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Mechanism and Kinetic Parameters of the Thermal Decomposition of Gibbsite $Al(OH)_3$ by Thermogravimetric Analysis

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In this study, the mechanism and the kinetic parameters of the thermal decomposition of gibbsite $Al(OH)_3$ were studied by differential thermogravimetry technique under non-isothermal conditions, between room temperature and 1200 K at heating rates of 5, 10, 15 and 20 °C min^{-1}. The obtained differential thermogravimetry curves show clearly three distinct peaks. The first peak is due to the partial dehydroxylation of gibbsite. Among the 32 types of differential equations of non-isothermal kinetics, we have found that the most suitable mechanism is ($A_{3/2}$: $g(x) = [-\ln(1-x)]^{2/3}$) also called Avrami-Erofeev equation of order 2/3. The values of the activation energy E_A and of the pre-exponential factor K are 157 kJ mol^{-1} and 7.58×10^{15} s^{-1}, respectively. The second peak corresponds to the decomposition of gibbsite to boehmite. Decomposition is controlled by the rate of second-order reaction (F_2: $g(x) = (1-x)^{-1} - 1$), under the applied conditions. The activation energy E_A and pre-exponential factor K correspond to 243 kJ mol^{-1} and 3.73×10^{22} s^{-1}, respectively. The third peak is due to transformation of boehmite to alumina. However the mechanism for such transformation is better described by the 3/2 rate order reaction ($F_{3/2}$: $g(x) = (1-x)^{-1/2} - 1$). In addition, the values of E_A and K were determined to be around 296 kJ mol^{-1} and 1.82×10^{19} s^{-1}, respectively. The results of differential thermogravimetry were supplemented by the differential thermal analysis. X-ray powder diffraction analysis was carried out for samples of gibbsite treated at different temperatures between 200 and 1200 °C in 200 °C steps.

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1. Introduction

The thermal decomposition of gibbsite, also named aluminium trihydrate, $Al_2O_3{\cdot}3H_2O$ has many industrial uses, such as, for example, the preparation of technical ceramic materials (functional and structural applications) [1]. It is well known that gibbsite undergoes a series of reactions and finally forms alumina γ-Al_2O_3. It had been established that gibbsite transforms to partial alumina, almost amorphous phase, than to boehmite and finally to χ-Al_2O_3 [2]. The main causes for differences in this series of reactions are the variations in size of particles, the surface area and the synthetic of gibbsite [3]. The techniques of thermal analysis are remaining to be the essential tools among the huge variety of methods which are used for analysis the kinetics of gibbsite dehydroxylation. The thermogravimetry (TG) and X-ray diffraction are other tools, used to evaluate the phase transitions of gibbsite [4].

Under non-isothermal conditions and by applying the 32 types of non-isothermal kinetic differential equations, for each stage the overall activation energy E_A and pre-exponential factor K were evaluated from a series of thermogravimetric experiments from room temperature to 1200 K at various heating rates.

The aim of this paper is to study the mechanism and the kinetic parameters (activation energy E_A and pre-exponential factor K) of the thermal decomposition of gibbsite.

2. Materials and methods

The material used in this work is gibbsite, called also aluminum hydroxide $Al(OH)_3$. It is a commercial powder which has a lot of uses in ceramic applications, such as catalysts, catalyst supports, absorbents and as refractory castables in refractories industries. Its typical composition is 65% Al_2O_3, 0.15% Na, 0.005% Fe and 0.002% SO_4. TG analysis of gibbsite powder was conducted at variable constant heating rates of 5, 10, 15 and 20 °C min^{-1}, from room temperature to 1200 K, using Setaram LA-Bevo TG-DSC 1600 °C equipment, operating under argon atmosphere. The phases formed of aluminum hydroxide samples at different temperatures were identified by using diffractometer system XPERT-PRO with scanning step size of 0.0167.

Initially, the kinetics and mechanism of phase transformation of gibbsite have been studied using isothermal and non-isothermal methods. Each technique has given important information about the thermal activities of gibbsite.

