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Note

The effect of sample preparation on the thermal decomposition of $CaCO_3$

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Abstract

It is pointed out that many of the thermal analysis techniques commonly utilized to measure the rates of thermal decomposition reactions are plagued with problems of mass and energy transport limitations. Because the technique employed here, dynamic X-ray diffraction (DXRD), allows for in situ observations of the solid reactants, intermediates, and products, and for better control of the heat and mass transfer resistance, most of these problems are obviated. Results are presented which not only compare the dramatic differences in global reaction rates between TGA and DXRD experiments, but also demonstrate the effects of sample preparation on calcite decomposition. Specifically, it is shown that sample cleaning, which tends to remove nucleation sites, as well as sample de-gassing, which probably removes water vapor, can lead to very different calcite decomposition rates.

Keywords: Calcite; DXRD; Preparation; Surface; TGA

1. Introduction

Modern cement manufacture includes substantial calcination (60–90%) of the limestone feed in "precalciners", prior to injection into the traditional rotary kiln. In order to facilitate the efficient design, improvement, and assessment of the precalciners, many researchers have studied the thermal decomposition kinetics of $CaCO_3$. It is evident that in the normal range of calcination temperatures (600–1000°C), the only products are CO_2 and CaO with the decomposition occurring at

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a definite boundary between the CaO and $CaCO_3$ phases [1]. The three potential rate-limiting processes involved in the decomposition [2] are: heat transfer to the particle surface and through the CaO product layer to the reaction interface, mass transfer of CO_2 released at the reaction zone away from the interface, mass transfer of CO_2 released at the reaction zone away from the interface through the product layer, and chemical reaction. However, the actual rate-limiting step has been the subject of considerable controversy and the effects of factors such as sample quantity, particle size, heating rate, decomposition temperature range, CO_2 partial pressure, sample diluent, gaseous environment, purge gas velocity, and crystalline structure on the rate-controlling step have all been previously reported [3–7].

The product layer is apparently a major resistance to heat and mass transfer in large particles under mild conditions. In order to obtain the intrinsic kinetics, most investigations have been focused on powdered samples; this has been reviewed by Beruto and Searcy [8]. Even with powdered samples, it is generally observed that sample quantity, heating rate/decomposition temperature range, and CO_2 partial pressure have marked effects on $CaCO_3$ decomposition and these experimental variables are closely interrelated. An increase in CO_2 partial pressure within a powdered bed may be brought about by any of these major variables. In order to obtain the intrinsic decomposition kinetics, efforts have been made to minimize the effects of heat and mass transfer [3,6,9]. However, as pointed out by Beruto and Searcy [8], the thermal gravimetric analyzer (TGA) is the most widely used means of studying the decomposition kinetics of $CaCO_3$. Although it is possible to control experimental variables such as heating rate, decomposition temperature range, gaseous environments, etc., sample quantity is usually an uncontrollable variable with TGA because it is directly related to experimental sensitivity and 1–10 mg samples are typically employed. For the purpose of overcoming this difficulty, dynamic X-ray diffraction (DXRD) has recently been successfully applied in the study of calcite decomposition [7]. However, in addition to the aforementioned experimental variables, we have observed that sample preparation also has an effect on calcite decomposition. Consequently, the results of an investigation of the effects of experimental conditions, particularly sample preparation, on the calcite decomposition kinetics are presented in this paper.

2. Experimental procedure

The Iceland Spar calcite sample used in this study was purchased from Ward's Natural Science Establishment, Inc. The sample was crushed, ground, sieved, and collected in the range <38 μm and 53–75 μm. The fraction collected in the range <38 μm was initially ground in a Chemplex SpectroMill Ball Pestle Impact Grinder (model 1100-II) for 10 hours and then stirred in acetone. A "muddy" suspension was separated from the sediment, dried in air and then gently ground into powder form. The mass average particle diameter for this sample was determined by X-ray micro-scan analysis to be 1.87 ± 0.50 μm [7]. A portion of the 1.87 ± 0.50 μm sample was also degassed overnight under vacuum at 200°C prior to the kinetic measurements. Also, a portion of the fraction with particle sizes of 53–75 μm was subjected to ultrasonic washing (10 times) prior to the kinetic experimentation. Subsequent measurements of BET area and particle size distribution were unaffected by this procedure.

