

Catalysis, Kinetics and Reaction Engineering

Non-isothermal decomposition kinetics of hydrogarnet in sodium carbonate solution[☆]



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ABSTRACT

Carbonation decomposition of hydrogarnet is a significant reaction of the calcification–carbonation new method for alumina production by using low-grade bauxite. In this work, non-isothermal decomposition kinetics of hydrogarnet in sodium carbonate solution was studied by high-pressure differential scanning calorimetry (HP-DSC) at different heating rates of 2, 5, 8, 10, 15 and 20 K·min⁻¹, respectively. The activation energy (E_a) was calculated with the help of isoconversional method (model-free), and the reaction mechanism was determined by the differential equation method. The calculated activation energy of this reaction was 115.66 kJ·mol⁻¹. Furthermore, the mechanism for decomposition reaction is Avrami–Erofeev ($n = 1.5$), and the decomposition process is diffusion-controlled.

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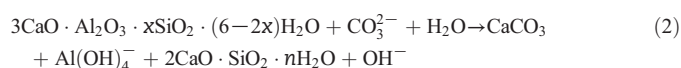
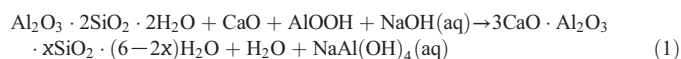
1. Introduction

As the leader of alumina production in the world, China produced more than 40 million tons of alumina, which accounts for approximately 40% of the global output in 2012 [1]. However, the lack of bauxite resource, especially high-grade bauxite is in stark contrast to the huge amount of the alumina output in China. More than 65% of bauxite in China is low-grade ore with the mass ratio of Al₂O₃ to SiO₂ (A/S) below 7, and only 18.5% of bauxite with the A/S higher than 9. It is estimated that the high-grade bauxite will be used up within 10 years in China [2].

Bayer process is the most common method for alumina production both in China and abroad. However, it is not suitable for processing the low-grade bauxite because of the high consumption of caustic alkali and the low recovery of alumina [3]. Although the sintering process can be employed for the low-grade bauxite, it is being phased out gradually due to its complex process and high energy consumption. Furthermore, alumina industry in China results in severe environmental problems, due to the huge amount of the red mud with a high alkaline after alumina refinery [4]. Therefore,

an environment-friendly method to efficiently utilize the abundance of the low-grade bauxite resources is urgently needed to be developed in China.

In order to produce alumina with low-grade bauxite, a novel calcification–carbonation method was proposed by our team [5,6]. In the calcification process, silica-containing phase in bauxite is transformed into hydrogarnet, which is a kind of hydroxy aluminosilicate with the general chemical formula of 3CaO · Al₂O₃ · xSiO₂ · (6 - 2x)H₂O (0 < x < 3). Thereafter, the generated hydrogarnet is decomposed as CaCO₃, 2CaO · SiO₂ · nH₂O and Al(OH)₃ through the carbonation process. After that, the Al(OH)₃ is extracted by NaOH solution at temperature below 373 K. The final red mud is composed of alkali-lean and alumina-lean CaCO₃ and 2CaO · SiO₂ · nH₂O. This process provides an eco-friendly design for the effective use of low-grade bauxite. The main reactions involved in this process can be presented as:



In previous works, the effect of reaction conditions on calcification process and transformation of equilibrium phase during the

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process has been investigated in detail [7–9]. However, as a significant intermediate process, the kinetics of carbonation decomposition reaction (Eq. (2)) of hydrogarnet is still unclear.

The differential scanning calorimetry (DSC) technique is widely used to determine the kinetics of reactions [10,11], curing [12], crystallization [13] and thermo-decomposition [14–16]. As reported by BAO *et al.* [10,11], a high-pressure DSC was used to determine the kinetics of gibbsite, boehmite and diasporite dissolving in caustic solution. Mechanism functions and kinetic parameters were featured by model-fitting method. SULTANIA *et al.* [12] studied the cure kinetics of vinyl ester–styrene system by non-isothermal DSC at four different heating rates (2.5, 5, 7.5, 10 K·min⁻¹), and obtained the apparent activation energy (E_a) of curing process by isoconversional method. Their results indicated that there is a good agreement between experiment and model.

In this paper, the decomposition kinetics of hydrogarnet in sodium carbonate solution was studied by means of a high-pressure differential scanning calorimetry (HP-DSC). The isoconversional and differential equation methods were used to analyze the DSC curve data. Furthermore, the apparent activation energy was calculated and the most probable mechanism of this reaction was proposed.

