Thermochimica Acta, 223 (1993) 177–186
Elsevier Science Publishers B.V., Amsterdam

Intrinsic kinetics of the thermal decomposition of sodium bicarbonate

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(Received 11 December 1992; accepted 18 January 1993)

Abstract

The intrinsic kinetics of the thermal decomposition of $NaHCO_3$ to Na_2CO_3 has been studied by non-isothermal thermogravimetric analysis. $NaHCO_3$ powder of 47 μm mean particle size was heated to decomposition at three constant heating rates (1.25, 2.5, and 5°C min^{-1}) in flowing nitrogen. The range in which the decomposition occurred was about 360–450 K. A graphical method and Friedman's method were both used to analyze the experimental data: close agreement was obtained. The reaction rate showed a first-order dependence on the amount of unreacted $NaHCO_3$ and the values for the activation energy and pre-exponential factor were 25.3 kcal mol^{-1} (105.8 kJ mol^{-1}) and 6.7×10^{12} min^{-1}, respectively.

LIST OF SYMBOLS

E	activation energy in J mol^{-1}
k	rate constant in min^{-1}
k_0	pre-exponential factor of the rate constant in min^{-1}
n	reaction order
R	gas constant, 8.314 J mol^{-1} K^{-1}
T	absolute temperature in K
t	time in min
W	weight of sample in mg
W_0	initial weight of sample in mg
x	conversion

INTRODUCTION

For the various sorbents used in dry flue gas desulfurization (FGD), investigations have confirmed that sodium compounds have an excellent

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capability for reducing SO_2. Among the sodium compounds, nahcolite, a naturally occurring mineral containing 70%–90% $NaHCO_3$, is more reactive than trona which contains about 50% Na_2CO_3 [1, 2].

Using a nahcolite injection process, more than 70% of the SO_2 in flue gas can be removed [3]. The overall reaction for this process is

$$2NaHCO_3(s) + SO_2(g) + 0.5O_2(g) \rightarrow Na_2SO_4(s) + 2CO_2(g) + H_2O(g) \qquad (1)$$

This reaction does not occur in a single step, as written above, but instead involves a series of three steps: thermal decomposition of $NaHCO_3$ to Na_2CO_3; reaction between Na_2CO_3 and SO_2 to form Na_2SO_3; and oxidation of Na_2SO_3 to Na_2SO_4. Thus the overall reaction rate may be controlled by either the rate of thermal decomposition of $NaHCO_3$ to Na_2CO_3 or the rate of uptake of SO_2 by the Na_2CO_3 to form Na_2SO_3 [1]. In order to determine the rate-controlling step, information on the kinetics of the thermal decomposition of $NaHCO_3$ are required.

The kinetics of the thermal decomposition of $NaHCO_3$ have been studied by many previous investigators [4–10]. The experimental conditions and the kinetic parameters reported by some previous studies are summarized in Table 1. These kinetic results are not in good agreement. Reaction orders of 2/3 or 1, and activation energies ranging from 65.1 to 112.4 kJ mol^{-1} have been reported. The discrepancies between these results may be caused by factors such as particle size, particle shape, method of kinetic analyses, etc. For example, the reaction of a large particle may be affected by external heat and mass transfer, and by internal conduction and diffusion effects. In this case, the kinetic parameters obtained are not the intrinsic values.

In this study, a $NaHCO_3$ powder of 47 μm mean particle size was used.

TABLE 1

Comparison of experimental conditions and results of various investigators for the thermal decomposition of $NaHCO_3$

Investigators	Experimental setup	Temperature range/°C	Particle size/μm	Reaction order
Jepson et al. [5]	Transfer lines		<40	1
Subramanian et al. [7]	DTA			1
Shefter et al. [6]	X-ray	82–95		2/3
Tobola [8]	DTA, DPA			
Galogaza and Mitrovic [4]	TGA in vacuo	99.9–128.5	95–625	2/3
Hartke et al. [9]	Circulating fluidized bed	127–203	137	2/3
Keener et al. [10]	Fixed bed	107–177	51–140	2/3
This study	TGA in N_2 gas	87–177	9–106	1

The intrinsic kinetics of the thermal decomposition of $NaHCO_3$ in flowing nitrogen gas was analyzed using thermogravimetric analysis.

