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The Thermal Decomposition of Calcium Carbonate

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Abstract: The thermogravimetry(TG) and derivative thermogravimetry(DTG) curves of the thermal decomposition reaction of calcium carbonate have been measured at five different heating rates. The kinetic parameters and the reaction mechanism of the reaction were evaluated from analysis of the TG and DTG curves by using the Ozawa method, the combined integral and differential methods and the reduced equations derived by us.

Keywords: Calcium carbonate, kinetic parameters, non-isothermal kinetics, TG-DTG.

The thermal decomposition reaction of calcium carbonate is a typical thermal decomposition reaction of the solid state. A great deal of studies on this reaction have been performed by previous investigators. This paper reports a procedure for estimating the non-isothermal kinetic parameters and the reaction mechanism of calcium carbonate.

TG-DTG experiments were carried out on a LCT-1 model thermobalance and a WF-1 model differentiator with a TG-DTA-DTG simultaneous device. The size of aluminium oxide crucible is 4×Φ5mm; heating rates are 5, 10, 15, 20, 30°C min^{-1}; TG: 10 mg; DTG: 2 mv min^{-1}; in a static air atmosphere and the sample mass was about 10 mg. The sample was G.R. grade precipitated calcium carbonate (E. Merck,Germany).

According to the Ozawa equation [1]:

$$\log\beta+0.4567E/RT=\text{constant} \quad (1)$$

The activation energy can be obtained by linear relation between the logarithm of the heating rate and the reciprocal of the absolute temperature at the maximum rate of conversion T_m. The values of T_m at five different heating rates (5, 10, 15, 20 and 30°C min^{-1}) are 1034, 1059, 1071, 1084 and 1110K, respectively. The activation energy is calculated to be $E = 214.9$ kJ mol^{-1} with linear correlation coefficient $r=0.9900$.

For the kinetic analysis by the combined integral and differential methods[2], the differential equation of Achar *et al.*[3] and the modified Coats-Redfern integral equation[4] were used. The equations are as follows:

$$\ln[(d\alpha/dt)/f(\alpha)]=\ln A-E/RT \quad (2)$$
$$\ln[g(\alpha)/T^2]=\ln[AR/\beta E]-E/RT \quad (3)$$

The common 19 forms of f (α) and g (α) reported in literature[5] were applied in this work.

The kinetic analysis were completed with the linear least-squares method and the basic data are linear fitted to Eq. (2) and Eq. (3) on a computer. The data of kinetic analysis at five different heating rates clearly show that the values of E and lnA from the two methods are approximately the same, and the relative deviation for E and lnA are minimal, when the most probable mechanism function is function No.12 and function symbol is R_2(the function forms: $f(\alpha)=2(1-\alpha)^{1/2}$, $g(\alpha)=1-(1-\alpha)^{1/2}$)[6]. The mean values of E at five heating rates, 223.26, 214.01, 207.22, 205.41 and 202.01kJ mol^{-1}, were obtained respectively; The mean values of lnA at five heating rates, 19.35, 19.06, 17.56, 17.34 and 16.84, were also obtained respectively.

The reduced equations derived by us are as follows[5]:

$$E/(RT_m^2)+(A/\beta)f'(\alpha_m)\exp(-E/RT_m)=0 \qquad (4)$$

$$E/(RT_i^2)+(3A/\beta)f'(\alpha_i)\exp(-E/RT_i)-2/T_i=0 \qquad (5)$$

Where $f'(\alpha)$ is the differentiation of $f(\alpha)$ with respect to α. Substituting T_m, α_m, T_i and α_i into the reduced equations, the kinetic parameters E and lnA were obtained using our own computer program edited by Quick Basic language. It is seen from the calculation results that only one group of data for E and lnA(R_2:E=224.86, 216.41, 209.48, 207.45, 204.11kJ mol^{-1}, lnA=19.16, 18.11, 17.47, 17.19, 16.58, at five heating rates respectively) is in agreement with those calculated by the combined integral and differential methods and the Ozawa method.

R_2 was taken as the possible mechanism. This was based on a two-dimensional geometrical model. The analysis results show that the reactions are governed by the surface area. D. Dollimore *et al.* found that the possible mechanism of this reaction was D_4 and pointed out the surface area may become significant in desiribing the kinetic behavior[6].

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