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Decomposition kinetics of $CaCO_3$ dry coated with nano-silica

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ABSTRACT

Non-isothermal decomposition kinetics of surface coated calcium carbonate ($CaCO_3$) was investigated using different wt.% of nano-silica. The activation energy was calculated from model-free isoconversional technique using Kissinger–Akahira–Sunose method. The result indicates that $CaCO_3$ with lower wt.% (0.25% and 1.0%) of nano-silica has low activation energy than pure and 2% nano-silica coated $CaCO_3$. This is possibly because nano-silica acts as heat receptor and creates defects inside the crystal which is dominant at lower percentage of coating. However, higher % of nano-silica coating increases resistance to CO_2 diffusion which increases the activation energy. The corresponding reaction model for decomposition was predicted by Málek's method. Experimental data was in good agreement with the theoretical model proposed by Šesták Breggren (SB). The parameters (m and n) in SB model and invariance of activation energy in the entire conversion range strongly signify that decomposition mechanism is single step in nature.

1. Introduction

Thermal decomposition of calcium carbonate ($CaCO_3$) is an extensively studied decomposition reaction due to various industrial applications in manufacturing of lime, additives, cosmetics, foods, plastics, printing ink, metallurgy, construction, cement, agriculture, medicine, filler in rubber, plastic, paper and paint, etc. [1–4]. Decomposition kinetics of $CaCO_3$ is studied with various experimental parameters such as influence of heating rate [5], particle size [6,7], atmosphere [8], impurities [9]under both isothermal [10,11] and non-isothermal [12–15] conditions. Most of these studies identified various resistances which influence the kinetics and basic mechanism of decomposition reaction. However, most of the previous studies are only limited to decomposition kinetics of pure $CaCO_3$ [5,8,10,16]. Presently, $CaCO_3$ is found to be functionalized or surface modified in many cases for specific applications such as biological labels [17,18], optical resonances [19,20], catalysis [21,22], magnetics [23], ceramics [2,24], and pigments [25]. Surface modification of $CaCO_3$ increases the dispersibility and helps to improve the strength and interaction between filler and substrate [26]. Also it improves the thermal stability of $CaCO_3$ [27]. Thus, decomposition kinetics of surface modified calcium carbonate is an interesting research for many new applications and can provide immense value to industrial applications. However, it is not well studied in the literature except very few cases [4,16]. [4] studied the kinetic parameters and dissociation mechanism for continuous silica coated nano-$CaCO_3$ using thermo-kinetic analysis. They reported the influence of coating on activation energy and concluded that dissociation kinetics changes from reaction controlled mechanism in spherical geometry (contracting volume mechanism, R_3) for uncoated $CaCO_3$ to one dimensional diffusion controlled mechanism (D_1) for continuous silica coated $CaCO_3$. Similar kind of study reported by [16] where continuous coating was performed with the help of AlOOH by wet coating method. They have found that the decomposition kinetics changes from reaction controlled mechanism in a disk geometry (contracting area mechanism, R_2) for uncoated $CaCO_3$ to one dimensional diffusion controlled mechanism (D_1) for surface coated $CaCO_3$. Both the studies used conventional Master plot method [28] for predicting the kinetic model for coated $CaCO_3$. The change in controlling mechanism from surface reaction to diffusion controlled is believed to be due to additional diffusional resistance offered by continuous layer of silica or AlOOH. However, the reason for changing the geometric model from two dimension to one dimension (after coating) is not explained clearly in the literature. In both the works, the coating was done by wet method, which involves handling of solvent. Also the coating is continuous in nature, which provides additional diffusional resistance to CO_2. In contrast, dry coating [29] is an environmentally benign surface modification technique which requires intimate rigorous mixing between nano-particle (guest) and micron particle (host) and high impaction shear force. It helps nano-particle to adhere on the surface of micron particle. The dry

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coating avoids complexity associated with solvent handling and its drying. In addition, the technique can also effectively improve the properties of fine powder such as flowability [30,31], dispersibility [32,33], solubility [32], wettability and resistance to humid environment [34,35]. However, there is no evidence of published study on decomposition of dry coated $CaCO_3$.

In the present work, decomposition kinetics of dry coated $CaCO_3$ with different (wt.%) of nano-silica is explored and compared with the uncoated (as received) $CaCO_3$ using dynamic thermal analysis. The main objective of this study is to investigate the characteristics of thermal decomposition of nano-silica coated calcium carbonate with different wt.% of coating and determine the suitable reaction model along with kinetic parameters. The effect of different percentages of nano-coating on kinetic parameters is also explored. The activation energy was calculated by employing the model free isoconversional method (Kissinger–Akahira–Sunose method). The selection of appropriate reaction model was performed using conventional Master plot analysis technique and Málek's approach.

