

THERMAL DECOMPOSITION KINETICS OF SIDERITE

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ABSTRACT

The kinetic region of the thermal decomposition of siderite is determined as a function of the single particle size. The kinetic constants are calculated from this region. Data are reported on the thermal decomposition of the $\text{FeCO}_3\text{-SiO}_2$ and $\text{FeCO}_3\text{-Al}_2\text{O}_3$ mixtures.

INTRODUCTION

Less attention is given in the literature to the investigation of the thermal decomposition kinetics of the siderite than other carbonate [1,2], although the ferrous oxides from pyrite and siderite have great industrial importance because of their use in covering the surfaces for heat transmission in the boilers. There are special difficulties in the case of fuels containing many inorganic mineral components because of the possible eutectics. Consequently, the formation kinetics of ferrous oxides have frequently been studied in different countries [3–5]. The mechanism and the peculiarities of the siderite decomposition have been investigated, but under isothermal conditions, the samples had 20% additives only and the limits of the kinetic region of the process were not determined [6,7]. So, the applicability range of the kinetic equation is questionable. Beyond that, the mutual effects of the various minerals have to be taken into consideration and it is not known whether the Al_2O_3 and SiO_2 , as very important components in the inorganic mineral part of the solid fuels, have some effect on the thermal decomposition of siderite or not. This work tries to eliminate these gaps.

EXPERIMENTAL

Natural crystals of siderite were used for the measurements. The chemical composition of the samples has been checked both with chemical analysis

and X-ray diffraction. The FeCO_3 content of the natural siderite mineral was 86.70 wt%. The thermal decomposition of siderite was measured thermogravimetrically [2]. Nitrogen, as purging gas, was used to eliminate the outer diffusional complications. The heating rate varied from 0.021 to 0.333 K s^{-1} . The sample mass was limited to 50 mg and a multi-plate sample holder [8] was used to eliminate the diffusional complications in the sample layer. Each sample particle was in contact with the platinum holder, thus monolayer sample arrangement was secured. The sample mass for each fraction has to satisfy the following correlation

$$M \leq \rho s d \quad (1)$$

where M = sample mass on one plate; s = plate surface; d = diameter of the sample particle; ρ = density of the particles.

If the condition in eqn. (1) is fulfilled for the smallest fraction, then it can be fulfilled for the more coarse fractions as well, ensuring the condition that $M = \text{constant}$ for the series of these measurements. $M = 25.46$ mg falls under the above conditions with $d = 25 \mu\text{m}$ particle size for siderite.

Looking for the effect of the internal diffusion on the decomposition kinetics, the particle size of the siderite has been varied between 25 and $6 \times 10^3 \mu\text{m}$ in the course of the investigations. In connection with the increasing particle diameter the internal diffusion of CO_2 toward the surface of the single particles can only influence the kinetics of the examined process. The increasing influence of the internal diffusion may shift the kinetic curves $\alpha = \alpha(T)$ towards the higher temperature because of the decreasing velocity of the process. In this way, the limits of the kinetic region could be determined and it becomes possible to calculate the kinetic constants for the decomposition of the siderite in this region.

The influence of SiO_2 and Al_2O_3 on the decomposition of siderite was also investigated as a connected problem. The concentration of the FeCO_3 in the mixtures was changed from 10 to 90 wt% in steps of 10%. Cylindrical platinum crucibles were used for these series of measurements. The heating rate was 0.167 K s^{-1} . As an application of the above results, the particle size of FeCO_3 has been chosen from the kinetic region (100 μm) and the particle size of the SiO_2 and Al_2O_3 used for the mixtures was the same.

RESULTS AND DISCUSSION

Our results correlate with others [6,9] where attention was drawn to the spontaneous split of one part of the siderite crystals by heating but before the chemical decomposition reaction begins. The split of crystals does not change on decreasing the heating rate from 0.333 to 0.021 K s^{-1} , so heating shock is not the cause of this phenomenon. The size of fragments seems not to depend on the chemical reaction.

