

KINETICS OF THERMAL DECOMPOSITION OF SYNTHETIC GIBBSITE ①

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ABSTRACT

The thermal decomposition of synthetic gibbsite has been investigated by means of DSC and X-ray diffraction methods. The mechanism of thermal decomposition and kinetic parameters were determined at temperatures ranging from room temperature to 400 °C.

Key words: synthetic gibbsite decomposition kinetics DSC

1 INTRODUCTION

The calcining of aluminum hydroxide, i. e. synthetic gibbsite, is the final technological stage of industrial production of aluminum oxide. Many properties of alumina, especially specific surface area, amount of α - Al_2O_3 , angle of release, etc., depend highly on calcining conditions. It is very important for the selection and improvement of the technological conditions of the calcining process of aluminum hydroxide that the kinetics of the thermal decomposition of aluminum hydroxide be investigated clearly. However, since the dehydration of aluminum hydroxide and phase transformation of the produced aluminum oxides are very complicated^[1], there have been few studies on the kinetics of the thermal decomposition of synthetic gibbsite, although many studies on this process of decomposition have been made^[2].

In the present work, DSC and XRD methods were used to determine the mechanism and to measure the kinetic parameters of the thermal decomposition of synthetic gibbsite in the temperature range from room temperature to 400 °C.

2 EXPERIMENTAL

The samples of synthetic gibbsite used in the present experiments were prepared by the method of Chen, which was described in a previous paper^[3]. The samples were confirmed as pure synthetic gibbsite by X-ray diffraction and as a stoichiometric composition of $\text{Al}(\text{OH})_3$ by gravimetric analysis. Sieving of dried synthetic gibbsite powder led to samples with sizes between 325 and 500 mesh.

A DSC-111 type differential scanning calorimeter was used for the kinetic studies of the decomposition of synthetic gibbsite. The temperature and sensitivity of the calorimeter had been carefully calibrated before the experiments. Eight runs with heating rates of 1.0, 1.5, 2.0, 3.0, 4.0, 5.0, 7.0, and 10.0 °C / min respectively, were conducted. The full scale of amplifier was 1 mV. In each run, a sample of 30.0 ± 0.1 mg was placed in a platinum boat, over which a flow of pure argon was passed to remove the water vapor evolved during the decomposition of gibbsite. All the eight runs at various heating rates were conducted under almost the same conditions. Eight runs were carried out one by one

after the DSC equipment was stabilized for more than one hour.

A personal computer (HP-85) was used on line to collect and save the experimental data amounting to about 2 400~4 500 points. The saved data were then processed with another personal computer with larger memory (HP-87) using special software developed by us^[4].

3 RESULTS AND DATA PROCESSING

The heat flow-temperature curves of eight runs of DSC measurement at various heating rates are shown in Fig. 1 and Fig. 2.

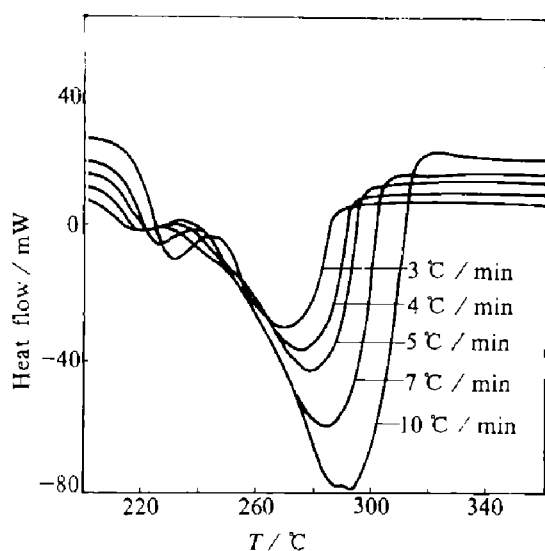


Fig. 1 The heat flow-temperature curves of DSC measurements at heating rates of 3, 4, 5, 6, 7, and 10 °C / min

From Figs. 1, 2, it can be found that two endothermic peaks appear on each curve of all the eight runs, which means that there are two reactions or phase transformations during the thermal decomposition of synthetic gibbsite when the temperature is lower than 400 °C. Therefore Kissinger's method^[5] is not suitable for the data treatment of our experimental results.

