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Effects of particle size on the decomposition of ammonium carbonate

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Abstract

The decomposition of ammonium carbonate having three different particle size distributions has been studied by DSC. The samples consisted of large particles (302 ± 80 μm), intermediate particles (98 ± 36 μm) obtained by grinding the larger particles, and small particles (30 ± 10 μm) obtained by fracturing the large particles with ultrasound. Data from the decomposition of the intermediate particles gave the best fit with a first-order rate law. The bulk of the data for decomposition of the larger particles followed either a D3 or F1 rate law while a D3 rate law fit most of the data from decomposition of the smallest particles.

Keywords: Ammonium carbonate; Decomposition; Mechanism; Particle size

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1. Introduction

While particle size is known to affect the behavior of some materials in the solid state, the effects are diverse [1–4]. A reaction must be studied kinetically to determine the ways in which the physical condition of the particles is related to the rate of a reaction of the particles. It has been observed that particle size can affect the temperature and ΔH of phase transitions [5,6]. In earlier work, we studied the decomposition of $(NH_4)_2CO_3$ and NH_4HCO_3 to determine the nature of sample-to-sample variations [7,8]. It was found that analysis of the kinetic data by the Coats and Redfern procedure [9] gave the best fit with the first-order rate law. However,

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the rate law on which the Coats and Redfern method is based cannot represent several types of processes. Therefore, it is necessary to determine the kinetics of the decomposition using a more comprehensive data analysis technique. Also, it is desirable to determine how particle size affects the decomposition of $(NH_4)_2CO_3$. In this work we have studied three samples of $(NH_4)_2CO_3$ which have different particle size distributions.

2. Experimental

Reagent grade $(NH_4)_2CO_3$ was used without further chemical purification. A Nikon metallurgical microscope was used to determine the particle size distribution by examining a minimum of 100 particles using a previously described method [10]. The particle size of the original sample (designated as Sample I) was 302 ± 80 μm (mean ± standard deviation). Another sample was pulverized using a mortar and pestle. That sample (designated as Sample II) had a particle size distribution of 98 ± 36 μm. A third sample (Sample III) having a particle size distribution of 34 ± 10 μm was obtained by fragmenting the large crystals using ultrasound. Sonication of a suspension of $(NH_4)_2CO_3$ in dodecane was carried out using a Sonics and Materials Vibra Cell VC-60 ultrasonic generator operating at 20 kHz.

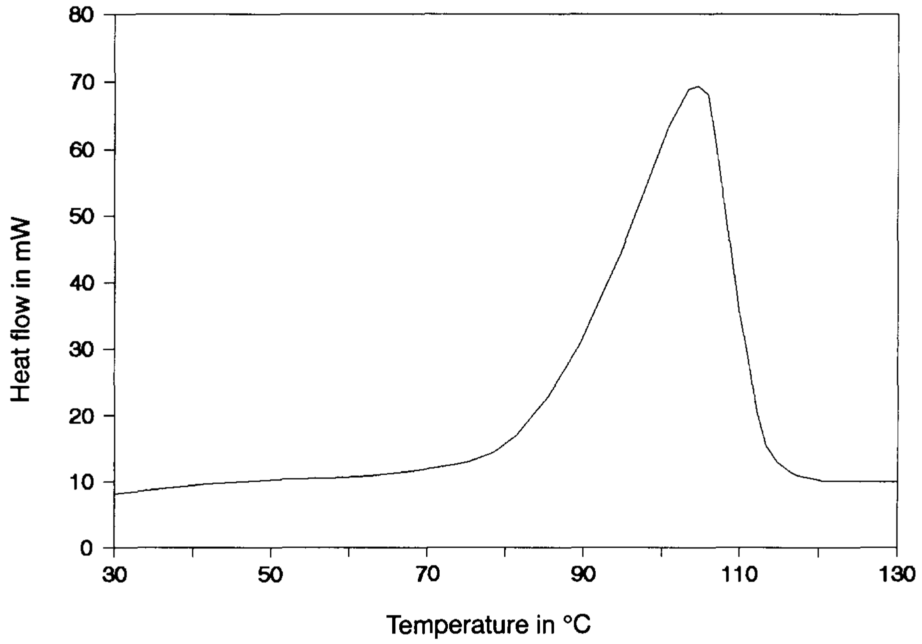

Fig. 1. A typical DSC curve for the decomposition of $(NH_4)_2CO_3$.

