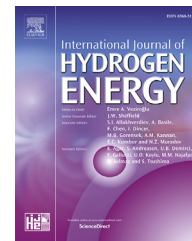




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Kinetic model analysis and mechanistic correlation of ammonia borane thermolysis under dynamic heating conditions

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ABSTRACT

Solid state decomposition of ammonia borane has been extensively reported to follow the Avrami-Erofe'ev equation. In this work, thermal analysis of ammonia borane is carried out under dynamic heating conditions under heating rate of 1–5 °C/min. The experimentally derived kinetic data is fitted against various solid state decomposition and autocatalytic kinetic models. It has been observed that the two steps of ammonia borane decomposition reactions follow different kinetics. The first step is more likely to be associated with the homogeneous autocatalytic reactions where the second part demonstrates the traditional nucleation growth kinetics.

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Introduction

Ammonia borane has been widely researched as solid state hydrogen storage material, because of its high gravimetric hydrogen storage capacity (GHSC) and low decomposition temperature. Despite its advantages, the decomposition reaction suffers various hindrances, including sluggish kinetics and generation of unwanted by-products [1]. Hydrogen generation from the thermolysis of AB also involves release of other by-products *e.g.* borazine, which indicates that the thermolysis reaction involves multiple parallel reactions. Since all thermolysis reaction depends upon exothermicity, it is expected that during decomposition, the extent of these individual by-product producing pathways will have different

thermal dependent kinetics. Therefore, in order to understand and improve the thermal dehydrogenation of ammonia borane, it is necessary to understand the decomposition kinetics of AB. Several attempts in the literature have been undertaken towards determining the activation energy of ammonia borane decomposition. The underlying assumption of these activation energy (E_a) analyses is that AB principally decomposes through a singular reaction mechanism regardless of heating conditions [2].

The kinetic models applicable for solid state decomposition reactions are observed to change with variation in reaction mechanisms [3]. Therefore, unlike consideration of singular pathway, accounting for the multiple parallel decomposition mechanisms, may provide with more accurate

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and detailed understanding about the complexity of AB decomposition reaction kinetics and dynamics.

Therefore, in this work, thermolysis of ammonia borane has been carried out under different dynamic heating rates. The as-obtained thermal analysis data are fitted against valid solid state reaction kinetic models, to understand their applicability under different heating conditions. Moreover, the change in decomposition mechanism, associated with the variation in reaction kinetics is addressed in following discussion.

Any solid state decomposition reaction follows the rate equation where the rate of the reaction can be expressed as:

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (1)$$

where, $\frac{d\alpha}{dt}$ is the rate of the reaction, k is rate constant, α is the extent of reaction, and time t , it can be further expressed as

$$\alpha_t = \frac{m_i - m_t}{m_i - m_f} \quad (2)$$

where, m_i, m_t and m_f are the mass of the reactant at $t = 0, t = t$ and $t = final$ respectively and

$f(\alpha)$ expresses the associated model for the decomposition reaction.

The expression (1) is commonly used to describe isothermal decomposition reactions. However, kinetic equation under dynamic heating condition can be derived from Eq. (1) by

$$\frac{d\alpha}{dT} \times \frac{dT}{dt} = kf(\alpha) \quad (3)$$

$$\frac{d\alpha}{dT} \times \beta = kf(\alpha) \quad (4)$$

$$\frac{d\alpha}{dT} = k \times \frac{1}{\beta} \times f(\alpha) \quad (5)$$

where, β is the heating rate.

Here, β and k are considered constant throughout a particular experiment. Hence, a plot of $\frac{d\alpha}{dT}$ vs α provides a curve and by fitting of various models, it is possible to find out the most appropriate solid state reaction model for ammonia borane decomposition reaction under dynamic heating condition. Thus, the complete kinetic analysis by model fitting may lead to further insight into validity of mechanistic assumptions, which can experimentally be validated [3].

In order to account for the involved heterogeneous interaction between the solid-solid interfaces, of reactant and product, various models have been proposed for solid state reaction based on different mechanistic assumptions. The various solid state models employed for thermal decomposition reaction in literature are listed below.

1. Order law models
2. Geometric contraction model
 - i. Cylindrical symmetry
 - ii. Spherical symmetry
3. Nuclei growth model
 - i. Avrami Erofe'ev equation
 - ii. Prout Tompkins equation

Order based models

This is the simplest decomposition model widely used after the common kinetics equation for homogeneous reactions. The rate is proposed to be directly dependent upon the fraction of reactant left at a certain time during the reaction. The model is being represented by the expression

$$f(\alpha) = (1 - \alpha)^n \quad (6)$$

where,

n is expressed as the order of the reaction. $n = 1, 2, 3, \dots$

The first order model is also known as the Mampel model. Oxidation of Silicon [4] and desorption of 2-phenylethylamine [5] are a few examples to follow such kinetic rate equations.

Geometric contraction models

Geometric contraction models are based on the assumptions that solid state reactions start from the surface of the reactant crystals followed by the product phase formation on the surface. The reaction interface then uniformly proceeds toward the centre of the reactant phase crystal, representing geometrically progressive increase in the product phase. Therefore, depending on the crystallite geometry the reaction model will be different. Decomposition of calcium oxalate monohydrate is observed to follow geometric contraction model [6], which can be expressed as

$$f(\alpha) = n(1 - \alpha)^{1-\frac{1}{n}} \quad (7)$$

where

$n = 2$, for spherical particles and

$n = 3$ for cylindrical particles or crystallites

Nuclei growth models

Avrami-Erofe'ev model

The major assumption in case of the geometric contraction model is the homogeneous growth of the product phase which advances from surface towards the centre. In real cases, however, at high temperature, due to various crystal lattice imperfections and temperature gradient, the reaction is proposed to follow through product nuclei formation rather than the homogeneous phase propagation.

Hence, the nuclei growth model demonstrates the reaction progress as.

1. Nucleation: The product phase starts to form on the surface of reactant crystal, where there is maximum concentration of lattice defects.
2. Nuclei growth: The product nuclei either coalesce with other product nuclei or ingest them in order to grow further and reach towards centre of the reactant nuclei [7].
3. Deceleration: The product nuclei, after occupying its maximum volume, begins to merge with one another, leading to decrease in reaction rate, signifying the deceleratory period and ultimately leading to completion of the reaction.

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