2. Materials and Methods

2.1. Preparation and characterization of materials

The hydrogarnet used in this experiment was synthesized by hydrothermal synthesis in a 2 L scale autoclave with a magnetic stirring. The materials for preparing hydrogarnet were analytical reagent CaO, NaOH, Al(OH)₃, and Na₂SiO₃·9H₂O (Sinopharm Chemical Reagent Co., Ltd, China). 1 L sodium aluminate solution with concentration of 240 g·L⁻¹ Na₂O and 197 g·L⁻¹ Al₂O₃ was prepared as the hydrothermal medium, which was subsequently mixed with 50 g CaO and 25 g Na₂SiO₃·9H₂O (SiO₂ 5 g·L⁻¹) and reacted in the autoclave at 513 K for 4 h. Then, the product was filtered and washed with distilled water to weak alkaline, and dried in an oven at 353 K for 8 h. The percentages of oxides of sample, as determined by X-ray fluorescence (XRF), are shown in Table 1. The mineralogy of sample was characterized by X-ray diffraction (XRD, D8 ADVANCE of Bruker company, 40 kV, 40 mA, CuK_α, 2θ 10°–90°, increment 0.0095°) as shown in Fig. 1.

Table 1
Chemical composition of the synthesized hydrogarnet

Composition	Al ₂ O ₃	SiO ₂	CaO	Na ₂ O	Loss on ignition
Content (by mass)/%	25.80	4.69	40.09	1.85	25.14

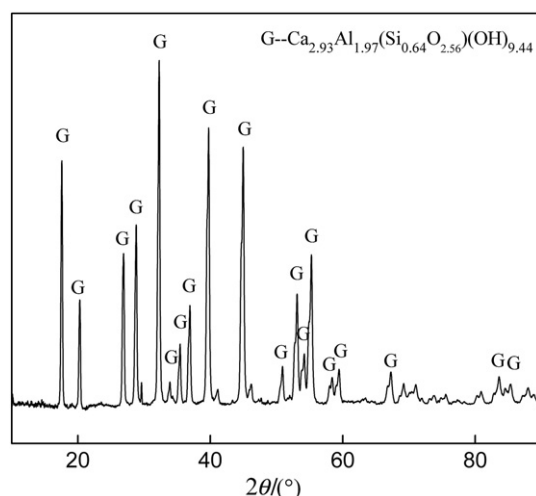


Fig. 1. XRD patterns of sample prepared by hydrothermal synthesis.

Fig. 1 proves that the hydrogarnet is synthesized successfully. The data in Table 1 show that the mass percentages of oxides of calcium, aluminum and silicon are 40.09%, 25.80% and 4.69%, respectively. The molar ratio of CaO:Al₂O₃:SiO₂ is 2.83:1:0.31, which corresponds to the stoichiometry of 2.83CaO·Al₂O₃·0.31SiO₂·5.38H₂O.

2.2. DSC measurements

The DSC measurements were performed with a high-pressure DSC (204HP, NETZSCH, Germany). Dry argon was used as the purge gas at a rate of 20 ml·min⁻¹, and a baseline was obtained with DSC crucible first. The mixture of prepared hydrogarnet and saturated sodium carbonate solution was sealed in a gold crucible with a stainless steel cap at the heating rate of 2, 5 and 10 K·min⁻¹ when the DSC was performed. The Proteus Software was used to collect and analyze the DSC data.

2.3. Calculation of kinetic parameters

According to non-isothermal kinetics theory, the general decomposition reaction rate can be expressed by [17]:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) = A \exp\left(-\frac{E_a}{RT}\right)f(\alpha) \quad (3)$$

where α is the reaction fraction, $k(T)$ is the rate constant, $f(\alpha)$ is the differential mechanism function, T is the absolute temperature, E_a is the apparent activation energy, A is the pre-exponential factor and R is the universal gas constant ($R = 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$).

When a sample is heated at a constant rate under non-isothermal conditions, $\beta = dT/dt$, and Eq. (3) is modified as follows:

$$\beta \frac{d\alpha}{dT} = A \exp\left(-\frac{E_a}{RT}\right)f(\alpha). \quad (4)$$

Taking the logarithm of Eq. (4) and the Friedman–Reich–Levi equation can be described as follows [18]:

$$\ln \left[\beta \frac{d\alpha}{dT} \right] = \ln [A f(\alpha)] - \frac{E_a}{RT}. \quad (5)$$

The Friedman–Reich–Levi method is considered as one of the most reliable isoconversional methods to calculate activation energy (E_a) of reactions without preselecting a reaction model [19]. By this method, activation energy can be evaluated from the slope of linear fitting $\ln(\beta d\alpha/dT)$ against T^{-1} under a given value of reaction fraction (α).

In order to obtain a reliable value, the activation energy E_a was determined by the isoconversional method (Friedman–Reich–Levi), which avoids the choosing of mechanism function. Herein, the differential equation method of non-isothermal kinetics was applied to study the reaction mechanism of the decomposition reaction, and it can be presented as follows [20]:

$$\ln \left\{ \frac{d\alpha/dT}{f(\alpha) \left[\frac{E_a(T-T_0)}{RT^2} + 1 \right]} \right\} = \ln \frac{A}{\beta} - \frac{E_a}{RT} \quad (6)$$

where $f(\alpha)$ is a differential expression for mechanism functions listed in Table 2.

3. Results and Discussion

3.1. XRD analysis of decomposition products

In order to characterize the product after decomposition of hydrogarnet by sodium carbonate solution, 6 g synthesized

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