EXPERIMENTAL

The sodium bicarbonate powder used in this experiment was obtained from Wako Pure Chemical Industries (Japan), purity >99.6%. A sample of the powder was examined using a scanning electron microscope. The particles were found to be tablet-like in shape. The particle surface was essentially smooth and non-porous. The particle size, determined by laser diffraction (Microtrac), was in the range 9–106 μm with a mean size of 47 μm. The BET surface area of the powder was measured as 0.37 $m^2\,g^{-1}$ by Quantasorb. Thus, the average particle thickness was calculated to be about 1.3 μm, assuming the particles to be flat plates.

The thermal decomposition of $NaHCO_3$ was performed using a Perkin-Elmer TGS-2 thermogravimetric analysis apparatus. Samples were heated from room temperature at three different constant heating rates (12.5, 2.5, and 5.0°C min^{-1}) until the decomposition was completed.

External and inter-particle transport effects were eliminated by using a sufficiently high flow rate of nitrogen gas and a small amount of solid particles spread thinly on the platinum sample pan. The minimum gas flow rate at which the effect of external transport became negligible was determined by continuously increasing the flow rate until the conversion versus temperature relationship no longer changed for the highest heating rate. This ensured the absence of external transport effects. The nitrogen gas flow rate used in this experiment was about 45 $cm^3\,min^{-1}$. Experiments were also carried out for various sample weights to verify the inter-particle transport effects being negligible. The weight of sodium bicarbonate used was about 4.5 mg.

KINETIC ANALYSIS

The stoichiometric equation of the thermal decomposition of $NaHCO_3$ is

$$NaHCO_3 \rightarrow 0.5Na_2CO_3 + 0.5CO_2 + 0.5H_2O \tag{2}$$

The rate equation of this reaction can be expressed as

$$dx/dt = kf(x) = k_0 \exp(-E/RT)\, f(x) \tag{3}$$

where x is the conversion of reactant, k is the rate constant, k_0 is the pre-exponential factor of k, E is the activation energy, and $f(x)$ is a function of the rate dependence on conversion.

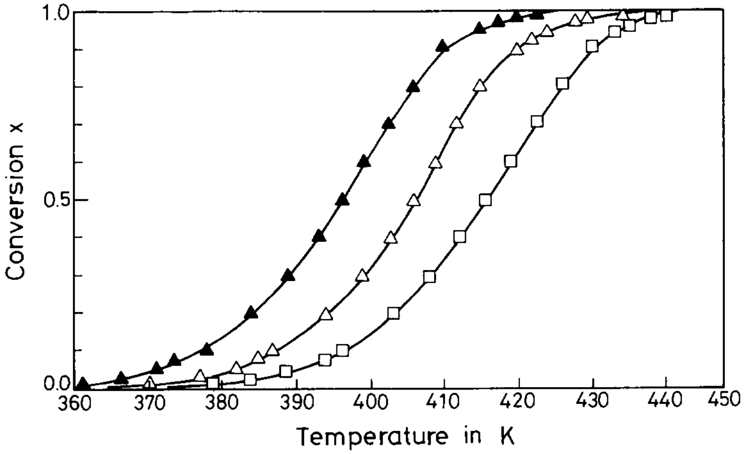

Fig. 1. Conversion vs. temperature for different heating rates: ▲, 1.25°C min^{-1}; △, 2.5°C min^{-1}; □, 5°C min^{-1}.

From the curves plotted by the TGA recorder, the variations in the fraction of weight remaining W/W_0, and the rate of weight change dW/dt with temperature were obtained directly. These data were transformed to x versus T and dx/dt versus T relationships, as shown in Figs. 1 and 2,