2. Theory

2.1. Thermo-kinetic analysis: estimation of kinetic parameters

The kinetics of solid-state decomposition is extensively studied by nonisothermal methods [10,36–38]. In non-isothermal decomposition study, kinetic parameters or kinetic triplet (activation energy, pre-exponential factor and reaction model) are easily calculated from thermo-kinetic analysis [39–41]. Dollimore et al. [42] summarized various existing reaction models which are given in Table 1. Heterogeneous solid-state thermal decomposition is generally expressed by,

$$\frac{d\alpha}{dt} = k(T)\ f(\alpha) \tag{1}$$

$$\beta\frac{d\alpha}{dT} = A\ \ \exp\left(\frac{-E_a}{RT}\right)\ \ f(\alpha) \tag{2}$$

where α is the degree of conversion,

$$\alpha = \frac{(m_0 - m_t)}{(m_0 - m_f)} \tag{3}$$

m_0 is the initial sample mass, m_t is the sample mass at time t, m_f is sample mass at the end of the decomposition. $f(\alpha)$ is the reciprocal of the differentiation of $g(\alpha)$ with respect to α. The forms of $g(\alpha)$ and $f(\alpha)$ for different models are listed in Table 1. $k(T)$ is the reaction rate constant and it follows the Arrhenius equation $k(T) = A\ \exp(-E_a/RT)$, where A is the pre-exponential factor, E_a is the apparent activation energy and R is the gas constant, T denotes temperature and β is the heating rate ($\beta = dT/dt$). In isoconversional approach [43–45] sample is decomposed under minimum three heating rates and apparent activation energy is evaluated without assuming any reaction model. Usually both differential and integral methods are employed to determine the activation energy and its dependence on α [46,47]. However, according to ICTAC recommendations [47], differential method [48] was avoided due to its inaccuracy and imprecision associated with this method. Among the integral methods, Kissinger–Akahira–Sunose method [49] gives more accurate apparent activation energy (E_a) as compared to Ozawa–Flynn–Wall method [50]. Thus, in this work Kissinger–Akahira–Sunose method was used which was originally recommended by Coats and Redfern [51]. The equation is expressed as follows,

$$\ln\left(\frac{\beta}{T_\alpha^2}\right) = -\left(\frac{E_a}{RT_\alpha}\right) + \ln\frac{AR}{E_a g(\alpha)} \tag{4}$$

At a particular α with different heating rates, the plots of ln (β/T^2) against $1/T$, gives a straight line. The slope of the corresponding line gives the value of apparent activation energy at corresponding α value.

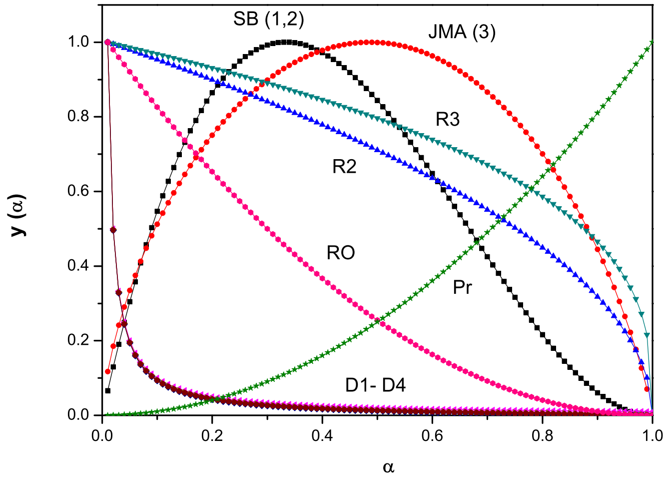

Fig. 1. Typical shapes of $y(\alpha)$ functions for several kinetic models.

2.2. Model selection

To find a proper dissociation mechanism and selection of reaction model, both the Master plot and the Málek's method were employed in the present work.

2.2.1. Master plot approach

Master-plot method [52] is found to be one of the accurate methods which is highly insensitive to experimental conditions. It has been used for non-isothermal data treatment for decomposition of coated $CaCO_3$ [4,16]. The Master plot method is introduced as follows,

$$z(\alpha) = f(\alpha)g(\alpha) \tag{5}$$

The experimental data is described in the following form (Eq. (6)) and compared with theoretical standard plot (Eq. (5)) corresponding to each model,

$$z(\alpha) = \frac{\pi(x)}{\beta}\left(\frac{d\alpha}{dt}\right)T \tag{6}$$

where $x = E_\alpha/RT$ and $\pi(x)$ is mentioned as [53],

$$\pi(x) = \frac{x^3 + 18x^2 + 88x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120} \tag{7}$$

The mechanism of corresponding system is defined by the model equation which is in close accord with the experimental data.

2.2.2. Málek's method

Málek's method is quite acceptable because of its simplicity and accuracy [53,54]. The two functions $y(\alpha)$ and $z(\alpha)$ in Málek's method are used to determine the kinetic model. Where function $z(\alpha)$ is expressed similar to that of Eq. (6) of Master plot method and function $y(\alpha)$ which is proportional to $f(\alpha)$ is represented by,

$$y(\alpha) = \left(\frac{d\alpha}{dt}\right)e^x \tag{8}$$

$y(\alpha)$ and $z(\alpha)$ are normalized with respect to α to find out the appropriate kinetic model. α_M, α_P^∞ and α_p are the maximum values of normalized functions $y(\alpha)$ vs. α, $z(\alpha)$ vs. α and $d\alpha/dt$ vs. α, respectively. The shape of $y(\alpha)$ vs. α curve (Fig. 1) and value of parameters (α_M, α_P^∞ and α_p) help to identify the suitable reaction model. As $y(\alpha)$ is proportional to $f(\alpha)$, the function $y(\alpha)$ is a characteristic curve (Fig. 1) for selection of kinetic model. The theoretical values