

# Thermal decomposition of layered double hydroxides: Kinetic modeling and validation



Mostofa Shamim, Kausik Dana\*

Refractory and Traditional Ceramics Division, CSIR-Central Glass and Ceramic Research Institute, Kolkata-700032 India, India

## ARTICLE INFO

### Article history:

Received 5 January 2016

Received in revised form 21 March 2016

Accepted 23 March 2016

Available online 24 March 2016

### Keywords:

Thermal decomposition

Kinetic modelling

LDH

Activation energy

Layer charge

## ABSTRACT

Solid state kinetic process during the multistage thermal decomposition of Layered Double Hydroxide (LDH) reaction has been modeled utilizing model-free and model-based multivariate non-linear regression analysis. The physically most meaningful kinetic triplet for each of the stages [reaction model  $f(\alpha)$ , activation energy ( $E_a$ ) and pre-exponential factor ( $A$ )] is reported for multiple layer charges. The first two stages involved removal of water from interlayer and brucite layer respectively, of the material and follows an  $n$ -dimensional Avrami-like model. The removal of  $\text{NO}_x$  from interlayer nitrate anion (third stage) follows a 3-dimensional diffusion model of Jander type. The proposed kinetic model is validated by the comparison of the reaction extent (for each of the stages)—both theoretically (chemical formula) and experimentally (from fitting curve) for LDH of multiple layer charges. The isothermal prediction based on the assigned kinetic model predicted the degree of decomposition of LDH with reasonable accuracy.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Solid state reactions are ubiquitous with materials science. Sintering of ceramics, calcination of compounds and reaction between different oxides are few important examples of such thermal treatment required to synthesize a material. Although these heat-induced transformations have been practiced at industrial scale, the complex kinetics of these solid state reactions are yet to be understood using unambiguous model. The conventional 'homogenous kinetic' approach applicable for liquid phase reactions are not valid in solid state, since the rate of reaction in a solid state system varies not only with time, temperature, concentration, but across the reaction mixture too. This process is further complicated by the size of the reactant, heat transfer, diffusion, structural defects, geometrical constraints, complex nature of removal of products and others.

Layered double hydroxides (LDH) are promising synthetic material with lamellar texture. It's layered structure, wide spectrum of possible chemical compositions, controllable layer charge density, reactive interlayer space, ion-exchange, rheological and colloidal properties are similar to clay minerals. The structure of LDH is related to layered  $\text{Mg}(\text{OH})_2$  brucite structure, where some of the edge connected octahedral  $\text{Mg}^{+2}$  ions (or divalent cations) are replaced by  $\text{Al}^{+3}$  ions (or trivalent cations). This aliovalent lat-

tice substitution leads to positive charge which is neutralized by extraneous exchangeable anions in the interlayer position. The general formula for this family is  $[\text{M}^{\text{II}}_{1-x}\text{M}^{\text{III}}_x(\text{OH})_2][\text{X}^{q-}_{x/q}\cdot n\text{H}_2\text{O}]$  where first half represents the layer and the second half the interlayer composition, and  $\text{M}^{\text{II}} = \text{Mg}^{+2}, \text{Ni}^{+2}, \text{Zn}^{+2}, \text{Cu}^{+2}$ ,  $\text{M}^{\text{III}} = \text{Al}^{+3}, \text{Fe}^{+3}$  etc.  $x$  is the trivalent cation substitution degree and is usually  $0.2 \leq x \leq 0.33$ . Intercalation of LDH is an important reaction to modify the surface chemistry of the layered hydroxides to render several useful properties. LDH find a wide range of applications as fire retardants, improvement of polymer properties, control drug release, dye intercalation, heavy metal adsorption, pesticide adsorption etc.