Because TGA can only be used to study reactions involving gaseous reactants or products, it is the most widely used means of studying the decomposition kinetics of $CaCO_3$. The main drawback with TGA is that heat and mass transfer complications are usually unavoidably involved. In this study, kinetic measurements were performed in situ under isothermal conditions using DXRD, the details of which have been previously described by Thomson [10]. The advantages of DXRD are two-fold: (1) the solid reactants, intermediates and products can be identified in situ, and (2) the sample can be dispersed on the heating strip in a single particle size depth, which minimizes heat and mass transfer effects. The loading of very thin $1.87 \pm 0.50\,\mu m$ samples on the DXRD heating strip was characterized using scanning electron microscopy (SEM) and these results are shown in Fig. 1. In this SEM micrograph, the dark, uniform background represents the DXRD heating strip, and the calcite samples are nearly dispersed in a single particle size manner (bed thickness is within 5 μm) which helps to minimize interparticle diffusion resistance. As a result, even under closely regulated experimental conditions,

Fig. 1. Scanning electron micrograph of the dispersion of 1.87 ± 0.50 μm Iceland Spar calcite on the DXRD heating strip.

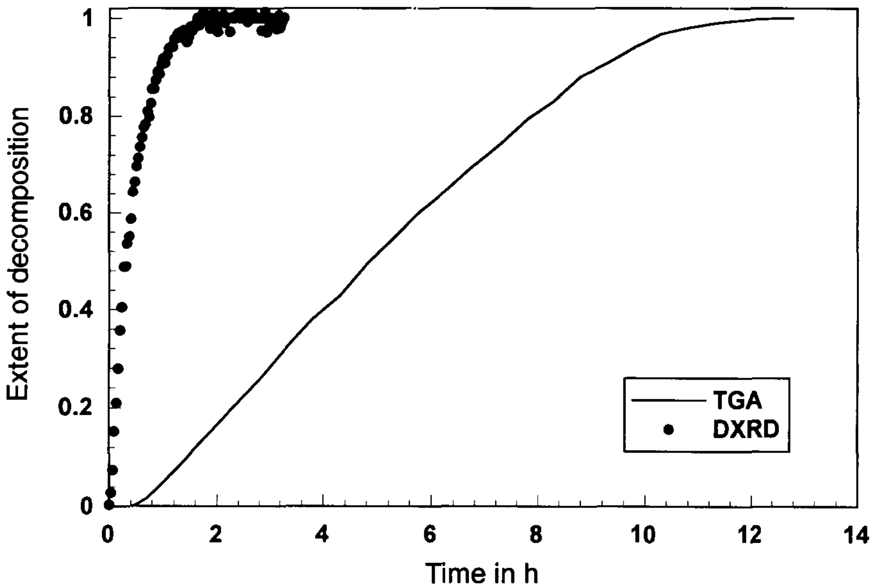

Fig. 2. Comparison of TGA and DXRD experiments: decomposition of 1.87 ± 0.50 μm Iceland Spar calcite at 490°C in helium environment.

significantly different calcite decomposition rates were observed between DXRD and TGA measurements. One such comparison is shown in Fig. 2, where the extent of decomposition for the 1.87 ± 0.50 μm sample is shown for both a DXRD and a TGA experiment at 490°C in helium. Obviously, calcite decomposes completely in a much shorter time (≤ 1 h) in the DXRD experiment than in the TGA experiment (12 h) even though the gaseous flow-rate in the TGA measurement was 10 times higher than in the DXRD experiment (42.5 vs. 4.25 cm min^{-1}) which should help to alleviate external mass diffusion resistance. However, the sample thicknesses are quite different in the two experiments. As stated above, the thickness in the DXRD experiment was one particle size, or about 2 μm, whereas the sample thickness in the TGA experiment (with a 1 mg loading) was about 50 μm. That is, interparticle diffusion resistance in the TGA experiment retards the removal of CO_2, resulting in a greatly inhibited decomposition rate, particularly at these lower decomposition temperatures.