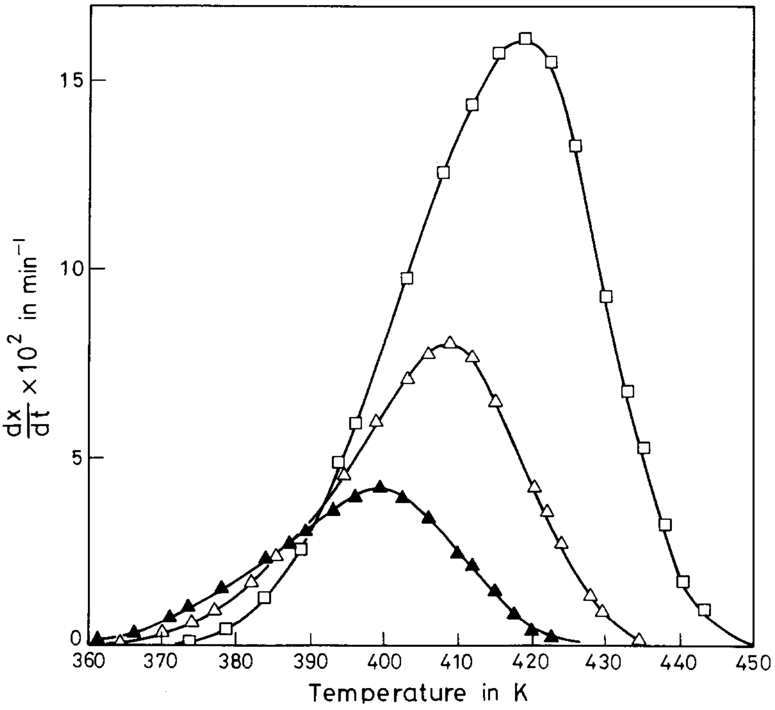

Fig. 2. Instantaneous reaction rates vs. temperature for different heating rates: ▲, 1.25°C min^{-1}; △, 2.5°C min^{-1}; □, 5°C min^{-1}.

respectively, using

$$x = 2.71\left(1 - \frac{W}{W_0}\right) \tag{4}$$

$$\frac{dx}{dt} = \frac{-2.71}{W_0}\left(\frac{dW}{dt}\right) \tag{5}$$

The temperature range in which the decomposition occurred depended on the heating rate. The overall temperature range for $NaHCO_3$ decomposition was about 360–450 K for the three heating rates used in this study.

There are many methods for analyzing non-isothermal kinetic data [11]. However, the results obtained using different methods may be different, due to the approximations made and the different data treatment techniques [12]. Thus, in this study two methods were used and their results are compared.

Graphical method

The form of the rate dependence on conversion $f(x)$ can be determined by the graphical method proposed by Criado [13] and Shih [14]. This method is based on the relationship

$$\left(\frac{T}{T_\alpha}\right)^2 \frac{(dx/dt)}{(dx/dt)_\alpha} \approx \frac{f(x)g(x)}{f(\alpha)g(\alpha)} \tag{6}$$

where α denotes the conversion x being equal to α, and

$$g(x) = \int_0^x \frac{dx}{f(x)} \tag{7}$$

By choosing a value of α (e.g. 0.5), curves for $f(x)g(x)/f(\alpha)g(\alpha)$ can be constructed for different forms of $f(x)$. Curves thus obtained are then compared with $(T/T_\alpha)^2(dx/dt)/(dx/dt)_\alpha$ calculated from experimental data to find the best form of $f(x)$. Figure 3 shows that the curve for $f(x) = (1-x)^{1.2}$ is in good agreement with the experimental data. The advantage of this graphical method is that the rate dependence on conversion or reaction order can be determined directly without knowledge of the activation energy. Because the reaction order is close to unity, it would be advantageous to simplify the kinetics to first-order. This would greatly simplify the subsequent use of the rate expression in the modeling of the thermal decomposition of $NaHCO_3$ in the FGD process. Thus, eqn. (3) can be rewritten

