Thermal Analysis and Structural Characterization Studies of Calcite Mineral at Different Microns

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Thermal analysis methods provide convenient method for quantification study of minerals, which is of great importance in various industries. Intensive studies have been made over years for calcite mineral obtained from mining area as such. In present work, the effect of particle size towards decomposition process of calcite mineral is studied using three particle size ranges which are 125, 50 and 25 mu. Decomposition reactivity is conducted using thermal gravimetric analyzer at heating rate of 20 °C/min in inert nitrogen atmosphere. Structural investigation using X-ray diffraction shows calcite is made up of 75 % calcium element and CaO is produced after decomposition is conducted, which is also been analyzed by X-ray diffusivity analyzer. The chemical composition is unaltered for different size. No structural variation for various particle sizes. Decomposition rate increased as the particle size is larger. The sample with smallest particle size exhibits to have minimum decomposition rate among the other sizes. It occurred at 811 °C with decomposition rate of 0.066/min. It is also observed that the time taken for decomposition of smallest particle size is shorter compared to the sample with larger particle size. Particle size really becomes a factor to the thermal decomposition process as it determines the surface area of the sample. Besides, smallest particle size exhibits the minimum decomposition rate. To conclude, calcite is a promising source for CaO and based on three different particles sizes used, sample at maximum size offers the highest decomposition rate.

Keywords: Calcite, Thermal decomposition, X-ray diffraction, Decomposition rate.

INTRODUCTION

Most physical, chemical and biological processes on earth are either influenced to some degree by the properties of minerals. Minerals are more complex than previously thought because of the discovery that their chemical properties vary as a function of particle size[1]. It has been established that these variations may make a difference in important geochemical and biochemical reactions and kinetics. Industrial minerals are geological materials which are mined for their commercial value, which are not fuel and are not sources of metals. They are used in natural state or either as raw materials or as additives in a wide range of applications[2].

The decomposition behaviour and temperature changes in carbonate samples are interrelated. A decomposition reaction, which is endothermic, tends to arrest the temperature rise, the lowered temperature slowing down the reaction rate. Calcium carbonate like many other similar simple chemical compounds forms different anhydrous polymorphs (calcite, aragonite, vetarite). The polymorphic modifications of $CaCO_3$ and the factors affecting their formation have the subject for many years[3]. It is of great importance to understand the formation and stability conditions for all $CaCO_3$ crystal modifi-

cations, as well as the rules of their phase transformations, especially in the studies of complex metamorphic and sedimentation process in geology. The carbonates of calcium and magnesium occur under various geological conditions. The natural occurance of carbon aggregate is often highly complex. Thermal analysis appeared to offer the means of defining the fraction of each mineral lattice in such mixtures and the concentration of each cation in each lattice. The correlation of the thermal data with the structural pattern should provide a broaden understanding of these minerals in their natural occurrence[4].

Calcite contains about 75-85 % by weight of $CaCO_3$ which has enable it to be applied for quite a number of purposes[5]. Thermal decomposition process known as calcination, $CaCO_3$ can be converted into CaO which is used in industries and daily practice such as in construction material, glass production, waste water and sewage treatment, agricultural and more[5]. Eqn. 1 represents the decomposition process of $CaCO_3$. CaO also been used as the based material to adsorb carbon dioxide, CO_2.

$$CaCO_3 \text{ (s)} \rightarrow CaO \text{ (s)} + CO_2 \text{ (g)} \qquad (1)$$
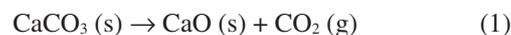
Limestone and dolomite is resistible to high-temperature process (500-1000 °C) other than it can be regenerated and

sustained to a number of CO_2 adsorption and calcination cycles[6]. Stanmore and Gilot[7] mentioned that kinetics of calcination is complicated by three factors which are concentration of CO_2, sizes of the particle and also impurities. Calcination favours high temperature as it is an endothermic reaction and it needs low decomposition pressure of $CaCO_3$ in order to drive the equilibrium reaction forward[7]. Previous studies found that atmospheric pressure could be achieved when calcination temperature reached 800-900 °C[6-8]. Besides, Cheng and Specht[8] stated that the resistances introduce by particle size of the sample can be avoided by having the sample size in millimetre or micrometer range. However, the extent of particle size effect is uncertain since it also depend on the calcination condition such as temperature, flow rate and calcination atmosphere[8].

Thus the aim of this paper is to study the decomposition behaviour of the calcite at different particle size range by demonstrating the fraction of decomposed sample according to temperature changes, the highest temperature that calcite can resist.