In order to obtain the value of the activation energy E_A many methods have been proposed. in this study we will use just three of them, which are Ozawa-Flynn-Wall (OFW), Boswell and Kissinger-Akahira-Sunose (KAS) methods described by the following three formulas:

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$$\ln[\phi] = -1.0518\frac{E_A}{RT_P} + C, \tag{1}$$

$$\ln\left[\frac{\phi}{T_P}\right] = -\frac{E_A}{RT_P} + C_1, \tag{2}$$

$$\ln\left[\frac{\phi}{T_P^2}\right] = \ln\left[\frac{RA}{E_A}\right] - \frac{E_A}{RT_P}, \tag{3}$$

where the frequency factors A and C are constant, φ is the heating rate in the differential thermogravimetry (DTG) analysis, E_A is the activation energy and T_P is the absolute temperature in DTG curves. The plot of $y = \ln[\varphi]$, $\ln[\varphi/T_P]$ and $\ln[\varphi/T_P^2]$ vs. $1/T_P$ should be linear, so the activation energy E_A is calculated using the obtained slope.

The calculation of kinetic parameters of solid-state reactions in the dehydroxylation process of gibbsite was carried out using thermal analysis techniques. Usually, isothermal and non-isothermal methods are used in the study of reaction parameters of homogeneous and heterogeneous reactions. Non-isothermal kinetic parameters are more reliable in heterogeneous reactions than the isothermal ones. In non-isothermal analysis of thermal data, with the provided information, it is possible to propose a single mechanism for each stage of the reaction.

In this paper, we analyzed the TG data by applying the 32 mechanisms of the basic solid-state kinetic equations as shown in Appendix [5]. In this case of dehydration reactions series, three probable mechanism were determined ($A_{3/2}$, $F_{3/2}$ and F_2). The least squares fit method has been employed for determining the linearity of the equation using corresponding correlation coefficients r and R^2, respectively. The mechanism of the decomposition was described by the function $g(x)$, where x is the degree of conversion. The following relationships are functions of three parameters, (i) the pre-exponential factor in the Arrhenius equation K, (ii) the activation energy E_A and (iii) the function of reaction mechanism $g(x)$. A number of models have been developed for study the mechanism of solid state decomposition processes [5–9]. Method of Redfern and Coats was found to be the most convenient [10, 11]. Thus the equations for determination of the E_A and K are as follows:

$$\ln\left[\frac{g(x)}{T^2}\right] = \ln\left[\frac{KR}{\phi E}\left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT}, \tag{4}$$

$$\ln\left[\frac{g(x)}{T^2}\right] = \ln\left[\frac{KR}{\phi E}\right] - \frac{E}{RT}. \tag{5}$$

Here $T = T_P$ is the absolute temperature at the specified fraction, K is the gas constant and φ is the heating rate. Plot of $\ln[g(x)/T^2]$ vs. $1/T$ gives a straight line. Thus values of E_A and K can be calculated [11].

3. Results and discussion

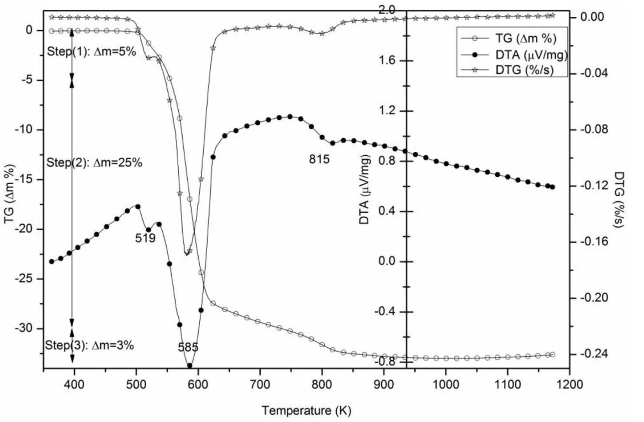

Fig. 1. DTA and TG/DTG curves of gibbsite powder heated at 20 °C min^{-1}.

