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Activation energy for calcination of lime stone by means of a temperature programmed reaction technique

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Abstract

Calcination of lime stone is considered in order to demonstrate the performance of a temperature programmed reaction technique to determine apparent activation energies for decomposition in the solid state. Influences of sample weight, particle size and sweep gas (He and Ar) are discussed, and comparisons made with thermogravimetric studies in the literature. © 1997 Elsevier Science B.V.

Keywords: Activation energy; Calcination; Temperature programmed reaction technique

1. Introduction

Calcination of limestone, $CaCO_3$, to form CaO(s) and CO_2(g) has been studied extensively in the past. The three key processes, articulated by Satterfield and Feakes [1], controlling the rate of calcination are (i) heat transfer, (ii) mass transfer (i.e. as CO_2 is removed from the carbonate-oxide interface, through the oxide and into the gas phase), and (iii) the actual chemical reaction. Khinast et al. [2] complemented this list by also including CO_2 diffusion in the pore system of the particles.

Apparent activation energies for calcination in the 35–50 kcal/mol range have been reported, while the activation energy for the chemical reaction was determined to be 50 kcal/mol [3,4]. The lower apparent activation energies were understood as resulting from heat and/or mass transfer limitations.

Indeed, both heat and mass transfer limitations have been proven to influence the rate of calcination. Caldwell et al. [5] demonstrated the improved heat conductivity of the selected sweep gas (He, N_2 or Ar) to increase the rate of calcination, while Gallagher and Johnson [6] showed sample weight to be a crucial factor in the determination of the activation energy. In fact, an extrapolated *infinite* apparent E_a in the limit of zero sample weight was produced, which led the authors to doubt the existence of a unique activation energy for calcination. Finally, the effect of particle size on the reaction kinetics has been demonstrated [2], suggesting decreasing sample size leading to suppression of heat and mass transfer effects.

Here, a temperature programmed desorption (TPD) approach will be attempted to determine the apparent activation energy for calcination of natural lime stone. The influence of sample weight, sample size, and sweep gas will be discussed.

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2. Model

The use of TPD technique is a common practice when activation energies for heterogeneous reaction/desorption processes are sought, e.g. see Refs. [7,8]. The method is based on the measurements of temperatures and adsorbate coverages for different heating rates. The activation energy is determined from the slope in an $\ln(T_m^2\theta_m^{n-1}\beta^{-1})$ versus T_m^{-1} plot (n being the reaction order, T_m and θ_m temperatures and coverages at the desorption maxima, and β the heating rate in K/s). An extensive discussion on this technique can be found in a work by Lord and Kittelberger [9], the mathematical treatment of which will be repeated here. The purpose is to explore possible applicability of the TPD approach to calcination in a bulk material.

Let θ be the ratio between amount of reacted, and the initial amounts of $CaCO_3$. Write the reaction rate

$$\frac{d\theta}{dt} = -k\theta^n \tag{1}$$

where n is the reaction order. Insertion of the Arrhenius expression for the reaction constant and the relation between temperature and heating rate $T = T_0 + \beta t$, produces

$$\frac{d\theta}{dT} = -\theta^n \frac{A}{\beta} e^{-E_a/RT} \tag{2}$$

Assuming the forward reaction to dominate in the calcination process, then the partial pressure of CO_2 becomes proportional to the reaction rate. These are the crucial assumptions of the present effort. The maximum reaction condition is given by

$$\left[\frac{dP_{CO_2}}{dT}\right]_m = \left[\frac{d^2\theta}{d^2T}\right]_m = 0 \tag{3}$$

which is equivalent to

$$\frac{n}{\theta_m}\left(\frac{d\theta}{dT}\right)_m = -\frac{E_a}{RT_m^2} \tag{4}$$

and by virtue of Eq. (2) we obtain the expression

$$n\theta_m^{n-1}\frac{A}{\beta} e^{-E_a/RT_m} = \frac{E_a}{RT_m^2} \tag{5}$$

Elementary manipulations of Eq. (5) finally produce the sought result

$$\ln(T_m^2\theta_m^{n-1}/\beta) = \frac{E_a}{RT_m} + \ln\left(\frac{E_a}{nAR}\right) \tag{6}$$

3. Experimental

Köping lime stone is calcined in a quartz reactor of 22 mm inner diameter and a length of 500 mm. The reactor, which has an asymmetric construction to avoid heating up of the metal fitting and the vacuum tight Viton O-ring, is placed in a furnace. The amount of lime stone in the bed material is varied between 0.5 mg and 1 g. It is mixed with quartz sand to control the residence time. The bed material is placed on a sintered quartz filter placed 80 mm below the middle of the reactor. The temperature is measured with a K-type thermocouple 4 mm below the quartz filter. A Eurotherm thermoregulator steered by a second K-type thermocouple, in contact with the heating coil, controls the furnace to produce the heating ramps. The heating rates (β) used are 3.75, 7.5, 22.5 and 30 K/min. A mass spectrometer (Balzers type QMG 421-3), set on mass 44, is connected to the reactor outlet.

The calcination behaviours of two different particle size distributions have been considered, and these are given in Table 1. Influence of heat transport on the apparent activation energy was tested for the coarse particle size, and for two different sweep gases (He and Ar). The gases were delivered by AGA. Gas flows between 200 and 265 ml/min were used.