EXPERIMENTAL

Calcite mineral used in this experiment were taken from Alathiyur, Virudachalam district Tamil Nadu, India. The mineral were crushed using jaw crusher which was then been ground into the powder form using pulverizer. The powder was then subjected to planatery milling for 5 to 0.5 h to segregate according to the ranges of particle sizes. The particle size was estimated using particle size analyser (CILAS 1064).

The characterization analysis have been done in this study were using X-ray diffraction (XRD). The chemical composition of limestone was analysed using induced coupled plasma (Model: Perkin Elmer optima 2000DV) while the crystal structure of the sample were estimated using X-ray diffraction, XRD (Model: Shimadzu XRD-6000), which was run in 2 theta range 1 to 80° with step size of 0.02 and scan speed 1 °C/min. Calcination of the sample were analysed by conducting the thermal decomposition using thermo-gravimetric analyzer, TGA (Model: Netzsch STA 449F3 jupiter). 10-20 mg of sample powder in the size of 125 mu was placed in the ceramic sample holder. It was heated up to 1000 °C at 20 °C/min under nitrogen gas flow at 20 mL/min. Nitrogen was used to ensure inert environment around the sample. The sample was cooled down to room temperature after been hold for 0.5 h at 850 °C to ensure the completion of the process. The procedures were repeated for different particle size at the same heating rate.

RESULTS AND DISCUSSION

Characterization of calcite mineral: Chemical analysis using inductive coupled plasma (ICP) has been conducted to estimate the mineral composition of the sample. The result demonstrates that the sample is made up of calcium (Table-1). The chemical composition was same for different particle sizes.

The analysis of crystal structure using XRD confirms that raw mineral is made up of calcite, $CaCO_3$. It is one type of crystal form of limestone (calcium carbonate) other than aragonite and vaterite[9]. Calcite is the most stable polymorphism of calcium carbonate, aragonite has higher density and hardness which make it very suitable material in plastic, paper, glass fiber and other industry. The analysis also indicates the presence of lime, CaO, in the calcined. Thus, these findings suggest that thermal decomposition of calcite converts $CaCO_3$ into CaO[10].

Fig. 1, (a) shows the XRD pattern of calcite for various particle size, where c indicates $CaCO_3$. (b) Shows the calcite decomposition pattern at 900 °C, where c indicates lime CaO. XRD pattern for different particle size are same, which reveals that no structural variations at different particle size. The peaks are quite sharp with little background absorption. There is a slight variation in the intensities of the peaks for different particle sizes.
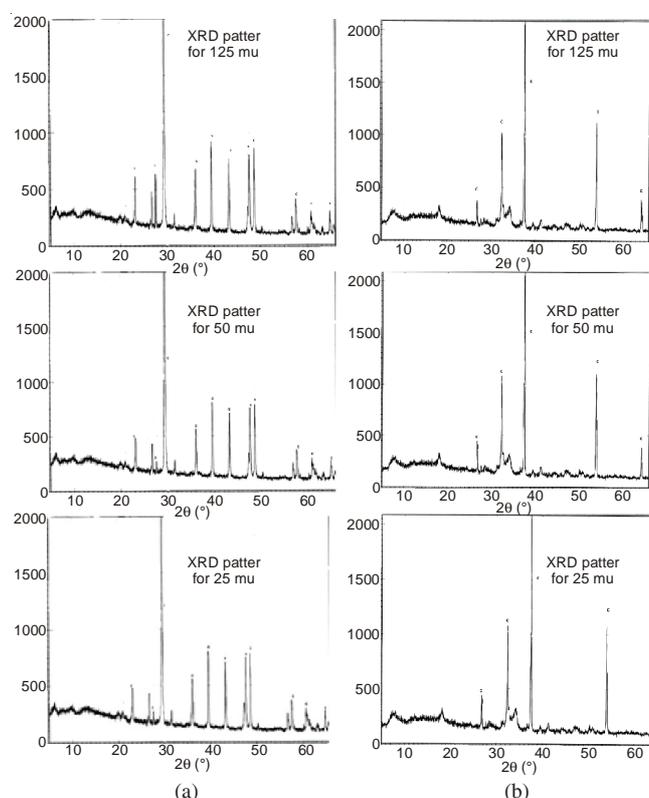
Fig. 1. XRD Spectra of (a) Calcite [c- $CaCO_3$] and (b) decomposed Calcite [c-CaO]

Thermal decomposition of calcite: Thermal decomposition of carbonate usually is assumed to suit Shrinking Core Model (SCM) where it visualizes the reaction begin to occur at the outer layer of the particle then move into the solid which finally leaving the completely converted material and inert solid that is known as 'ash'[11]. Fig. 2 illustrates weight loss of the sample during the process. By taking sample with particle