Structural changes occur when LDH is heated with progressive removal of interlayer water, hydroxyl water and interlayer anions occur at higher temperatures. Interestingly, this calcination step opens up the possibility of preparing LDH-like materials with controlled structure, bonding and surface chemistry. Heat-treated dehydroxylated LDH is often reacted with water in presence of desired anions to produce intercalated LDH. This 'reformation' reaction allows facile intercalation of large or difficult-to-intercalate anions. Calcination of LDH at further higher temperatures  $\sim 800^\circ\text{C}$  lead to formation of a mixed metal oxide (MMO) [1], where  $\text{M}^{\text{II}}$  and  $\text{M}^{\text{III}}$  are statistically distributed in edge shared octahedral sheet. Several studies on MMO suggest it to be a very promising as catalytic material [2] and got promising application in different organic synthesis reaction [3], oxidative steam reforming of bio-ethanol [4] etc. If the kinetic pathway of the calcination process is discerned, it would be possible to optimize the calcination time

\* Corresponding author.

E-mail addresses: [kdana@cgcri.res.in](mailto:kdana@cgcri.res.in), [kausikdana3@gmail.com](mailto:kausikdana3@gmail.com) (K. Dana).

and temperature program and control the properties (structure and bonding) of the calcined product. It would also allow controlled/partial calcination of LDH, to generate further functionality to LDH. Thus, understanding this kinetics of calcination process shall enable engineering the LDHs properties and its application.

Decomposition kinetics of LDH has mostly been studied through non-isothermal kinetics. Velu et al. [5] investigated the non-isothermal decomposition kinetics of decomposition of ZnAl X LDH ( $X = \text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ). They proposed a multistage decomposition pathway and described the variation of activation energy ( $E_a$ ) with interlayer anions. However, there are no details of kinetic model ( $f$ ), decomposition mechanism and the software/algorithm used.

Non-isothermal kinetic method was also used by Rhee et al. [6] for studying dehydroxylation kinetics of Mg-Al  $\text{CO}_3$  LDH of different cation ratio (Mg:Al) using thermogravimetric analysis (TG). They reported only the  $E_a$  and pre-exponential factor ( $A$ ) for the dehydroxylation stage but did not suggest any reaction model for the stage. Moreover, no kinetic information about the removal of interlayer anions at the higher temperature was discussed.

A comprehensive report on LDH decomposition by Wang et al. [7] describes the kinetic parameters with reaction model and mechanism. They proposed a three stage decomposition pathway for the thermal decomposition of LDH (Ni/Al LDH nitrate with a Ni/Al = 3.0) by using the TG-DTA coupled with mass spectrometry (TG/DTA MS). Although a three stage decomposition mechanism was proposed but kinetic triplet [ $f(\alpha)$ ,  $E_a$  and  $A$ ] information for only two stages were provided. Also, the kinetic model was determined (by Popescu method) only after the values of the  $E_a$  and  $A$  were calculated by another method (Ozawa-Flynn-Waal method)—which is debatable. From the kinetic point of view, any multistage thermal decomposition (viz. LDH) should be understood with a single mathematical treatment to arrive at different kinetic triplets for each stage.

An interesting combination of iso- and non-isothermal decomposition kinetics of LDH was done by Valente et al. [8], who studied the thermal profiles and kinetic behavior of two different sol-gel samples of MgAl LDH by using TG-DTA and two kinds of model-free kinetic methods (Fourier transformed modulated TG and iso-conversional method) respectively. They found progressive change of  $E_a$  with progress of the decomposition reaction but did not illuminate on the reaction model and mechanism.

In summary, the previous works generally reported the  $E_a$  and discerned the structural evolution of LDH during multistage thermal decomposition, but a comprehensive report on kinetic triplet for all the stages along with quantification and validation of model is still needed in order to engineer the decomposition reaction to serve the purpose of different applications.

In the present study, using TG data, we report the solid state kinetic process involved with this multistage decomposition reaction and propose a comprehensive mechanistic pathway for the entire reaction with detailed kinetic parameters for each of the stages utilizing several approaches (viz., model free analysis and model-based multivariate non-linear regression analysis). The best fitted kinetic model has been validated by the comparing reaction extent (for each of the stages)—both theoretically (chemical formula) and experimentally (from TG fitting curve) for LDH of two layer charges.