Even though interparticle diffusion resistance can be effectively removed in the DXRD experiments, there is still the possibility of external mass transfer limitations. Consequently, the effect of gaseous flowrate on the decomposition of calcite samples with different particle sizes was also studied in connection with the DXRD experiments. As can be seen from Fig. 3, as long as flow rates are ≥ 500 ml min^{-1} (2.15 cm min^{-1}), there is no effect of gas–solid mass transfer on the decomposition rate and all of the experiments reported here were conducted with a flow rate of 1000 ml min^{-1}. As previously reported [11], when TGA was used to measure the thermal decomposition rate of $CaCO_3$, the rates were affected by the thermal conductivity of the gaseous environments. Interestingly, when DXRD was used to

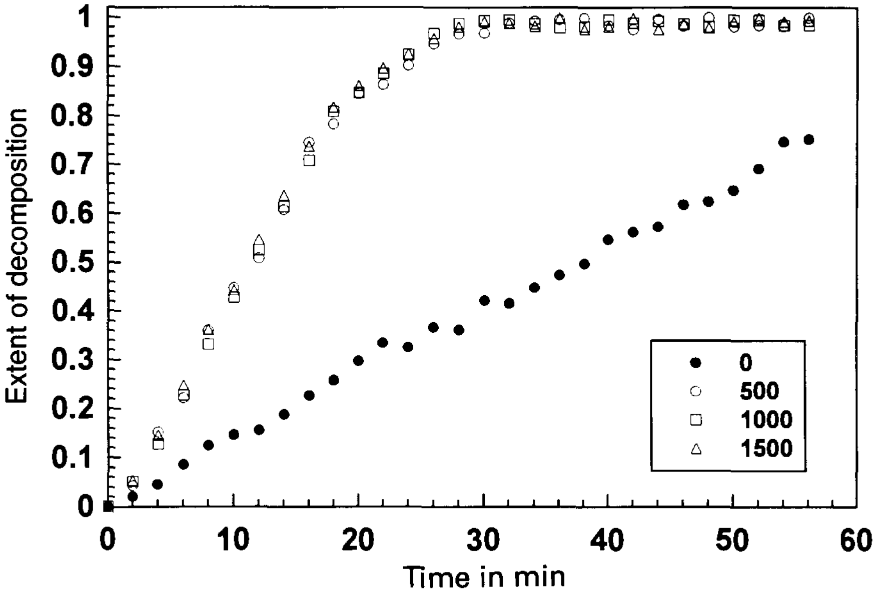

Fig. 3. Isothermal decomposition of 1.87 ± 0.50 μm Iceland Spar calcite at 500°C at various helium flow rates.

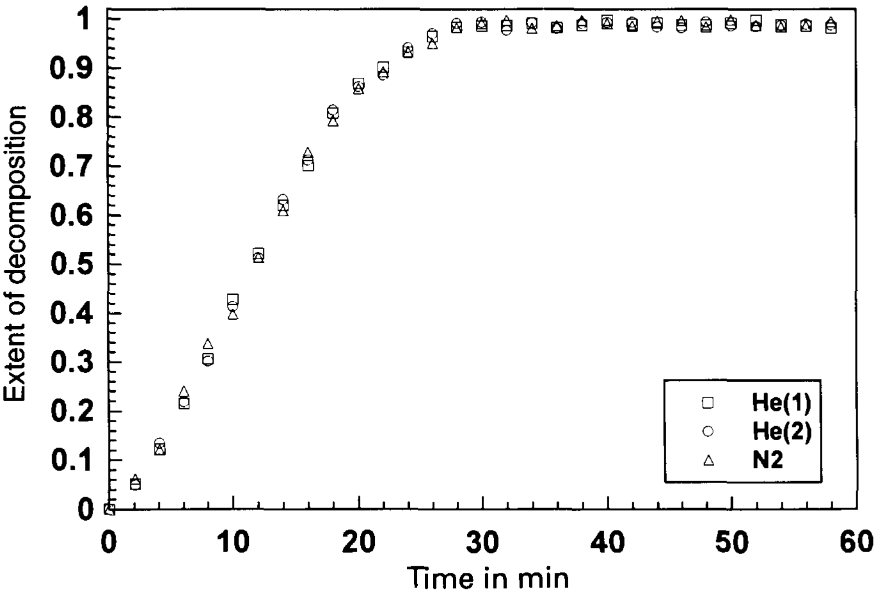

Fig. 4. Isothermal decomposition of 1.87 ± 0.50 μm Iceland Spar calcite at 500°C in various gaseous environments.