$$\frac{1}{(1-x)}\frac{dx}{dt} = k_0 \exp(-E/RT) \tag{8}$$

Taking logarithms of eqn. (8) gives

$$\ln\left(\frac{dx/dt}{1-x}\right) = \ln k_0 - E/RT \tag{9}$$

A straight line plot of $\ln((dx/dt)/(1-x))$ versus $1/T$, as shown in Fig. 4,

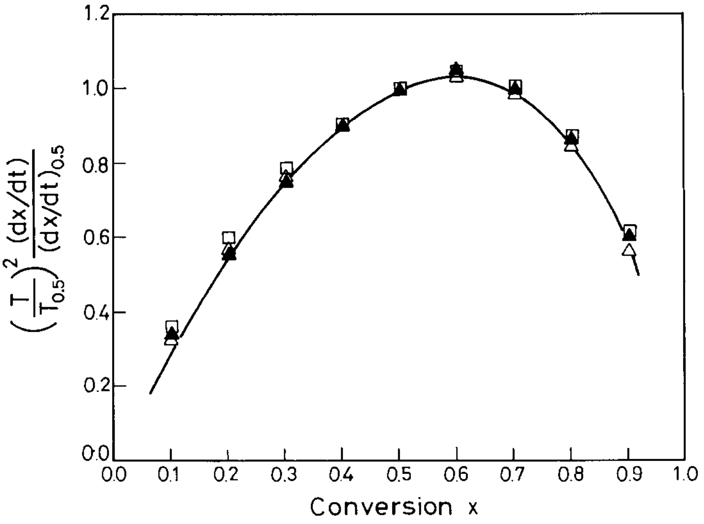

Fig. 3. Determination of reaction order by the graphical method: ▲, 1.25°C min^{-1}, △, 2.5°C min^{-1}; □, 5°C min^{-1}.

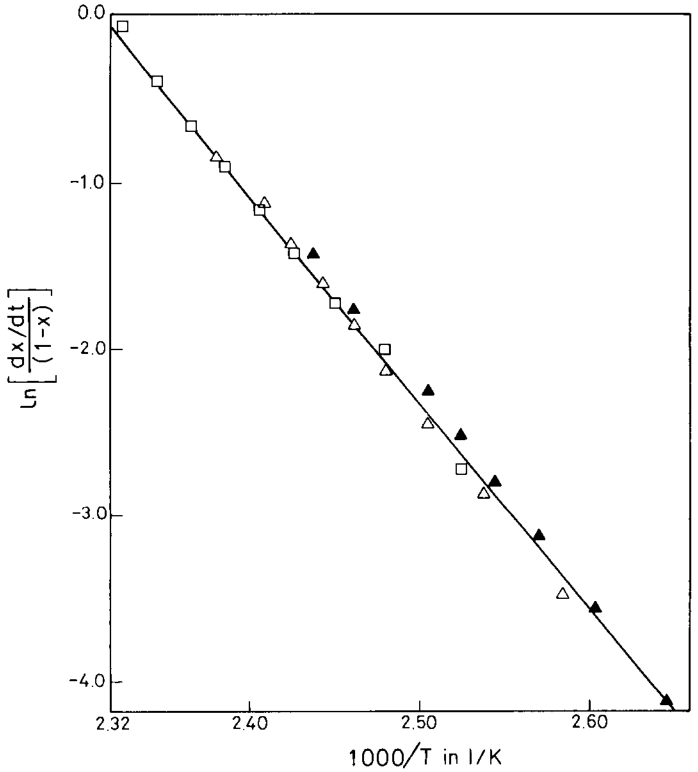

Fig. 4. Determination of the values of E and k_0 by plotting $\ln[(\mathrm{d}x/\mathrm{d}t)/(1-x)]$ vs. $1/T$: ▲, 1.25°C min^{-1}; △, 2.5°C min^{-1}; □, 5°C min^{-1}.

yields simultaneously the activation energy and the pre-exponential factor of the rate constant. The value of E is 105.8 kJ mol^{-1} and that of k_0 is 6.7×10^{12} min^{-1}. Consequently the rate equation of the thermal decomposition of $NaHCO_3$ to Na_2CO_3 can be expressed as

$$dx/dt = 6.7 \times 10^{12} \exp(-105\,800/RT)\,(1-x)\,(\text{min}^{-1}) \tag{10}$$

Friedman's method

Using Friedman's method [15], the activation energy can be determined without knowing the rate expression. Taking logarithms of eqn. (3) gives

$$\ln(dx/dt) = \ln k_0 - E/RT + \ln f(x) \tag{11}$$

Thus, for a certain value of x, the $\ln(k_0, f(x))$ and E values can be determined from the corresponding (dx/dt) and T values at different heating rates. Nine values of x were selected, ranging from 0.1 to 0.9, at equal intervals. Three sets of dx/dt and T values, one set for one heating rate, were taken for each x value from Figs. 1 and 2. Plots of $\ln(dx/dt)$ versus $1/T$ are shown in Fig. 5 for different values of x. The slope of each