Figure 1 shows the typical TG/DTG and DTA curves of gibbsite powder heated from room temperature to 1200 K at a heating rate of 20 °C min^{-1}. In the DTG curve shown in Fig. 1 we find the first and the smallest endothermic peak at 519 K, which is due to the partial dehydroxylation of gibbsite ($Al(OH)_3$; File Nr. 00029-0041) and formation of boehmite (AlOOH; File Nr. 00-021-1307). Endothermic peak at 585 K corresponds to two processes: (i) transformation of gibbsite to phase χ-Al_2O_3 and (ii) additional conversion of gibbsite to boehmite. The first process is in accordance with the results obtained in [12]. Another endothermic peak at 815 K is due to decomposition of boehmite and formation of alumina γ-Al_2O_3 [12]. The obtained TG curves show clearly three steps of weight loss. The weight loss in the first step (about 5 wt.%) is due to the partial transformation of gibbsite to boehmite; the second step (about 25 wt.%) corresponds to decomposition of gibbsite to boehmite, otherwise to χ-Al_2O_3. The last step of around 3 wt.% relates to the formation of γ-Al_2O_3. Further observations show that the total weight loss is equal to 33 wt.%. All these transformations of gibbsite and the chemical composition are confirmed by the XRD analysis, as shown in Fig. 2 [12].

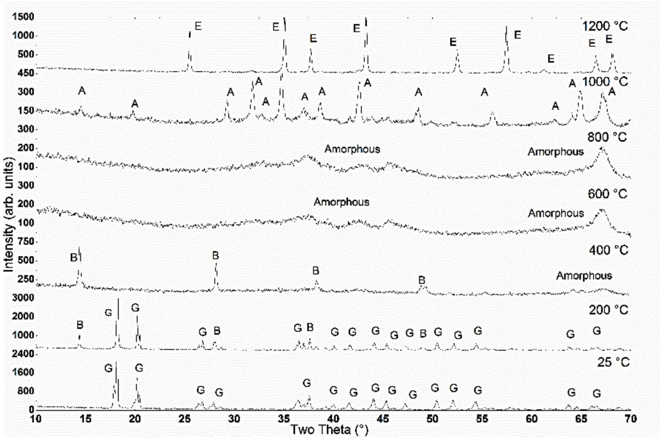

Fig. 2. X-ray patterns of gibbsite powder treated at different temperatures for 2 h, G: Gibbsite, B: Boehomite, A: χ-Al_2O_3 and E: γ-Al_2O_3.

TABLE I

The values of E_A, r and R^2 obtained using OFW, Boswell and KAS methods for reactions (A), (B) and (C).

Method	Reaction (A)			Reaction (B)			Reaction (C)		
	E_A [kJ/mol]	Pears. r	R^2	E_A [kJ/mol]	Pears. r	R^2	E_A [kJ/mol]	Pear. r	R^2
OFW	155.4	-0.9999	0.99996	248.8	-0.9995	0.99873	277	-0.9988	0.99666
Boswell	159.2	-0.9999	0.99996	256.9	-0.9995	0.99868	285	-0.9988	0.99652
KAS	154.9	-0.9999	0.99995	252.1	-0.9995	0.99864	278.5	-0.9987	0.99637

TABLE II

Kinetic parameters of the thermal decomposition of gibbsite.

Mech.	g(x)	Reaction rate deter. process	Activation energy E_A [kJ/mol]	Pre-exponential factor K [s^{-1}]	Correlation coefficient r	R^2
$A_{3/2}$	$g(x) = [-\ln(1-x)]^{2/3}$	Avrami-Erofeev eq. order 2/3	157.529	7.58×10^{15}	-0.99898	0.99792
F_2	$g(x) = (1-x)^{-1} - 1$	second-order	243.210	3.73×10^{22}	-0.99947	0.99858
$F_{3/2}$	$g(x) = (1-x)^{-1/2} - 1$	One and a half order	296.941	1.827×10^{19}	-0.99975	0.999755

The values of E_A, r and R^2 shown in Table I for the reaction (A), as an example, were determined from the slope of the straight line in Fig. 3. Noted that at 519 K reaction (A) corresponds to partial dehydroxylation of gibbsite and formation of boehmite, the activation energy E_A varies from 154.9 to 159.2 kJ mol^{-1}. We can say that these reactions are very quick. The second reaction (B) corresponds to the transformation of gibbsite to phase χ-Al_2O_3 at 580 K. Here the energy of activation is in range of 248.8–256.9 kJ mol^{-1}. The last reaction at 815 K due to the transformation of boehmite to alumina γ-Al_2O_3 is designated as reaction (C). Its activation energy E_A varied from 277 to 285 kJ mol^{-1}.