measure the decomposition kinetics, the choice of chemically inert gases did not affect the decomposition rate, as shown in Fig. 4 for the 1.87 ± 0.50 μm Iceland Spar calcite heated at 500°C (He(1) and He(2) are two repeatable experimental results). One possible reason is that the heating manner of the samples in TGA and DXRD is different. Because in TGA experiments, the samples are heated by the gaseous environment, the dependence of the decomposition rate on chemically inert gases could be expected if the decomposition is controlled by heat transfer. This is not a problem in the DXRD experiments because the samples are heated by the sample holder.

3. Results and discussion

3.1. The effect of sample washing

Even in previous work [3,6,9] where efforts have been made to minimize the effects of heat and mass transfer, the experimental results have been found to be compatible with a wide variety of rate models. For example, rate-limiting mechanisms for geometric rate models, i.e., contracting area equations [3,6,9], diffusion-controlled models [9] and even nucleation-controlled models [3] have all been observed. However, by careful scrutiny of the experimental procedures used by these investigators, it appears that sample preparation may not be an insignificant factor. In the DXRD results shown in Fig. 5, sigmoid and deceleratory reaction

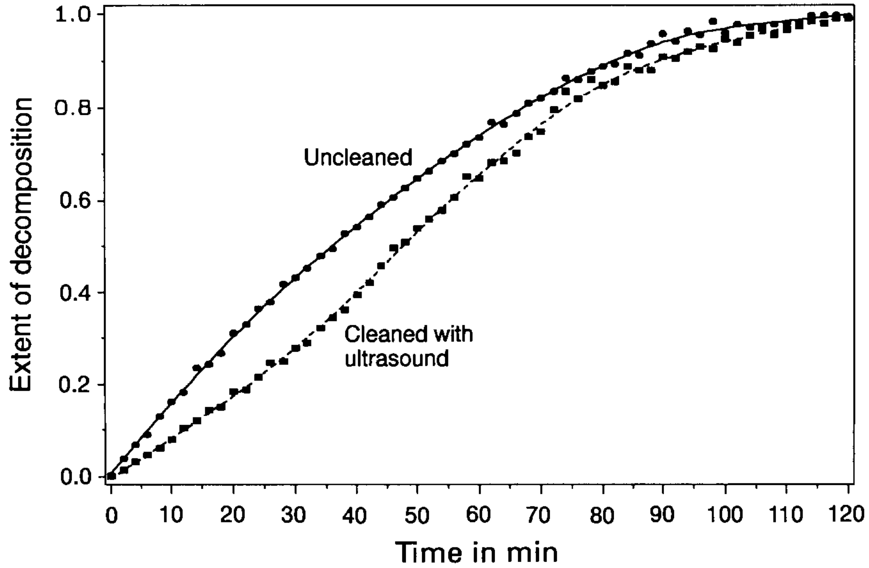

Fig. 5. Comparison of decomposition reaction curves: uncleaned vs. ultrasonically cleaned Iceland Spar calcite (particle size = 53–75 μm, at 565°C).