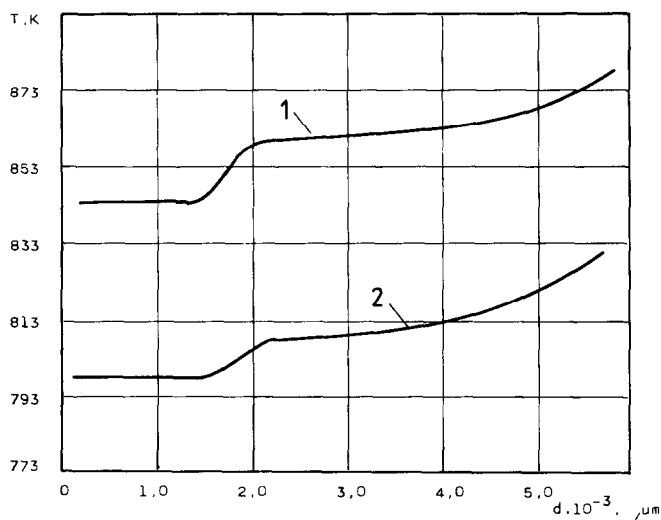


Fig. 1. Dependence of characteristic reaction temperatures on particle size. (1) Final temperature of reaction ($\alpha = 0.98$). (2) Temperature of maximal reaction rate/peak temperature.

By changing the particle size of the siderite from 25 to 1300 μm , the $\alpha = \alpha(T)$ functions remain identical. They do not depend on the particle size. This means that the chemical reaction is the rate determining step in this particle size interval. The CO_2 can easily diffuse through the grains and the layer of the solid phase does not influence the rate of the decomposition process and the reaction proceeds in the kinetic region (Fig. 1).

Changing the diameter of the particles from 1300 to 1400 μm , the reaction proceeds in the kinetic region to $\alpha = 0.7\text{--}0.8$ and only above this value does the diffusion of the gas through the solid phase become more and more important. The reaction rate decreases and the $\alpha = \alpha(T)$ functions are shifted towards the higher temperature zone (Fig. 2). The cause of this shift may be the internal diffusion only. This was proved by calculation, too; applying Lykov's formula [10] to the evaluation of measurements with particle size 2000 μm (heating rate 0.05 K s^{-1}) and with particle size 6000 μm (heating rate 0.5 K s^{-1}). In this case the kinetic measurements are correct only up to a 1400 μm particle size, because above this range (from 1400 to 2000 μm) the process goes on the transition region [11], the influence of diffusion increasingly shifts the characteristic temperature of the maximum reaction rate and the final temperature of the reaction toward the higher temperatures zone (Fig. 1). If the diameter of the particles is more than 2000 μm , the reaction proceeds in the diffusional region. In this case the formal kinetic description takes the form of second order. This means that the kinetic equation exists only as a polynomial [12].

It is seen in Fig. 1, that the characteristic temperatures increase slowly in the diffusion region though the layer thickness of the reaction product

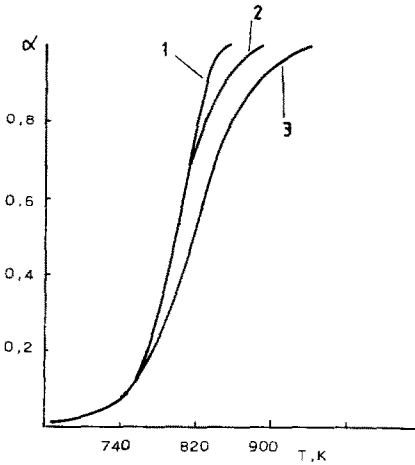


Fig. 2. Kinetic curves of thermal decomposition of siderite. (1) $d = 1300 \mu\text{m}$; (2) $1300 < d < 1400 \mu\text{m}$; (3) $1400 < d < 2000 \mu\text{m}$.

increases considerably. It could be supposed that the main diffusion flow proceeds through the cracks rather than through the porous layer of the ferric oxide. Consequently, the considerable increase in the layer of product leads only to a small decrease of the rate of the process in the diffusion range and results in a small shift of the kinetic curves toward the higher temperatures.

The data of the kinetic region were used only for the calculation of kinetic constants with the following equation

$$-\frac{d\alpha}{dt} = K_0 \exp(-E/RT)(1 - \alpha)^n \quad (2)$$

and with the Allakhverdov and Nirsha method [13].