It also can be seen that there is a small platform at the beginning of each peak in the runs which were conducted at a rate lower than 2 °C / min. It is reasonable to consider these small platforms as the induction period of reactions.

With the increase of heating rate, the platform of the induction period disappears. Ozawa's method^[6] was used with the data coming from the experiments at heating rates larger than 2 °C / min to determine the activation energies of the decomposition of gibbsite. The general equation of Ozawa's method could be expressed as

$$\lg \beta = [\lg(AE_a / R) - \lg g(\alpha) - 2.315] - 0.4567E_a / RT \quad (1)$$

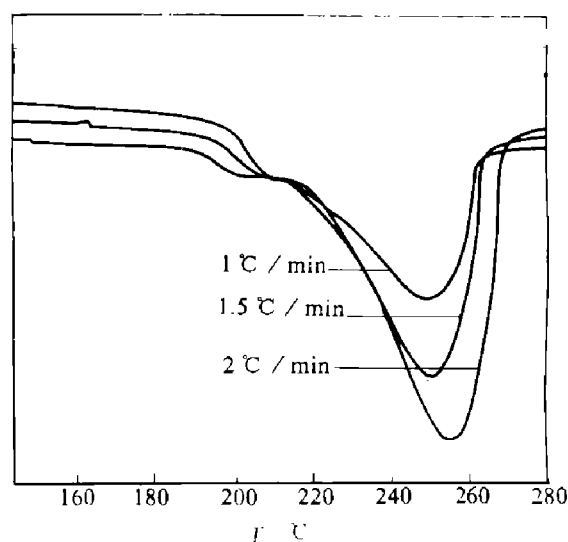


Fig. 2 The heat flow-temperature curves of DSC measurements at heating rates of 1, 1.5 and 2 °C / min.

For the same value of α , the values in the square brackets are constants. Therefore, the activation energies could be obtained from the slopes of the plots of $\lg \beta - T^{-1}$ at same α (see Fig. 3).

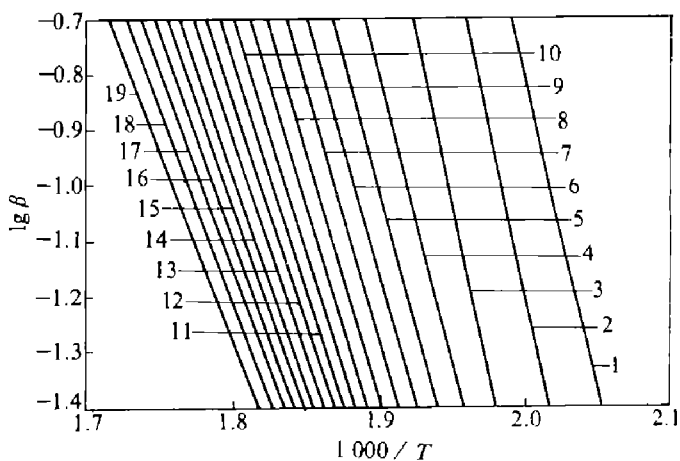


Fig. 3 $\lg \beta - T^{-1}$ plots for the determination of E_a using Ozawa's method

The linear relevant coefficients (R) are very closed to unit. The obtained values of E_a are shown in Table 1.

Table 1 The values of the activation energy of the decomposition of synthetic gibbsite (Ozawa's Method)

α	$E_a / \text{kJ} \cdot \text{mol}^{-1}$	R
0.05	196.648	-0.998 3
0.10	221.497	-0.997 7
0.15	217.555	-0.992 7
0.20	183.891	-0.996 1
0.25	173.234	-0.997 4
0.30	166.883	-0.997 8
0.35	162.398	-0.998 0
0.40	157.666	-0.998 1
0.45	154.624	-0.998 7
0.50	149.687	-0.998 8
0.55	146.720	-0.999 0
0.60	143.628	-0.999 1
0.65	141.616	-0.999 1
0.70	138.172	-0.999 2
0.75	135.896	-0.999 2
0.80	133.468	-0.999 2
0.85	131.014	-0.999 1
0.90	128.135	-0.998 9
0.95	125.035	-0.998 7

4 DISCUSSION

As shown in Figs. 1, 2, the thermal decomposition of synthetic gibbsite is a heterogeneous reaction with 3 stages. The first stage is an induction period which was reflected in platforms on the curves when the heating rates were lower than $2^\circ\text{C} / \text{min}$. When the heating rate was higher than $2^\circ\text{C} / \text{min}$, the induction period become so short that no platform appeared on the curve.