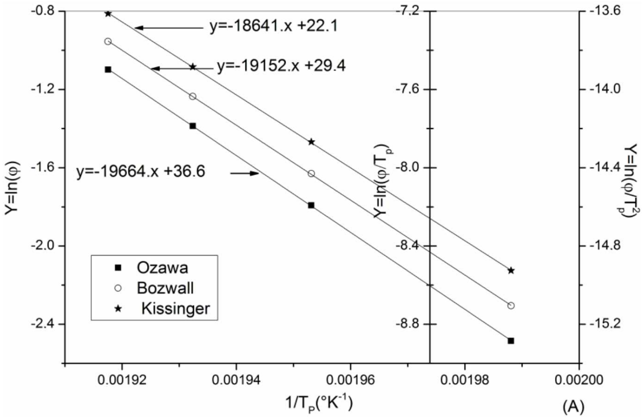

Fig. 3. Plot of $y = \ln[\varphi]$, $\ln[\varphi/T_P]$ and $\ln[\varphi/T_P^2]$ according to OFW, Boswell and KAS respectively.

The mechanisms obtained are depended on the values of $g(x)$. The most likely reaction mechanism was evaluated from the thermal analysis data, the $\ln[g(x)/T^2]$ vs $1/T$ functions, for each mechanism. An example of such analysis for $A_{3/2}$ at each degree of heating rate is shown in Fig. 4. The kinetic parameters of thermal decomposition of gibbsite for each mechanism are shown in Table II [11].

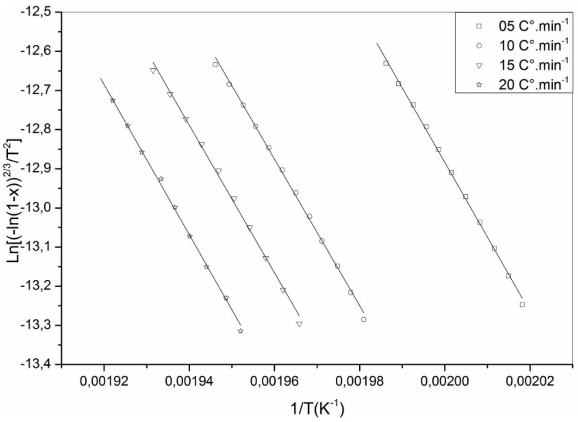

Fig. 4. The plot of $\ln[g(x)/T^2]$ versus $1/T$ for each heating rate for $A_{3/2}$.

4. Conclusions

The kinetics decomposition of gibbsite was studied using TG/ DTG techniques. The transformations of gibbsite are distributed in three stages:

- Gibbsite undergoes a partial dehydroxylation and it is transformed to boehmite (AlOOH) at 519 K.
- An additional conversion of gibbsite and transformation to amorphous phase χ-Al_2O_3 at 585 K.
- The last stage at 815 K is due to decomposition of boehmite and formation of alumina γ-Al_2O_3.

The kinetic parameters, such as activation energy and the pre-exponential factor, of the three reactions were calculated using two different techniques of isothermal and non-isothermal methods by applying 32 known mechanisms.

Appendix

Example of determination of solid-state kinetic equations using TG data for each heating rate. Table lists the values of R^2 obtained over interval $0.25 \leq x \leq 0.75$. The results in bold are marking the most probable kinetic mechanism [13].

Definition of the kinetic function			Heating rate φ [°C min^{-1}]			
Sign	Function name	Formula of $g(x)$	05	10	15	20
F_2	Second order	$\boldsymbol{(1-x)^{-1}-1}$	0.99692	0.99814	0.99943	0.99986
$P_{1/4}$	Maple power law	$x^{1/4}$	0.98521	0.97663	0.96913	0.95699
$A_{3/2}$	Avrami-Erofeev eq.	$[-\ln(1-x)]^{2/3}$	0.99782	0.99815	0.99751	0.99499
R_1	Power law	X	0.99138	0.98669	0.98256	0.97649
D_1	Parabolic law	x^2	0.99203	0.98773	0.98394	0.97843
G_1	Other kinetic	$1-(1-x)^2$	0.96537	0.95384	0.94769	0.93685

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