Table 1
Particle size distribution of the fine and coarse natural limestone

	Micrometer (μm)	Köping limestone Fine	Coarse
	500–1000	0	11.9
	250–500	0	18.6
Particle size (%)	125–250	0	29.5
	87–125	2.8	35.3
	62–87	2.8	3.8
	<62	94.4	0.9

4. Results and discussion

It is clear from Eq. (6) that TPD is not suitable for determining the order of reaction. This is accentuated if the left-hand side of Eq. (6) is written

$$2\ln T_m + (n-1)\ln\theta_m - \ln\beta \qquad (7)$$

and if it is, furthermore, noticed that $0.5 < \theta_m < 0.65$ is fairly independent of heating rates and temperatures in the ranges $3.75 \leq \beta \leq 30$ K/min, and $975 < T_m < 1075$ K. This observation is validated in Table 2. Two sample weights, 2.71 mg and 0.1000 g were considered, and the obtained activation energies for five hypothetical reaction orders in the range $0.1 \leq n \leq 2$ are listed. The observed insensitivity justifies the use of a convenient value, $n = 1$ in the following.

While TPD can be discarded as a method to determine reaction orders, in agreement with observations in Ref. [9], it is gratifying to find the activation energies of Table 2 in narrow ranges.

Sample weights are observed to affect the activation energies, i.e. 40 and 50 kcal/mol for the 0.1000 g and 2.71 mg samples, respectively. To extract the weight dependence of E_a, the apparent activation energies were determined for sample weights (W) in the range $0.5\text{ mg} \leq W \leq 1.0$ g with both He and Ar sweep gases and for two different particle size distributions (see Table 1). Fig. 1 displays apparent activation energies versus log(W). It is found that for sample weights less than 7 mg, the activation energies become independent of sweep gases and particle size. Extrapolation to zero sample weight produces $E_a = 49$ kcal/mol. This value, for which heat and mass transfer problems have apparently been removed, should be a good estimate of the activation energy for calcination of $CaCO_3$(s). In fact, other estimates in the literature give around 50 kcal/mol [3,4].

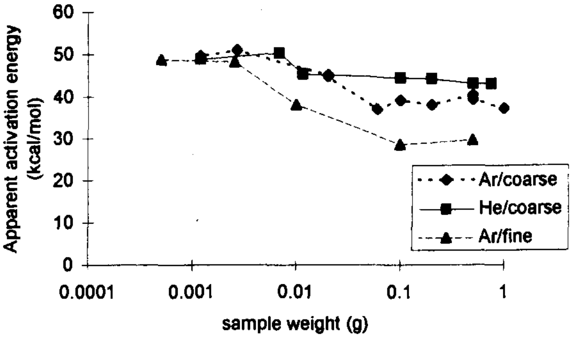

Fig. 1. The apparent activation energy as a function of sample weight for different sweep gases and particle sizes.

Indicative of heat-transfer effects are the differences between the activation energies obtained with helium and argon as sweeping gases, observed for sample weights greater than 7 mg. The main expected origin of this effect is the endothermic character of the calcination reaction, making the actual temperature

Table 2
Influence of the reaction order on the apparent activation energy for two different sample weights: (a) 0.1000 g, (b) 2.71 mg

β	T_m	$1/T_m \times 10^{-3}$	$\ln(T_m^2\theta_m^{n-1}/\beta)$				
(K/s)	(K)	(1/K)	$n = 0.1$	$n = 0.5$	$n = 1$	$n = 1.5$	$n = 2$
(a)							
0.0625	976	1.025	16.96	16.77	16.54	16.31	16.07
0.125	1000	1.000	16.29	16.12	15.89	15.67	15.45
0.375	1053	0.950	15.27	15.10	14.90	14.70	14.49
0.5	1073	0.935	15.00	14.84	14.64	14.45	14.25
corr			99.77696	99.7694	99.7692	99.7689	99.7686
E_a (kcal/mol)			42.79	42.17	41.41	40.64	39.87
(b)							
0.0625	914	1.094	16.84	16.65	16.41	16.17	15.92
0.125	934	1.071	16.17	15.99	15.76	15.53	15.30
0.375	972	1.029	15.18	14.98	14.74	14.49	14.24
0.5	982	1.018	14.98	14.75	14.47	14.42	13.91
corr			99.8537	99.9177	99.9641	99.9692	99.9588
E_a (kcal/mol)			48.66	49.39	50.30	51.22	52.13

lower at the interface between the $CaCO_3$ and CaO phases, than that measured in the gas phase. The greater apparent activation energies for helium than argon, bringing E_a(He) closer to the limiting value, is in line with a partially heat transfer controlled reaction for larger sample weights.

Decrease in particle size result in decreased apparent activation energies in the large and medium sample weight regimes. This could be understood to contradict the observation of Khinast et al. [2]. These authors interpret results to imply decreased mass and heat-transfer effects with reduced particle sizes. However, the opposite effect observed in Fig. 1 could be taken to imply inter particle diffusion effects to influence the results for the higher sample weights.

In conclusion, a fast and accurate tool is proposed to determine activation energies for decomposition of solids. The suggested approach attempts to make a three-dimensional analogy to a desorption process, which would make the temperature programmed reaction technique applicable. Activation energies for calcination, ascribed to the reaction step

$$CaCO_3(s) \Rightarrow CaO(s) + CO_2(g) \qquad (8)$$

have been determined, and found in agreement with the literature values. Removal of heat and mass transfer limitation effects produce an activation energy of 49 kcal/mol.

Acknowledgements

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