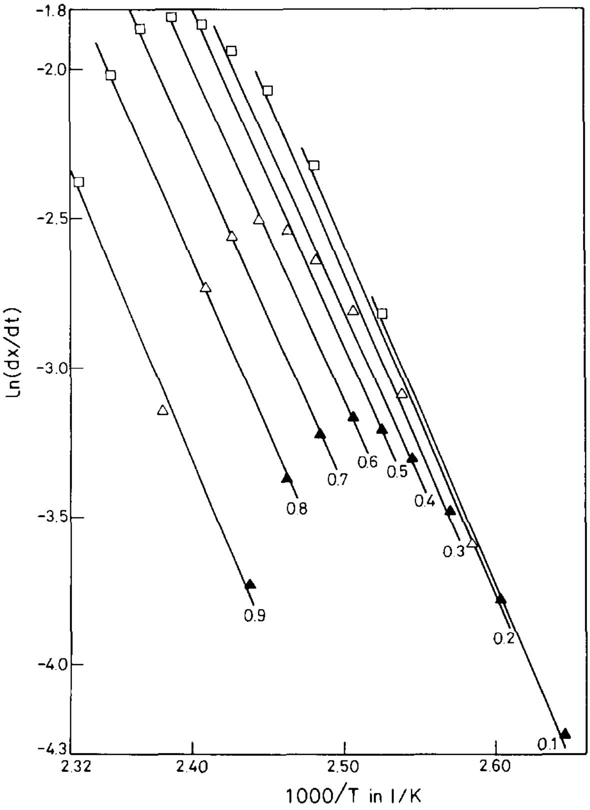

Fig. 5. Determination of kinetic parameters by Friedman's method: ▲, 1.25°C min^{-1}; △, 2.5°C min^{-1}; □, 5°C min^{-1}.

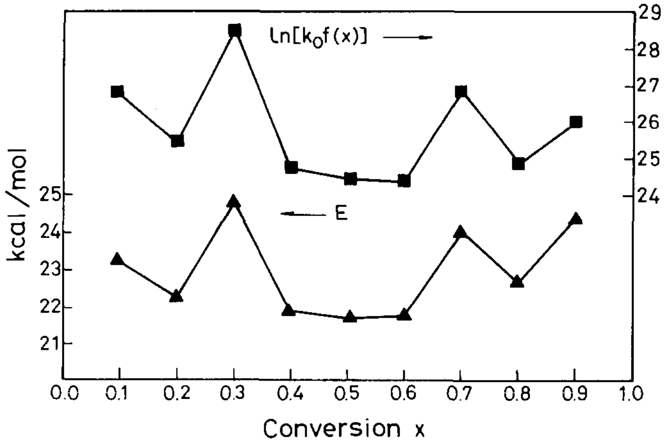

Fig. 6. The values of E and $\ln(k_0f(x))$ for different conversions determined using the Friedman method.

line gives the value of $-E/R$ and the intercept is equal to $\ln(k_0f(x))$. The values of E and $\ln(k_0f(x))$ are plotted against x in Fig. 6. It can be seen that E is fairly constant over the entire conversion range. The average value of E is 96.1 kJ mol^{-1}. Experimental data and the average value of E are substituted into eqn. (11) to determine the values of $\ln(k_0f(x))$. Average values of $\ln(k_0f(x))$ at each conversion are plotted as a function of $\ln(1-x)$ as shown in Fig. 7. A reasonably good straight line is obtained over the