The suspension consisted of 0.5 g of $(NH_4)_2CO_3$ in 5 ml of dodecane and it was sonicated for 2 h to reduce the particle size.

Thermal studies were carried out using a Perkin-Elmer DSC-7 differential scanning calorimeter controlled by TAC-7 controller with IBM compatible software. The instrument was calibrated using the heat of fusion of indium. Samples were heated at 2.0, 4.0, and 8.0 K min^{-1} in a dry nitrogen atmosphere with a flow rate of 30 cm^3 min^{-1}. The fraction of the sample which had decomposed, α, was calculated at various temperatures by comparing the partial peak areas to that for a complete reaction. The (α,T) data were analyzed by the method of Reich and Stivala [11] to determine the rate law describing the decomposition reaction. Five runs using each of the samples were made at each heating rate to provide for permutation of the data sets in order to maximize the kinetic analysis of the data [12–15].

3. Results and discussion

All of the samples of $(NH_4)_2CO_3$ were found to decompose in a single step yielding a DSC curve similar to that shown in Fig. 1. From the area of the endothermic peak, the enthalpy of decomposition was found to be 189.8 ± 4.1 kJ mol^{-1} for the 15 runs using Sample I (particle size 302 ± 80 μm) at the three heating rates. The pulverized sample (II) having a particle size distribution of 98 ± 36 μm gave an endothermic peak which corresponded to an enthalpy of decomposition of 191.7 ± 4.5 kJ mol^{-1}. Sample III containing small particles (34 ± 10 μm) produced by sonicating the large particles gave a mean ΔH of 181.4 ± 12.2 kJ mol^{-1}. Thus, it appears that the thermodynamics of decomposition of $(NH_4)_2CO_3$ is essentially unaffected by the particle size of the material. However, for phase changes, it has been observed that the particle size distribution can have a considerable effect on the temperature at which the phase transition occurs and the enthalpy of the transition [5,6]. No such effects were observed in this work.

Partial peak areas were determined at various temperatures to calculate α by comparing the partial area to that corresponding to the complete reaction. Five runs were made at each heating rate of 2.0, 4.0, and 8.0 K min^{-1} using Samples I, II, and III. The Reich and Stivala procedure makes use of values at specified temperatures when the heating rates differ by a factor of two [11]. Using all possible combinations of the data sets from the runs resulted in 25 combinations for the runs at 2.0 and 4.0 K min^{-1} and another 25 combinations for the runs at 4.0 and 8.0 K min^{-1} for Samples I and II. However, for Sample III some of the α values at specified temperatures did not allow for enough data points to provide a reliable kinetic analysis. For Sample III, there were 19 usable data sets from runs at the two lower heating rates and 18 combinations from the runs at the two higher heating rates. Results of the analysis to determine the applicable rate law are shown in Table 1.

Several conclusions can be drawn from the data shown in Table 1. First, it is readily apparent that the kinetic analysis of the data sets from runs using Sample

Table 1
Rate laws obtained for the decomposition of $(NH_4)_2CO_3$

Rate law	Frequency of best fitting rate law[a]		
	Sample I[b]	Sample II[c]	Sample III[d]
4.0 and 8.0 K min^{-1} runs			
D3	8	0	15
F1	7	16	0
D4	3	0	0
D1	3	1	0
D2	1	0	0
R3	1	0	0
R2	1	7	0
A1.5	1	1	0
A4	0	0	0
P3	0	0	3
2.0 and 4.0 K min^{-1} runs			
D3	5	0	12
F1	9	17	0
D4	2	0	0
D1	2	4	0
D2	1	4	0
R3	2	0	0
R2	2	0	1
A1.5	2	0	1
A2	0	0	1
P3	0	0	4

[a] Number of best fit cases out of 25 combinations for Samples I and II and number out of 19 combinations (4 and 8 K min^{-1} runs) or out of 18 combinations (2 and 4 K min^{-1} runs) for Sample III. [b] Particle size 302 ± 80 μm. [c] Particle size 98 ± 36 μm. [d] Particle size 34 ± 10 μm.