In order to determine the mechanism of the second stage, which performed as the first peak on the DSC curve, we checked the products of the first stage. The platinum boat was pushed out immediately after the first peak and cooled quickly. The sample was then analyzed by X-ray diffraction. Comparing the pattern (see Fig.4(a)) with the standard pattern of gibbsite showed that the pattern of our sample was mostly close to

that of gibbsite. Only a bit of it belonged to that of boehmite. From the above facts, we consider that the majority of the product of the second stage was $\text{Al}(\text{OH})_n$ with the value of n between 2 and 3.

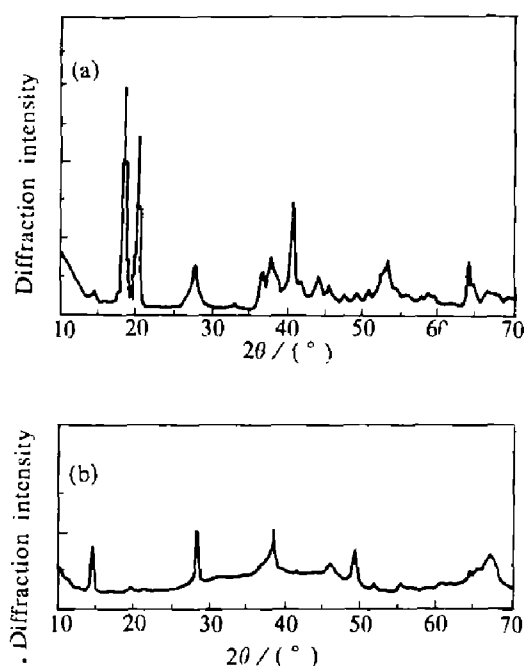


Fig. 4 XRD pattern of the product of the second (a) and third (b) stages

X-ray diffraction analysis(see Fig. 4(b)) of the product of the third stage which performed as the second peak on the DSC curve showed that the majority of the product of the third stage was boehmite with traces of $\gamma\text{-Al}_2\text{O}_3$.

The information for the first stage (induction period) was too sparse to determine kinetic parameters. The activation energies of the second and the third stages could be obtained from the results of Ozawa's method. We ignored the result when $\alpha=0.05$, since its relative error was too large. The activation energy of the second stage of the reaction (the first peak), responding to the section of $\alpha=0.10$ to $\alpha=0.15$, was $219.5 \pm 4.2 \text{ kJ/mol}$, which came from the average of the results of $\alpha=0.10$ and $\alpha=0.15$. Beside the transition section($\alpha=0.20$ to 0.30), we calculated the activation energy of the third stage (the second peak) using the results of the section between

$\alpha=0.35$ and 0.95 . The activation energy of the third stage is 142.2 ± 11.7 kJ/mol from the average of above section.

Goton *et al.* (1955) studied the decomposition of gibbsite using DTA and TGA at heating rate of $10^\circ\text{C}/\text{min}$. They also found that there were two endothermic peaks on their DTA curve at temperatures lower than 400°C [7]. Almost all water in gibbsite was lost after the second peak as we observed. Sato (1964^[8], 1985^[1]) found the products of the decomposition of synthetic gibbsite at about 300°C were boehmite and $\lambda\text{-Al}_2\text{O}_3$. The later could not be found in our experiment. Zhao and Chu (1991)^[2] investigated the mechanism of the decomposition of gibbsite. They considered the products after the first endothermic peak was $3\text{Al}(\text{OH})_3 \cdot \text{AlOOH}$ which was not a simple mixture but a stable phase. However, it seems to be no evidence for this from either their XRD patterns or our XRD pattern.

5 SUMMARY

DSC and XRD methods were used to determine the mechanism and kinetic parameters of the thermal decomposition of synthetic gibbsite.

When the temperature was lower than 400°C , the decomposition was a heterogeneous reaction which contained three stages. The first stage of reaction was an inductive period. The majority products of the second stage were $\text{Al}(\text{OH})_m$ and the activation energy was 219.5 ± 4.2 kJ/mol. After the third stage, almost all of the reactant became boehmite and the activation energy is 142.2 ± 11.7 kJ/mol. The reactions during both the second and the third stages were endothermic reactions.

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