TABLE 1
CHEMICAL ANALYSIS OF CALCITE BY INDUCTIVE COUPLED PLASMA

$CaCO_3$	SiO_2	Al_2O_3	Fe_2O_3	MgO	Na_2O	K_2O	Mn_2O_3	TiO_2	P_2O_5	Cr
76.56	13.45	3.46	3.05	0.38	0.25	0.36	0.05	0.22	0.05	0.01

size range of 125 mu as the example, the initial process started with a very small weight loss which is due to the moisture content that still left in the sample. As the temperatures increase between 700 to 900 °C, rapid weight change occur as the volatile material in the sample attempt to escape as decomposition begin to take place. However, the sample weight seemed to be constant after the temperature reach 900 °C. It signifies that the process was already done and sample left is known as 'ash'[11].
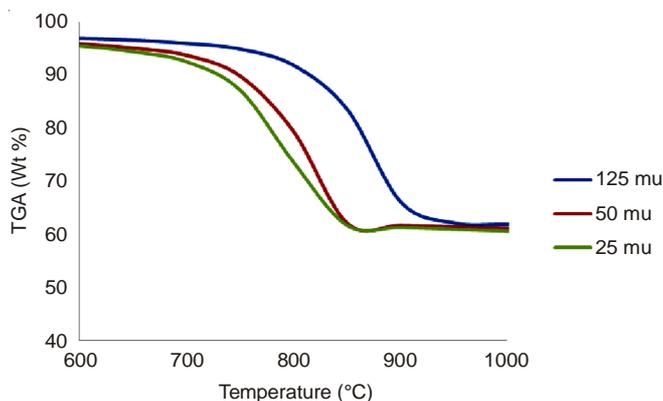
Fig. 2. TG Curves of limestone decomposition

Weight loss of the sample indicates the fraction of sample that been decomposed during the process. Fig. 3 represents the fraction of decomposed sample which was most probably involving the conversion of $CaCO_3$, into CaO. The assumption was supported by the analysis that been done using XRD.

Using the same computation method as Dollimore et al.[12] and Halali et al.[13], fraction of the decomposed sample during the calcination is denoted by α and computed using eqn. 2. The fraction was based on the current weight loss with respect to total weight loss of the sample. Initial weight is denoted by w_i while w_t represents current weight and final weight is denoted by w_f. Sample with larger particle size need higher temperature and longer time to get fully decomposed compared to sample with smaller particle size.

$$\alpha = (w_i-w_t)/(w_i-w_f) \qquad (2)$$
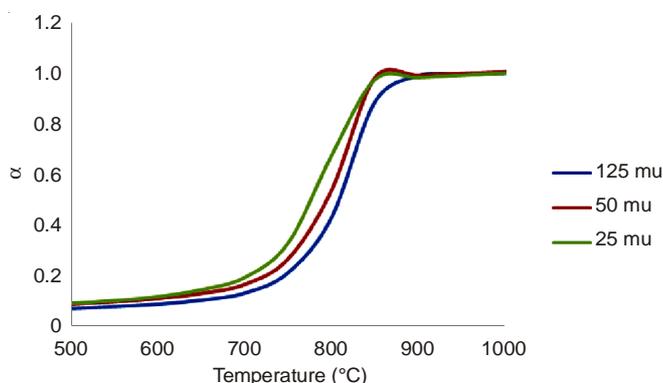
Fig. 3. Fraction of sample decomposed according to temperature change