I gave the best fit with a variety of rate laws. However, the first-order, F1, and three-dimensional diffusion control, D3, rate laws are indicated most often without a clear preference for either. Out of the 50 combinations of data sets for Sample I, 16 indicated a best fit with F1 and 13 gave a best fit with D3. A variety of rate laws gave the best fit in other cases with D1, one-dimensional control, and D4, Ginstling–Brounshtein, having five best-fitting cases each. It appears that the decomposition of the material consisting of the largest particles can best be considered as a first-order process in accord with our previous studies [7,8] which made use of the Coats and Redfern method of data analysis.

When the data from runs using Sample II, the pulverized sample having a particle size of 98 ± 36 μm, are examined, it is seen that the kinetic results are considerably more consistent. For example, out of 50 combinations of data sets, 33 gave the best fit with the F1 rate law while seven gave the best fit with the R2, receding area, rate law. Eight additional combinations gave the best fit with D1 and D2 rate laws (four each).

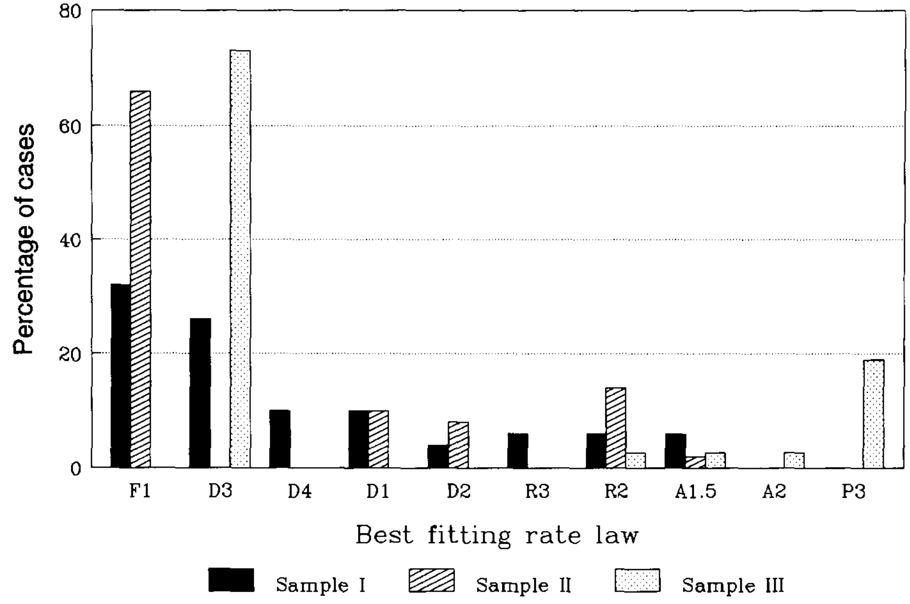

Fig. 2. Distribution of best-fitting rate laws for decomposition of the three samples of $(NH_4)_2CO_3$. Sample I consists of particles in the range 302 ± 80 μm; Sample II consists of particles in the range 98 ± 36 μm; and Sample III consists of particles in the range 34 ± 10 μm.

