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INVESTIGATION OF DEHYDROXYLATION OF GIBBSITE INTO BOEHMITE BY DSC ANALYSIS

J. Perić, R. Krstulović and M. Vučak

Faculty of Technology, University of Split, Teslina 10/V, 21000 Split, Croatia

Abstract

The dehydroxylation of gibbsite into boehmite was investigated by means of DSC analysis under non-isothermal conditions in the temperature range 453–673 K at heating rates from 2.5 to 20.0 K $\min^{-1}$. Mathematical analysis of the experimental DSC curves revealed the mechanism and kinetics of the gibbsite dehydroxylation process. The kinetic curves $\alpha=f(t)$ and $\alpha=f(T)$ are sigmoidal in shape; their inflection points and the v_m point of the curves $v=f(t)$ and $v=f(T)$ are interrelated and are defined by the concept of a stationary point. The activation energy for the first stage of gibbsite dehydroxylation in the temperature range 453–673 K is 132.92± 8.33–142.26±8.33 kJ mol^{-1}.

Keywords: boehmite, DSC, gibbsite

Introduction

A large number of methods have been suggested for the determination of kinetic parameters from dynamic thermogravimetric measurements and differential thermal analysis [1–5]. In previous work [5], the process of dehydroxylation of aluminium minerals was examined by means of non-isothermal thermogravimetric analysis. The present paper describes the treatment of experimental data obtained by means of differential scanning calorimetry (DSC) under non-isothermal conditions in order to establish the kinetic parameters of the dehydroxylation of $\gamma\text{-Al(OH)}_3$.

The reaction kinetics was examined only for the first stage of gibbsite dehydroxylation, i.e. the dehydroxylation of gibbsite to secondary boehmite in the temperature range 453–673 K. The choice of upper temperature limit was influenced by the characteristics of the apparatus.

Experimental

Sample

This was a gibbsite $\gamma\text{-Al(OH)}_3$ sample produced industrially in 1983 according to the Bayer process.

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X-ray diffractometry

A Philips X-ray diffractometer with CuK$_\alpha$ radiation was used to check the purity of the sample (Fig. 1). The gibbsite was observed to have been partially converted to boehmite by ageing under the normal pressure and temperature conditions.

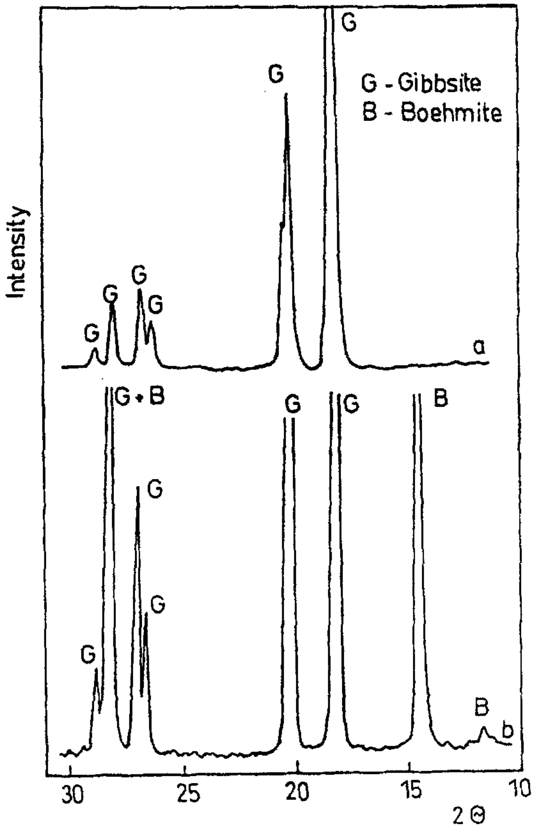

Fig. 1 Comparison of X-ray diffraction patterns of gibbsite sample. Diffractogram: a) recorded in 1983; b) recorded in 1992

DSC analysis

The DSC analysis was carried out under dynamic non-isothermal conditions with a flow of extra-pure nitrogen in a Perkin-Elmer DSC-4 differential scanning calorimeter [6]. The operating conditions were: temperature range: 453–673 K, heating rate: 2.5, 5.0, 10.0, 15.0 or 20.0 K min^{-1}, cooling rate: 320 K min^{-1}, flow rate of extra-pure nitrogen: 30 ml min^{-1}.