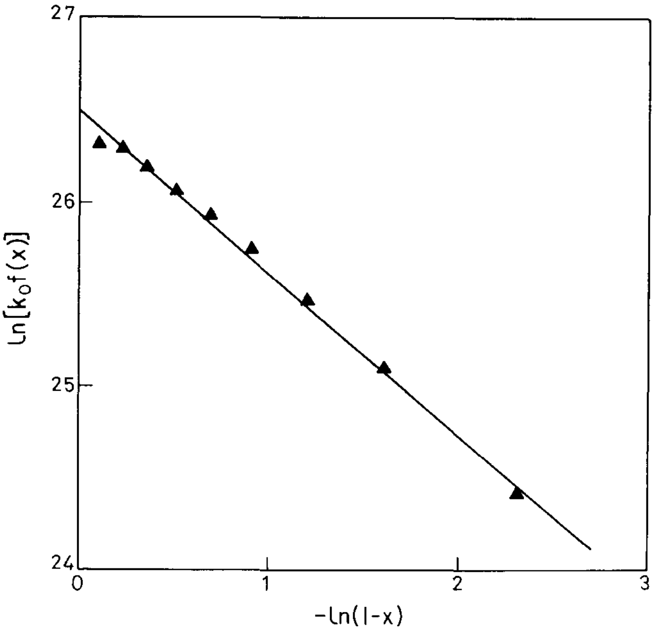

Fig. 7. Determination of the reaction order and the pre-exponential factor using the Friedman method.

entire range of conversion, indicating that the reaction order remains constant. According to the curve in Fig. 7 the reaction order is 0.9 and the value of the pre-exponential factor of the rate constant is equal to 3.2×10^{11} min^{-1}.

The reaction order determined by this method is lower than that determined by the graphical method; however, both values are close to unity. If the reaction order is taken as first-order, the activation energy must be recalculated by using eqn. (9). The result is identical to that shown in eqn. (10).

DISCUSSION

The kinetic analysis of the thermal decomposition of $NaHCO_3$ powder has shown that this is a first-order reaction. This indicates that the kinetics of the thermal decomposition of these $NaHCO_3$ particles can be described by the nucleation and growth model.

In Table 1, the kinetic parameters obtained in this study are compared with those of previous investigators. Some authors reported a reaction order of 2/3, which corresponds to shrinking-core model kinetics for a spherical particle, with chemical reaction being the rate-controlling step. Their activation energies are also lower than ours. The activation energy reported by Jepson et al. [5], however, is very close to ours, and they also reported a reaction order of unity. Their particle sizes were smaller than 40 μm, which is smaller than the particle sizes used by other investigators. Although some particles used in this work are larger than those used by Jepson et al., most are smaller than those used by others. Moreover, our particles are tablet-shaped with a very small average thickness (1.3 μm). Thus the differences in the reaction kinetics reported are believed to be caused by the differences in the particle sizes used. Most gas–solid reactions start by forming nuclei in the solid phase. For very fine solid particles, nuclei may form and grow within the entire volume of the particle. For large solid particles, these nuclei are formed at the surface of the solid and, as the reaction progresses, they grow in size and new ones are formed; eventually they overlap one another and cover the whole surface, thus forming the reaction interface in a shrinking-core system [16]. For large particles which react according to the shrinking-core model, the intraparticle diffusional resistance may be important, so the value of the activation energy for large particles may become smaller than that for small particles to which the nucleation and growth model is applicable.

A complete description of the thermal decompositon of $NaHCO_3$ to Na_2CO_3 in FGD processes must include intrinsic kinetics as well as transport effects. The results of this investigation will be used in subsequent work to analyze the thermal decomposition of large pellets of $NaHCO_3$. The transport effects will be more important for large pellets.

CONCLUSIONS

The kinetics of the thermal decomposition of $NaHCO_3$ was determined by a non-isothermal method. By using three constant heating rates, 1.25, 2, and $5°C\,min^{-1}$, $NaHCO_3$ powder of mean size 47 μm decomposed in the approximate temperature range of 360–450 K. Analyses by graphical and Friedman's methods gave results in agreement with each other. The reaction was first order, and its activation energy and pre-exponential factor were $105.8\,kJ\,mol^{-1}$ and $6.7 \times 10^{12}\,min^{-1}$, respectively. The kinetic parameters obtained here are believed to be intrinsic values. The differences in the reaction kinetics obtained in this work and previous investigations are caused by differences in the particle sizes used.

ACKNOWLEDGMENTS

The authors thank P.K. Haung and C.N. Lin for their assistance in the experimental work.

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