THE KINETICS OF THE THERMAL DEGRADATION OF CALCIUM CARBONATE*

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(Received May 21, 1985; in revised form July 26, 1985)

The decomposition of calcium carbonate fine powder in a flowing nitrogen atmosphere has been investigated by non-isothermal thermogravimetry at heating rates in the range, 10–50 deg min⁻¹. The analog percentage weight change record was digitized at 1 deg intervals. The resulting data, transformed into dimensionless extents of reaction and calculated rates of reaction, was then subjected to the Arrhenius, Friedman and Generalized Kissinger analyses, using a recently developed FORTRAN program system. The value of n namely 0.39 ± 0.04, resulting when the data is analyzed assuming an nth order reaction, strongly indicates that the most probable rate controlling step is a three-dimensional diffusion process (D4 mechanism), with $E = 172.4 \text{ kJ}\cdot\text{mol}^{-1}$ and $A = 1.97 \cdot 10^4 \text{ K}^{-1}\cdot\text{min}^{-1}$. Reasons for the wide disparity in previously reported kinetic data are discussed.

The ever-increasing impact of the acid rain problem has emphasized even more the need to develop efficient procedures for in situ removal of sulfur dioxide, produced from high sulfur coals in large combustion systems. Atmospheric Fluidized Bed Combustion (AFBC) utilizes naturally occurring limestone or dolomite admixed with the fossil fuel as feedstock. Calcination proceeds and theoretically the sulfur dioxide produced in the combustion zone is removed by lime absorption prior to stack emission. Flue Gas Desulfurization (FGD) may entail the use of calcined limestone physically separated from the burning fuel. The efficiency of either gettering process will be governed by the nature of the calcium sulfate (or sulfite) formation reaction. This may well be similar to the calcium carbonate formation process, which in turn may be analogous to the reverse dissociation reaction. An understanding of the nature of these reactions is considered to be of

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prime importance. This paper is concerned with the findings of a study of the calcination reaction.

The thermal degradation of calcite has been the subject of intensive study over the years [1]. Beruto and Searcy [2] find that most activation energy values \( E \) reported prior to 1974 are close to the enthalpy of degradation, 178 kJ·mol\(^{-1}\) (see ref. 733 in the Brown, Dollimore and Galwey review) [1]. At this time, Zsakó and Arz [3] analyzed previously reported experimental data from three sources. They employed the \( n \)th order function \( (1 - \alpha)^n \), to represent \( f(\alpha) \) in the general rate Eq. (1). For degradative studies carried out in an air atmosphere, \( E \) values ranging from 110–742 kJ·mol\(^{-1}\), and pre-exponential factors, \( A \), varying between \( 1.6 \cdot 10^2–3.2 \cdot 10^3 \) min\(^{-1}\), were obtained. When data obtained under various partial pressure carbon dioxide atmospheres was analyzed, even greater values were obtained; namely, \( E = 709–1558 \) kJ·mol\(^{-1}\), \( A = 1.6 \cdot 10^{32}–7.9 \cdot 10^{58} \) min\(^{-1}\). It is true, as Zsakó and Arz state, that the investigative conditions do influence the results. However, we strongly disagree with these authors who state that the great differences in the kinetic parameter values obtained are in no way related to the calculation procedures.

It is the purpose of this paper to show how non-isothermal thermogravimetry at medium heating rates, in the range 10–50 deg·min\(^{-1}\) can be used to study the calcination reaction, to derive the kinetic parameters for a reasonably mechanism, and to show why the calculation techniques are all important.

**Experimental**

All non-isothermal thermogravimetric measurements (NITG) were carried out in 100 ml·min\(^{-1}\) flowing 99.9% pure nitrogen in the Perkin–Elmer TGS–2/System 4 analyzer with the \( X-Y_1-Y_2 \) recorder, employing the previously-described [4] temperature control procedure. Analytical reagent-grade calcium carbonate (Mallinckrodt #4072) was used at a sample size 3.7–3.8 mg. In order that the weight loss was recorded over 100% of the recorder chart width, a 56% weight suppression was applied, and the data recorded in the percent initial weight mode. This analog data, amplified 100 ×, was digitized at 1 °C intervals and transferred to magnetic tape. This information was then transferred off-line to the in-house computer for analysis by programs TGDATCON/TGKIN as has been described [5, 6].

*J. Thermal Anal.* 31, 1986