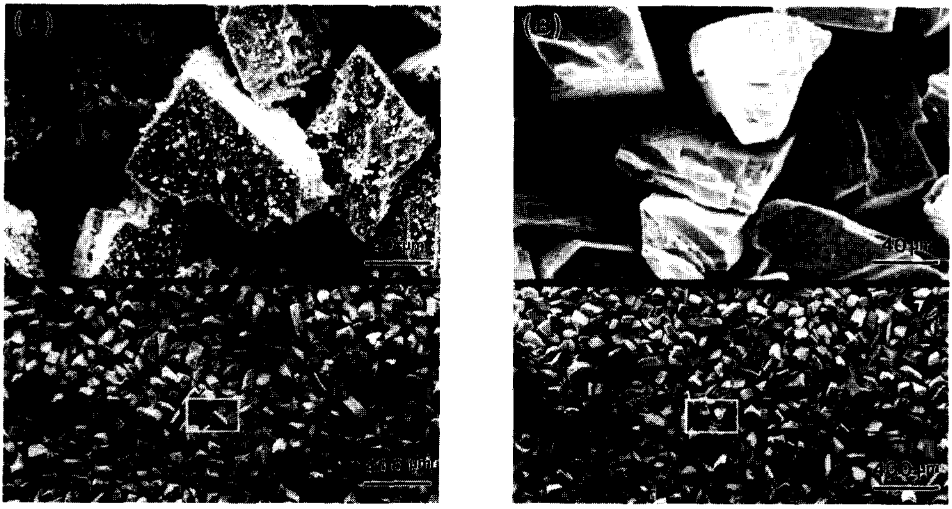

Fig. 6. Scanning electron micrographs (53–75 μm): (A) uncleaned Iceland Spar calcite, and (B) Iceland Spar calcite after ultrasonic cleaning ten times.

curves are respectively observed for an ultrasonically cleaned and an uncleaned Iceland Spar calcite. Sigmoid reaction curves such as observed for the cleaned sample normally represent a nucleation and growth controlled mechanism, whereas deceleratory reaction curves such as observed for the uncleaned sample usually result from diffusion or geometry controlled mechanisms. Scanning electron micrographs of these two samples before calcination (Fig. 6(A) and (B)) indicate that there are agglomerates (sizes <5 μm) adsorbed on the uncleaned samples while ultrasonically cleaned samples have clean surfaces. It is not unreasonable to hypothesize that the increased surface area of the uncleaned samples might eliminate the nucleation-controlled portion of the mechanism and thereby lead to enhanced decomposition rates. This is borne out by the data in Fig. 5 which shows that the extent of the uncleaned $CaCO_3$ decomposition was greater than that of the cleaned sample at any instant during the decomposition.

3.2. *The effect of sample degassing*

In addition to sample washing, degassing during sample perparation also appears to be an important factor affecting the calcite decomposition. Fig. 7 shows a comparison of the thermal decomposition (at 470°C) of degassed and un-degassed calcite samples of particle size 1.87 ± 0.50 μm. The decomposition rate of un-degassed sample is clearly faster than that of the degassed sample. It is possible that un-degassed samples adsorb small quantities of water vapor and, as reported previously [7], even this small concentration of water vapor can significantly enhance calcite decomposition.

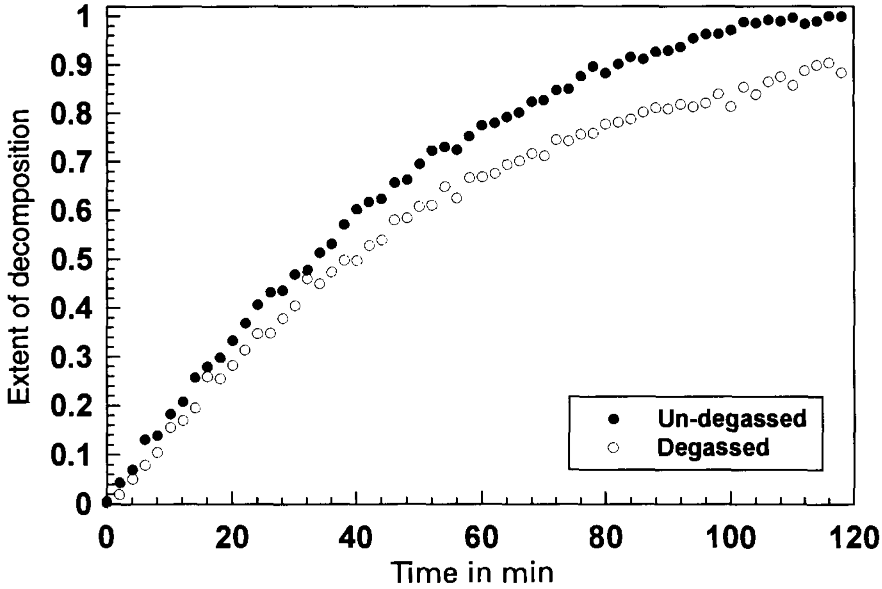

Fig. 7. Comparison of thermal decomposition of the degassed and un-degassed calcite samples at 470°C in helium.

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