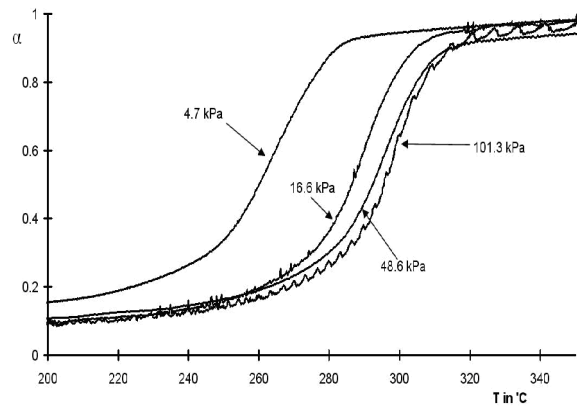
Equation (6) can be rewritten as:

$$Y = \ln\left[\frac{\frac{d\alpha}{dt}(1-\alpha)^{-\frac{2}{3}}}{\left(1 - \frac{p}{p^*}\right)}\right] = \ln A - \frac{E}{RT} \qquad (7)$$

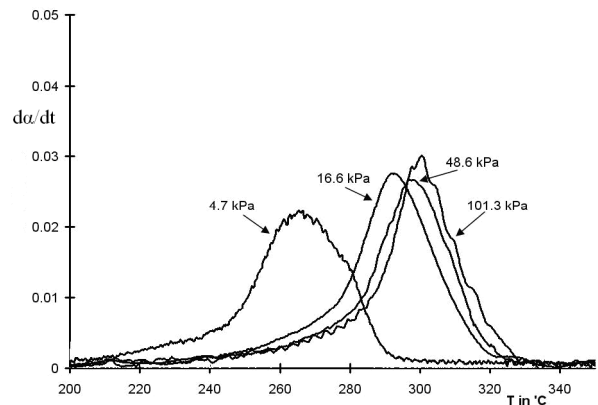Values of dα/dt are required for calculating Y. These values may be obtained from the following relationship:

$$\frac{d\alpha}{dt} = \frac{d\alpha}{dT}\frac{dT}{dt} \qquad (8)$$

And as it was mentioned before, dT/dt = 10 K/min.

In Figure 7 values of Y versus 1000/T have been plotted for different gas mixtures. The plots

exhibit linear behavior in the temperature range of this study. Therefore, the shrinking core model with phase boundary controlled reaction may be applied to samples satisfactorily.

4.2. Calculation of Activation Energy The slope of the Y versus 1000/T curve was found for each sample from Figure 7. As the slopes for these lines are $\frac{E_a}{R}$, the values of activation energy may be calculated. The intercept of these plots can be assumed as lnA. The calculated values for the activation energy and pre-exponential factors of calcination of zinc carbonate hydroxide samples in different carbon dioxide partial pressures are tabulated in Table 1. Table 2 exhibits a comparison between values of activation energy obtained by different researchers for this reaction.
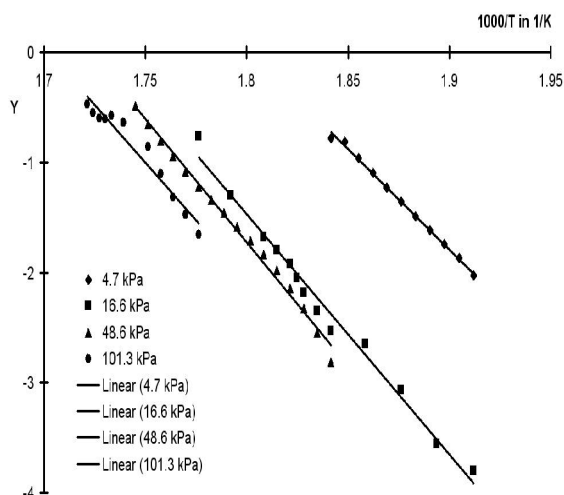
Figure 7. The Values of Y versus 1000/T

TABLE 1. Kinetic parameters values at different CO_2 partial pressure

CO_2 Pressure (kPa)	E (kJ/mol)	A (1/min)	Correlation Coefficient
4.7	151.398	1.77×10^{14}	0.9973
16.6	180.821	2.30×10^{16}	0.9871
48.6	185.934	5.41×10^{16}	0.9926
101.3	173.954	2.99×10^{15}	0.9094

TABLE 2. Comparison of activation energies obtained for calcinations of zinc carbonate

Reference	E (kJ/mol)	CO_2 pressure (kPa)
This study	152.4 – 174.0	4.7 – 101.3
Pysiak et al. [5]	160.0 – 180.7	0
Kanari et al. [7]	132 ± 5	0
Dollimore et al. [9]	94 ± 9	0

At the lowest CO_2 partial pressure of this study, that is 4.7 kPa, the activation energy of the reaction is calculated as 151. 398 kJ/mol. As the CO_2 partial pressure is increased, the activation energy approaches a mean value of 180 ± 5 kJ/mol. Other researchers studying similar reactions in air have found activation energies of 94 ± 9 kJ/mol [9] and 88.7 kJ/mol [10]. These values are obtained in the absence of CO_2 in the experiment atmosphere. It can therefore be deduced that the activation energy of calcination for this material is very sensitive to changes in carbon dioxide partial pressure at very low CO_2 partial pressures such that an marginal increases in the carbon dioxide partial pressure can raise the activation energy of the reaction by as much as 50 kJ/mol.

The values of calculated activation energy of reaction indicate that the rate controlling step is a chemical reaction, and this reaction is the chemical reaction at the surface of the unreacted core.

5. CONCLUSION

1. Calcination reaction of zinc carbonate hydroxide becomes significant at 240 ^{o}C under a CO_2 partial pressure of 4.7 kPa. Increasing the carbon dioxide partial pressure can shift the reaction temperature by up to 30 degrees centigrade.
2. The shrinking core model can justify the calcination reaction of zinc carbonate hydroxide and the reaction mechanism is phase boundary controlled.
3. In an inert gas atmosphere, incremental increase in the partial pressure of carbon dioxide may increase the activation energy for calcinations of zinc carbonate hydroxide by as much as 50 kJ/mol.
4. Increasing the carbon dioxide partial pressure up to 1 atm, does not change the thermal decomposition reaction and does not change reaction mechanism.

6. REFERENCES

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