The novelty of this work is related to the 'control' of the degree of decomposition reaction. By exploiting our proposed mechanistic pathway we successfully engineered the decomposition reaction to any extent viz. partial removal of hydroxyl groups. To best of our knowledge there is no such report which correlates the mechanistic pathway with quantification of mass loss regimes, reaction extent and utilizes the proposed mechanistic pathway to forecast the thermal decomposition under any thermal pathway.

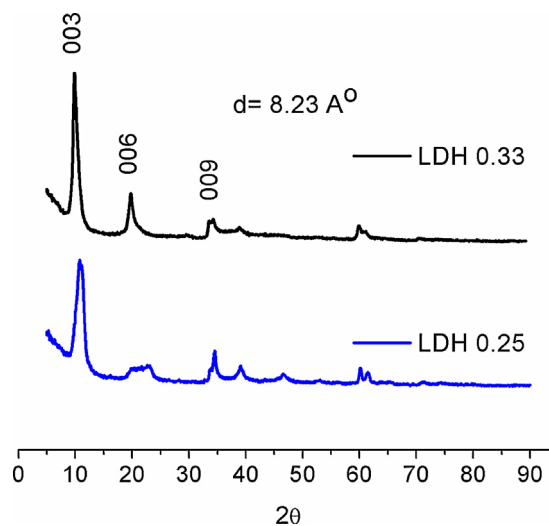


Fig. 1. XRD pattern of synthesized LDH 0.25 and LDH 0.33.

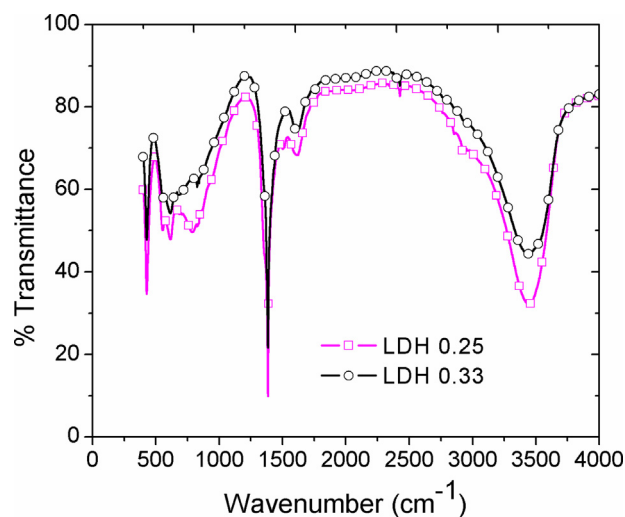


Fig. 2. FTIR spectra of LDH 0.25 and LDH 0.33.

### 1.1. Theoretical background: solid state kinetics

The rate of any solid state transformation reaction is

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \quad (1)$$

where  $A$  is the pre-exponential factor,  $E_a$  is the activation energy,  $T$  is absolute temperature,  $R$  is the gas constant,  $f(\alpha)$  is the reaction model and  $\alpha$  is the fractional conversion. Often, this trio viz.,  $A$ ,  $f(\alpha)$  and  $E_a$  is referred as kinetic triplet.

For a reaction involving mass loss (TG),  $\alpha$  may be expressed as

$$\alpha = \frac{m_o - m_t}{m_o - m_f} \quad (2)$$

where  $m_o$  is initial weight,  $m_t$  is weight at time 't' and  $m_f$  is final weight. In case of non-isothermal solid state transformation,  $\alpha$  may be expressed as

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

where  $d\alpha/dT$  the non-isothermal reaction rate,  $d\alpha/dt$  is the isothermal reaction rate and the heating rate ( $\beta$ ) =  $dT/dt$ . Substitution

Download English Version:

<https://daneshyari.com/en/article/672766>

Download Persian Version:

<https://daneshyari.com/article/672766>

[Daneshyari.com](https://daneshyari.com)