The dehydroxylation of gibbsite into boehmite is an endothermic process:

$$\mathrm{Al(OH)_3} \xrightarrow{\text{heat}} \mathrm{AlOOH + H_2O}$$

which can be seen from the DSC curves (Fig. 2): there is an endothermic peak in the temperature range 483–637 K.

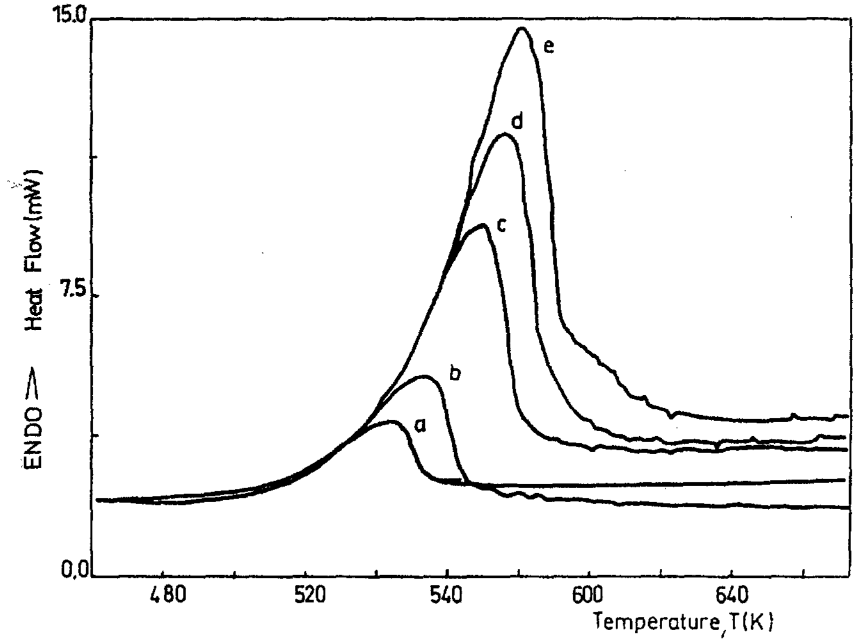

Fig. 2 DSC curves. Heating rates: curve a) 2.5 K min^{-1}; curve b) 5.0 K min^{-1}; curve c) 10.0 K min^{-1}; curve d) 15.0 K min^{-1}; curve e) 20.0 K min^{-1}

Results and discussion

The DSC curves were analysed mathematically in order to determine the mechanism and kinetics of the dehydroxylation of gibbsite by means of methods involving a number of experimental kinetic curves and the stationary point theory [7, 8]. The dehydroxylation rate v is expressed as a differential change:

$$v = \frac{d\alpha}{dt}$$

where the dehydroxylation degree α is determined from the ratio of the change of enthalpy $\Delta H_{\text{partial}}$ in time t and the total enthalpy change ΔH_{total} [6]:

$$\alpha = \frac{\Delta H_{\text{partial}}}{\Delta H_{\text{total}}}$$

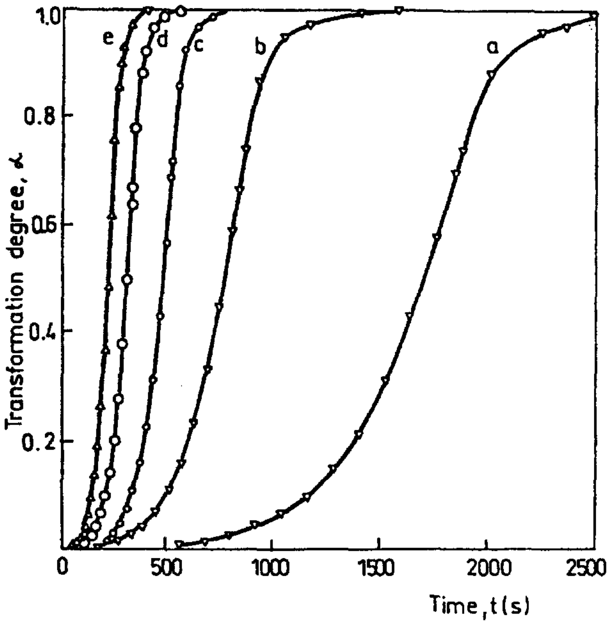

Fig. 3 Plots of degree of transformation *vs.* time. Curves as in Fig. 2

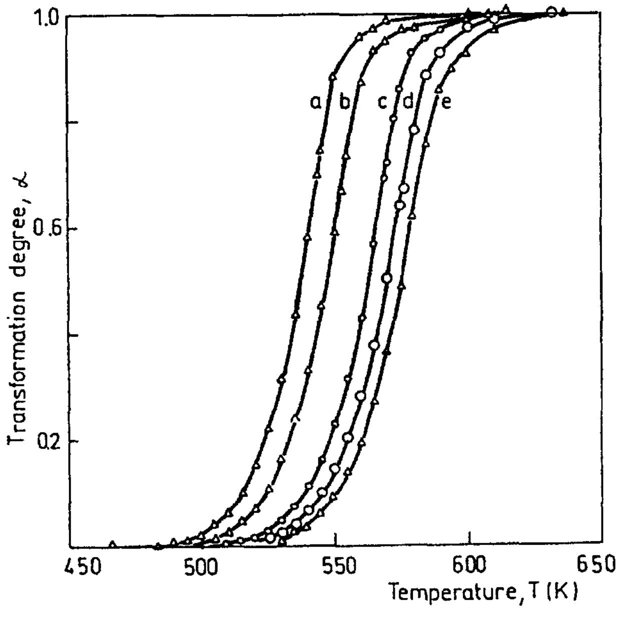

Fig. 4 Plots of degree of transformation *vs.* temperature. Curves as in Fig. 2

Figures 3 and 4 show graphically the calculated dehydroxylation degree as functions of temperature and time.

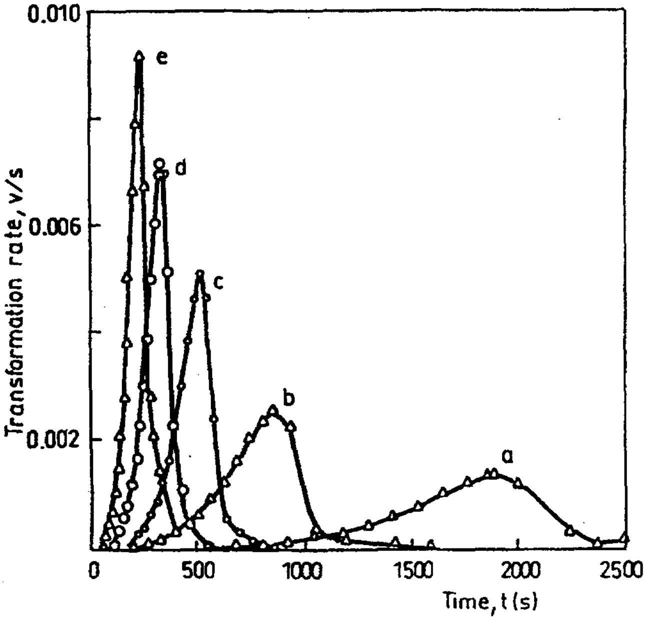

Fig. 5 Plots of transformation rate *vs.* time. Curves as in Fig. 2

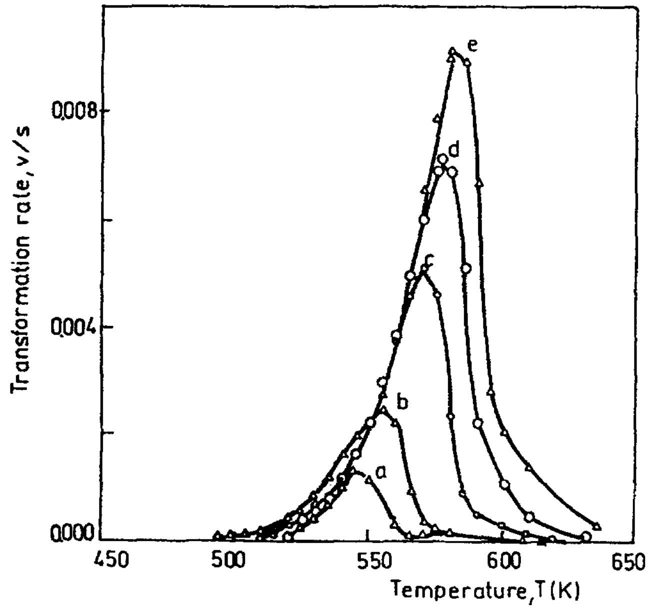

Fig. 6 Plots of transformation rate *vs.* temperature. Curves as in Fig. 2

The curves $\alpha=f(t)$ and $\alpha=f(T)$ are sigmoidal in shape, and $\alpha=0$ at zero time as concerns the beginning of change, which would indicate that this process is not characterized by an induction period.

