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Dehydration kinetics of boehmite in the temperature range 723–873 K

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ABSTRACT

The dehydration kinetics of boehmite prepared from the hydrothermal transformation of gibbsite has been comprehensively studied to clarify the mechanism of the dehydration process using a thermogravimetric technique under both isothermal and non-isothermal conditions. Selected residues were examined by XRD, SEM, TEM and selected area electron diffraction (SAED). Results indicate that the dehydration process is a topotactic reaction which brings about γ-Al_2O_3 with porous microstructure and poor crystallinity. The kinetic data were analysed using the model-free (isoconversional) methods. The results indicate that the activation energy of the dehydration process depends on the reaction extent, signifying the dehydration process is chemical controlled with a diffusion complication as the reaction extent increases. Prediction of the dehydration extent was accomplished using the kinetic parameter of the non-isothermal process and the isoconversional method. The predicted rate is in a reasonably good agreement with the measured values. Finally the mechanism of the dehydration process is discussed based on the auxiliary results from the physical examination of the reacted residues and the kinetic behaviour.

1. Introduction

In the Bayer process, bauxite is digested in caustic liquor for extracting alumina at temperatures dictated by the mineralogical forms of alumina present in bauxite. Boehmite is one of three main aluminium-bearing minerals (gibbsite, boehmite and diaspore) commonly found in bauxite ores. After digestion, both insoluble minerals and reaction products are removed as residue from the liquor. Gibbsite ($Al(OH)_3$) is precipitated from the supersaturated liquor after cooling and seeding, which is then calcined to product alumina (Al_2O_3) [1].

The final stage of the Bayer process is the calcination (to ~980 °C) of product gibbsite to Smelter Grade Alumina (SGA). This is energy intensive (~1.7 GJ ton^{-1} [2]) and thus contributes significantly to the overall cost of SGA production. It has long been recognised that calcining boehmite to SGA instead of gibbsite will result in energy savings [3,4] and so there has been a body of work aimed at the direct crystallisation of boehmite from Bayer liquor [3–6].

Outside the alumina industry, boehmite as a precursor is used through thermal treatment for preparation of many materials, which include catalysts, adsorbents, ceramics, refractories, electronic devices and bio-medical materials [7].

Despite the widespread interest in boehmite, studies of the kinetics of its thermal behaviour are limited and the results are difficult to compare due to different test conditions. Tsuchida et al. [8,9] investigated the effect of preparation conditions of boehmite on the reactivity of aluminas formed from the dehydration of boehmites. They found that the dehydration reaction was complex under isothermal conditions (below 480 °C) and the dehydration kinetics of boehmites with different crystallinities fit to different models.

Alphonse and Courty [7] investigated the thermal behaviour of nanocrystalline boehmite and processed the kinetic data using an isoconversional (model free) method. They found that the dehydration kinetics of the boehmite under non-isothermal conditions (up to over 1000 °C) with constant heating rates could be accurately modelled by four steps: desorption of physisorbed water, desorption of chemisorbed water, conversion of boehmite into transition alumina and dehydration of transition alumina.

Nordahl and Messing [10] studied the effect of corundum seed on the transformation kinetics of boehmite under non-isothermal conditions up to 1300 °C and analysed the data using a model-fitting method. They observed extremely high activation energy for the transformation of boehmite to corundum (522 kJ mol^{-1}) without seeding and a significant reduction (up to 115 kJ mol^{-1}) with seeding.

The dehydration of boehmite has long been regarded as a topotactic reaction [11–18]. Mechanistic studies show that the dehydration advances from the surface of layered boehmite

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through the elimination of water formed by the protons and hydroxy groups between adjacent layers. Counter-diffusion of protons and Al cations takes place in the plane of the reaction interface. This leads to a coherent skeleton of γ-Al_2O_3 which is intersected and of porous microstructure. The diffusion of Al cations from octahedral to tetrahedral sites is a necessity for the formation of spinel γ-Al_2O_3 and has been found to be a rate-determining step in the dehydration process. Theoretical studies demonstrate that the number of Al cations migrated to tetrahedral sites and the distribution of cation vacancies are important for the free energy change and the stability of structure formed at a given temperature [17,19].

In our previous study of the dehydration kinetics of gibbsite [20] under isothermal conditions, we found that the dehydration occurred through a set of chain reactions of gibbsite to transition alumina and gibbsite through boehmite to transition alumina. The activation energy of gibbsite to boehmite ($\sim$44 kJ mol^{-1}) is much higher than that of boehmite to transition alumina ($\sim$14 kJ mol^{-1}) while the rate of gibbsite to boehmite (3.9×10^{-3} s^{-1}) is slower than that of boehmite (5.9×10^{-3} s^{-1}) to transition alumina.

It is evident that there are discrepancies between the published results. The discrepancies could be caused by a number of factors such as the preparation and attributes of boehmite, the thermal dehydration conditions and the mathematical methods for processing the kinetic data [21–28].