Fig. 4, shows the first derivative weight loss curve. The first derivative peak temperature T_p for particle size range 125 mu is 845 °C, for 50 mu is 830 °C and for 25 mu is 811 °C. Hence, the decomposition for the sample with smaller particle size takes place at lower temperature compared to that of larger particle size (Fig. 5).
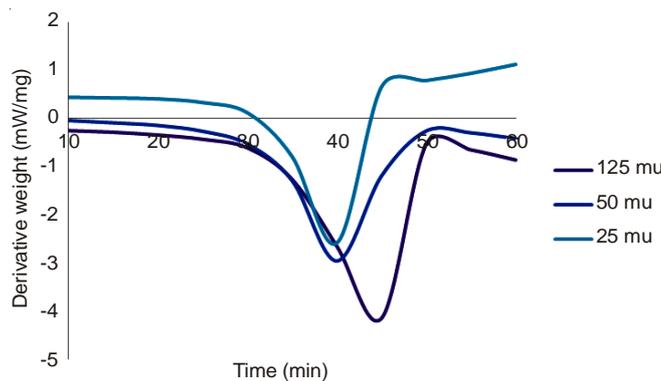
Fig. 4. Derivative weight curve as a function of time
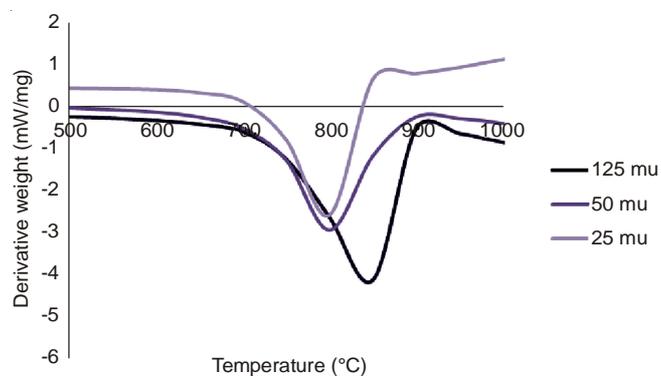
Fig. 5. Derivative weight curve as a function of temperature

Table-2 suggested that the particle with maximum size absorbed more heat to release CO_2 (to decompose) than that of smaller particle size. The time taken is also longer (41 min) for maximum particle size. Whereas the sample with minimum particle size decomposes faster (39 min). Exothermic peaks are also noticed which is due to the presence of impurities like silicon[14]. Fig. 6 shows decomposition rate of calcite, $d\alpha/dt$, which is computed using eqn. 3. Weight loss with respect to time, dw_t/dt, is the differential data of TG curves.

$$d\alpha/dt = \frac{-dw_t/dt}{w_i - w_f} \qquad (3)$$

TABLE-2			
Particle size	125 mu	50 mu	25 mu
Endotherms (J/g)	-856.3	-827.1	-720.5
Decomposition temperature (°C)	845	830	811
Decomposition time (min)	41	40	39

Decomposition rate is increased as the particle size is larger. The sample with smallest particle size exhibits to have minimum decomposition rate among the other sample sizes. It occurred at 811 °C with decomposition rate of 0.066/min. It is also observed that the time taken for maximum decomposition rate of the largest particle size is longer compared to the sample with smaller particle size. Particle sizes really become a factor to the thermal decomposition process as it determines the surface area of the sample. Smaller particle
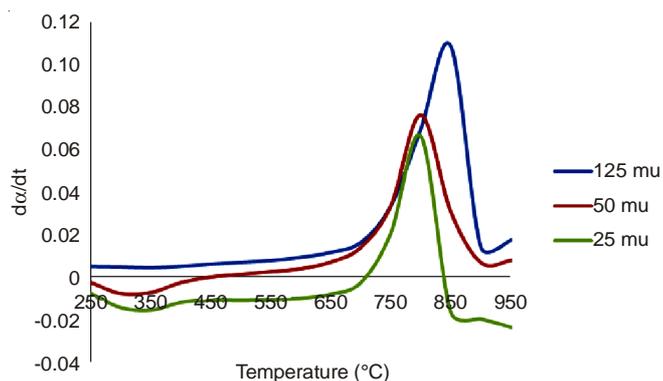
Fig. 6. Decomposition rate curve of calcite with different particle size

size tends to have large surface area that contributes to high efficiency of heat transfer. It can accelerate the process by reducing the thermal or heat resistance and other resistance such as mass transfer or gas diffusion[8]. The cause of CO_2 partial pressure can be neglected in this study as the process was conducted at 850-900 °C in which at this temperature the pressure is considered to be in equilibrium or atmospheric pressure[7,15].

Conclusion

Calcite mineral is a crystal form of limestone containing calcium carbonate. This is confirmed from the XRD analysis. The thermal decomposition process that been done managed to decompose a fraction of the sample into calcium oxide. Through thermogravimetric analysis, calcite begin to decompose at 800 °C and loss 45 % of the weight regardless the particle sizes. The findings confirmed that particle size influenced the process. Sample with smaller particle size decomposes at lower temperature compared to the larger particle size. The heat energy (endotherms) needed to decompose the sample is minimum for smaller particle size. Besides

these findings, the larger particle size possess higher decomposition rate and at lower temperature the smaller particle size possess lower decomposition rate. In this case, the highest decomposition rate is 0.108/min for the particle size range of 125 mu and 0.066/min for 25 mu at heating rate of 20 °C/min. The lowest decomposition rate for smaller particle size, in this regime demonstrates that the particle size is not the only factor that influences the calcite decomposition, but also the concentration of CO_2 and impurities present in the sample also to be considered.

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