The curves $v=f(t)$ and $v=f(T)$ (Figs 5 and 6) show that, as the heating rate decreases, the maximum rate v_m shifts towards higher times.

The activation energy was calculated by means of several methods of non-isothermal kinetics derived from the stationary point theory:

– the Antić-Colović method:

$$\frac{d\ln v_m}{d(1/T_m)} = -\frac{E}{R} \tag{1}$$

– the Kissinger method:

$$\frac{d\ln(q/T_m^2)}{d(1/T_m)} = -\frac{E}{R} \tag{2}$$

– the modified Kissinger method:

$$\frac{d\ln(q/T_m)}{d(1/T_m)} = -\frac{E}{R} \tag{3}$$

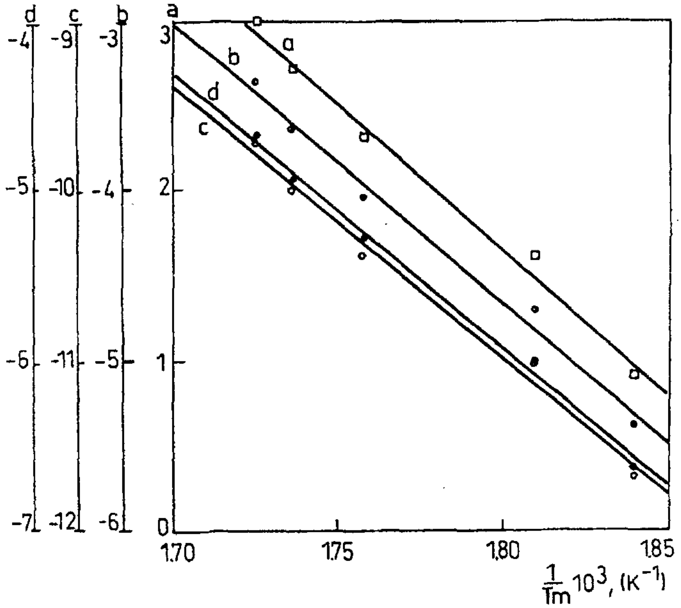

Fig. 7 Plots of: a, ln*q*: b, ln(q/T_m); c, ln(q/T_m^2); d, ln v_m *vs.* $1/T_m$. Correlation coefficients of the linear regression for plots a, b, c and d are 0.995, 0.995, 0.994 and 0.997, respectively

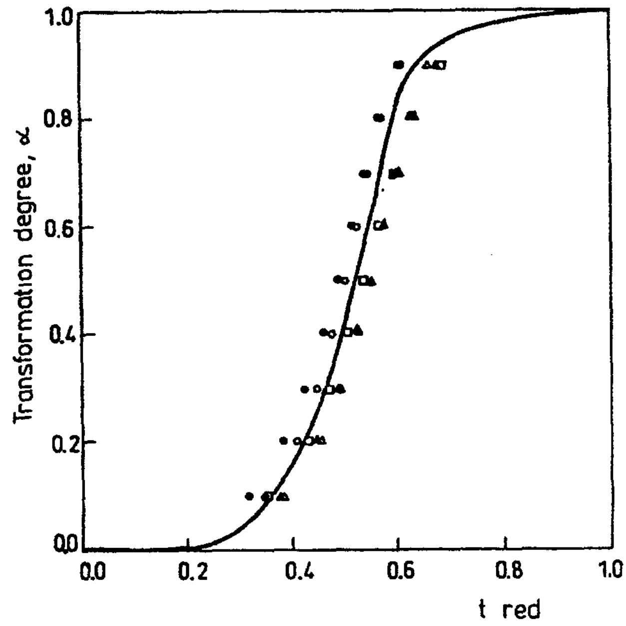

Fig. 8 Affine transformed curves. Heating rates: o, 2.5 K min^{-1}; •, 5.0 K min^{-1}; Δ, 10.0 K min^{-1}, ▲, 15.0 K min^{-1}, □, 20 K min^{-1}. $t_{red}=t_i/t_f$ where: t_i – the current time, t_f – the final time of the reaction development under non-isothermal conditions for the corresponding heating rate

– the Ozawa method:

$$\frac{\mathrm{d}\ln q}{\mathrm{d}(1/T_m)}=-\frac{E}{R} \tag{4}$$

where: E=activation energy, J mol^{-1}, R=gas constant, J mol^{-1} K^{-1}, q=linear heating rate, K s^{-1}, v_m=maximum transformation rate, and T_m and t_m=temperature and time at which v_m is achieved.