In this paper, we investigate the kinetics of boehmite dehydration in the temperature range similar to that used for the dehydration of gibbsite [20]. In contrast to boehmite as intermediate phase formed in the process of gibbsite dehydration in the previous work, the boehmite used in current work was hydrothermally prepared as a pure feed. The dehydration has been investigated under both isothermal and non-isothermal conditions in order to take advantage of both the heating regimes. The kinetic data have been processed using more reliable model-free methods recommended by the Kinetics Committee of the International Confederation for Thermal Analysis and Calorimetry (ICTAC Kinetics Committee) [32]. The results are compared with the published ones and the mechanism of the dehydration process is discussed.

2. Kinetic calculations

2.1. Calculation methods

Model-fitting and model-free (isoconversional) methods are two types of methods widely used in analysis of kinetic data from thermal reactions of solids. Although the model-fitting method has been the most popular method used in studying solid-state kinetics, it can produce some problems [28]. One problem originates from force-fitting data into assumed different models. Under isothermal conditions where the dependence of rate constant on temperature and the form of model are separated, the model can give rise to a single set of Arrhenius parameters as average values for an overall process. This however, may conceal a multistep mechanism. Under non-isothermal conditions, both the rate constant and the reaction model depend on temperature and cannot be separated – they are extracted by the model-fitting method from a single non-isothermal experiment. Therefore, almost any model can be satisfactorily fitted to non-isothermal data at the cost of drastic variations in the Arrhenius parameters which compensate for the difference between the assumed form of model and the true, but unknown kinetic model [22,25,29,30].

For this and other reasons, the ICTAC Kinetics Committee has conducted an extensive comparison study of the two methods on processing both isothermal and non-isothermal data [31] and found that the model-free and multi-heating rate methods are particularly successful in describing the multi-step kinetic processes. It has recommended to use model-free methods to analyse kinetic data from multiple temperature programmes [32]. This guideline has been followed in this work.

The dehydration of boehmite is a solid decomposition reaction,

$$2\mathrm{AlOOH}(s) \rightarrow \mathrm{Al_2O_3}(s) + \mathrm{H_2O}(g) \tag{1}$$

the rate of which can be expressed as

$$\frac{dx}{dt} = k(T)f(x) \tag{2}$$

where k is the rate constant, T is the absolute temperature, $f(x)$ is the reaction model function [25] and x is the conversion fraction

$$x = \frac{\Delta w_t}{\Delta w_e} \tag{3}$$

where Δw_t is the water weight lost at any time t and Δw_e is the total water weight lost at the end of test.

Under constant temperature condition, Eq. (2) can be integrated to

$$g(x) = kt \tag{4}$$

where $g(x)$ is the integral form of model. Commonly used models can be found in the review by Vyazovkin et al. [32]. The temperature dependence of the constant k is usually described by the classical Arrhenius relation

$$k = A\exp\left(\frac{-E}{RT}\right) \tag{5}$$

where A is the pre-exponent factor, E is the activation energy and R is the gas constant. Combining Eqs. (4) and (5) gives

$$g(x) = A\exp\left(\frac{-E}{RT}\right)t \tag{6}$$

Applying the isoconversional principle and some rearrangement to Eq. (6), an equation of an integral isoconversional method recommended by the ICTAC Kinetics Committee is obtained:

$$\ln t_{x,i} = \ln\left[\frac{g(x)}{A_x}\right] + \frac{E_x}{RT_i} \tag{7}$$

where $t_{x,i}$ is the time to reach a given reaction extent at different isothermal temperature T_i. The reaction extent dependent activation energy E_x can be calculated from the slope of the plot $\ln t_{x,i}$ vs $1/T_i$ without applying an actual model.

For a non-isothermal process with a constant heating rate $\beta = dT/dt$, Eq. (2) becomes

$$\frac{dx}{dT} = \frac{k(T)f(x)}{\beta} = A\exp\left(\frac{-E}{RT}\right)\frac{f(x)}{\beta} \tag{8}$$

Integration of Eq. (8) gives

$$g(x) = \frac{A}{\beta}\int \exp\left(\frac{-E}{RT}\right)dT \tag{9}$$

Eq. (9) has no analytical solution [26], but a number of approximate solutions have been developed over years. Among them an isoconversional equation developed by Starink [33] and also recommended by the ICTAC Kinetics Committee [32], has been proven more accurate and takes the form

$$\ln\left(\frac{\beta_i}{T_{x,i}^{1.92}}\right) = Const - 1.0008\left(\frac{E_x}{RT_x}\right) \tag{10}$$

To use Eq. (10), tests with different heating rates need to be conducted so that a constant conversion corresponds to several temperatures at these heating rates. The reaction extent dependent activation energy E_x can be determined from the slope of the plot of the left hand side of Eq. (10) vs $1/T_x$.