The reaction order was calculated using eqn. (3)

$$y(1 - \alpha_m) = n \frac{1}{1 - n} \quad (3)$$

where α_m is the fraction reacted at the peak temperature and

$$y = \sum_{i=1}^{\infty} (-1)^{i+1} i! x^{i-1} = 1 - 2!x + 3!x^2 - 4!x^3 + \dots \quad (4)$$

where

$$x = \frac{RT_m}{E}$$

The calculation starts with the first step, when $y = 1$.

Equation 5 served for the calculation of activation energy

$$E_i = n_i R \vartheta \quad (5)$$

where

$$\vartheta = \frac{T_m^2 \left(\frac{d\alpha}{dT_m} \right)}{1 - \alpha_m}$$

Index "m" means that all the values should be taken at the point of

$$\left(\frac{d\alpha}{dT_m} \right) = \text{maximum}$$

As the second step in the calculation, y_2 is calculated with eqn. (4), when $E = E_1$ and n_2 is determined using eqn. (3), where $y = y_2$.

The calculation can be continued until

$$(n_j - n_{j-1}) \geq \epsilon$$

where index "j" marks the number of the steps. In our case the prescribed value of ϵ is 10^{-3} .

The values of the pre-exponential factor K_0 comes from eqns. (6) and (7).

$$K_m = \left(\frac{d\alpha}{dT} \right)_m (1 - \alpha_m)^{-n} \quad (6)$$

$$K_0 = K_m \exp(E/RT_m) \quad (7)$$

The square of deviation was calculated with eqn. (8).

$$s^2 = \sum_{\nu=1}^N \frac{1}{N-1} [\alpha_{c_\nu}(T) - \alpha_{ex_\nu}(T)]^2 \quad (8)$$

where N = the number of points on the experimental curve α_{ex} . In this work $N = 20$. α_{c_ν} = the function calculated with constants n , E , K_0 .

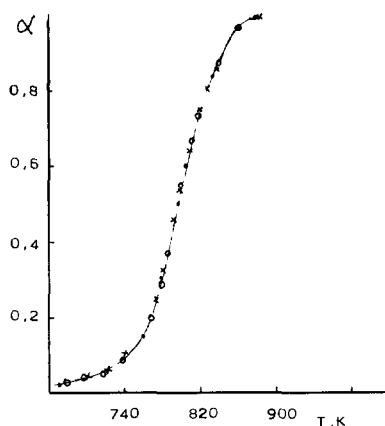


Fig. 3. Kinetic curves of decomposition of siderite mixed with SiO_2 or Al_2O_3 . (·) 10 wt% FeCO_3 + 90 wt% SiO_2 ; (×) 10 wt% FeCO_3 + 90 wt% Al_2O_3 ; (○) 100 wt% FeCO_3 . (Sample mass was the same in each experiment.)

Our measured data can be described with kinetic constants as follows: $n = 2.0$; $E = 238.13 \text{ kJ mol}^{-1}$; $K_0 = 2.96 \cdot 10^{13} \text{ s}^{-1}$; $s^2 = 5.9 \cdot 10^{-4}$.

The kinetic curves of pure siderite samples do not differ from the curves of its mixtures with SiO_2 and Al_2O_3 (Fig. 3). The kinetics of siderite decomposition in the mixtures of FeCO_3 and SiO_2 or FeCO_3 and Al_2O_3 do not depend on the concentration of SiO_2 or Al_2O_3 . Consequently, no influence of SiO_2 or Al_2O_3 on the thermal decomposition of siderite has to be taken into account in the practical calculations relating to the inorganic mineral parts of the solid fuels (combustion or industrial conversion of solid fuels).

CONCLUSIONS

The thermal decomposition process of siderite proceeds in the kinetic region, if the particle size is smaller than $1300 \mu\text{m}$ and it can be characterised with the eqn. (2).

If the particle size of the siderite is between 1300 and $2000 \mu\text{m}$, its decomposition proceeds in the transition region.

Diffusion becomes the rate determining step, if the particle size is greater than $2000 \mu\text{m}$.

The thermal decomposition kinetics of siderite was not influenced by the admixture of SiO_2 and Al_2O_3 .

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