The slopes of the straight lines drawn by a least squares method determine the values of the activation energy (Fig. 7).

As the kinetics curves $\alpha=f(t)$ and $\alpha=f(T)$ are sigmoidal in shape, and as the curves $\alpha=f(t_{red})$ overlap for the different heating rates (Fig. 8), the modified Kazeev-Erofeev equation (5) can be used to determine the pre-exponential factor k_o of the Arrhenius equation and the kinetic parameter n by the least squares method [7] (Fig. 9):

$$\frac{E}{RT_m}=\ln k_o-\ln[-\ln(1-\alpha_m)]+n\ln t_m \tag{5}$$

where α_m is the transformation degree at the stationary point, i.e. at the moment the maximum reaction rate is attained.

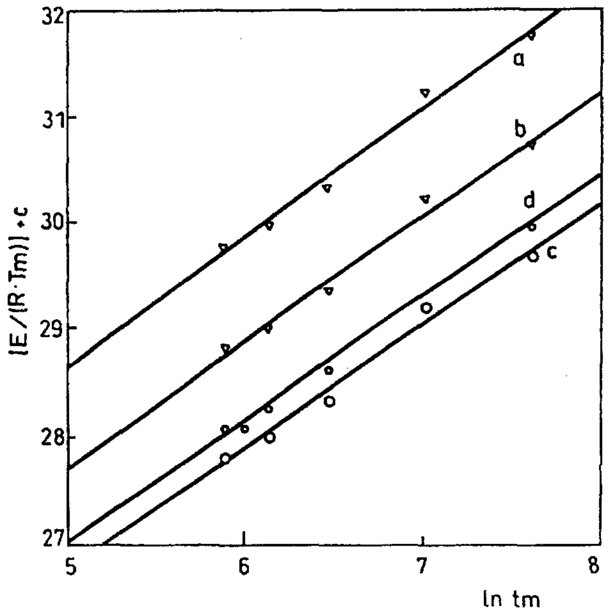

Fig. 9 Plots of $E/(RT_m)+k$ vs. $\ln t_m$. Symbols as in Fig. 7. Correlation coefficients of the linear regression for plots a, b, c and d which are equal and amounts to 0.992. Dimension of E=kJ mol^{-1}

Table 1 Values of kinetic parameters in the dehydroxylation process of gibbsite into boehmite

Method applied	E_a/ kJ mol^{-1}	n	$k_0 \cdot 10^{-9}$/ s^{-1}
Ozawa	142.26±8.33	1.21±0.09	6.4
Mod. Kissinger	137.59±8.33	1.17±0.08	3.1
Kissinger	132.92±8.33	1.13±0.08	1.5
Antić-Colović	134.18±5.79	1.14±0.08	1.8

Table 1 compares the calculated values of the activation energy and the kinetic parameters of the dehydroxylation of gibbsite into boehmite. The calculated activation energy of gibbsite dehydroxylation into boehmite displays a good correspondence with the value of E_a=121.1 kJ mol^{-1} obtained by means of non-isothermal thermogravimetrical analysis [5]. Recently, Candela and Perlmutter [9] carefully studied the kinetics of boehmite formation by the isothermal decomposition of gibbsite. Their E_a value (142±10 kJ mol^{-1}) agrees perfectly with our results.

Conclusion

DSC should become a widely used technique for kinetic analysis.

No significant differences were found between the activation energies calculated from the same DSC traces by different mathematical approaches. In the temperature range 453–673 K, for the first stage of gibbsite dehydroxylation the calculated activation energy was 132.92±8.33–142.26±8.33 kJ mol^{-1}. This is comparable with the 121.4 kJ mol^{-1} obtained by means of dynamic thermogravimetry.

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