Sample III which had been subjected to ultrasound was extensively fragmented and had a particle size of 34 ± 10 μm. Although five runs were made at each heating rate, only 19 usable combinations of data sets could be made from the runs at 2.0 and 4.0 K min^{-1} and 18 could be made from the runs at 4.0 and 8.0 K min^{-1}. The results of the kinetic analysis of data for the decomposition of Sample III are also shown in Table 1. The data show that the decomposition of the extensively fragmented $(NH_4)_2CO_3$ is more likely to be represented as a three-dimensional diffusion control D3 rate law. In fact, 27 of the 37 data combinations gave a best fit with the D3 rate law while seven others indicated the P3 rate law and three others gave the best fit with the A2, A1.5, or R2 rate law (one each). It appears that the decomposition of particles of $(NH_4)_2CO_3$ in the range 302 ± 80 μm is best modeled with an F1 or D3 rate law, those in the range 98 ± 36 μm with an F1 rate law and those in the range 34 ± 10 μm with a D3 rate law. While the enthalpy of decomposition appears to be independent of particle size, the rate law modeling the decomposition reaction varies with the particle size distribution. In view of the fact that $(NH_4)_2CO_3$ consisting of large particles decomposes according to an F1 rate law, the Coats and Redfern procedure, which can correctly model processes following rate laws based on reaction order, appears to be adequate. The decomposition of $(NH_4)_2CO_3$ was studied by TG in an earlier study of sample-to-sample variations with the data being analyzed by the Coats and Redfern method [7]. It was found that the best fit to most of the data was provided by a first-order rate law, although some runs gave the best fit with other indices of reaction. Although the present study utilized a different experimental technique and a more comprehensive data analysis technique, the rate law for decomposition of Samples I and II appears to be in agreement with the one previously identified [7].

Sample III which had been subjected to ultrasound was extensively fragmented and had a particle size of 34 ± 10 μm. Although five runs were made at each of the heating rates of 2, 4, and 8 K min^{-1}, some of the endothermic peaks accompanying decomposition were shifted in temperature slightly so that it was not possible to obtain α values at the same temperatures for all of the combinations of runs. Instead of having 25 combinations, 18 were available from the runs at 2 and 4 K min^{-1} and 19 were available from the runs at 4 and 8 K min^{-1}. The results of the kinetic analysis of data for decomposition of the sonicated material are also shown in Table 1. A comparison of the data for Sample III with those for Samples I and II shows that the decomposition of the fragmented crystals having a particle size distribution of 34 ± 10 μm are much more likely to follow a D3 law. In fact, 27 of the 37 data combinations gave a best fit with the D3. A comparison of the data from all three samples is shown in Fig. 2. Since there were different numbers of data sets involved, this figure makes it easier to compare the results from the three samples because it is based on the percent of runs fitting the various rate laws.

Clearly, the F1 and D3 rate laws fit most of the data for Sample I and the F1 rate law fits the majority of the data for Sample II, the pulverized sample. After sonication of the particles, the D3 rate law fits most of the data. For the untreated sample and the pulverized sample, the rate of decomposition appears to be dependent on the amount of material present as represented by particle size and is first order. After sonication, the rate of decomposition appears to be quite clearly governed by a diffusion-controlled process. This may indicate that the process of sonication causes localized heating or high-energy collisions between particles which remove existing nuclei or causes the particles to be more uniform dimensionally. At any rate, there is clearly a considerable difference between the kinetics of decomposition of ground $(NH_4)_2CO_3$ and that which has been subjected to ultrasound. It is quite likely that these results are characteristic of many other reactions of solids, and we are currently investigating these effects for other systems.

References

[1] M.E. Brown, D. Dollimore and A.K. Galwey, in C.H. Bamford and D.F.H. Tipper (Eds.), Comprehensive Chemical Kinetics, Vol. 22, Elsevier, Amsterdam, 1972.
[2] C. Kutal and J.C. Bailar, Jr., J. Phys. Chem., 76 (1972) 119.
[3] H. Tanaka, S. Ohshima, S. Ichiba and H. Negita, Thermochim. Acta, 48 (1981) 137.
[4] D.A. Young, Decomposition of Solids, Pergamon Press, Oxford, 1966.
[5] M.J.M. Van Oort and M.L. Cotton, Thermochim. Acta, 219 (1993) 245.
[6] T. Okamoto, N. Nalamura and H. Chilhara, Bull. Chem. Soc. Jpn., 52 (1979) 1619.
[7] J.E. House, Jr., Thermochim. Acta, 47 (1981) 379.
[8] J.E. House, Jr., Inorg. Nucl. Chem. Lett., 16 (1980) 185.
[9] A.W. Coats and J.P. Redfern, Nature (London), 201 (1964) 68.

[10] J. Stockham and E. Fochtman, Particle Size Analysis, Ann Arbor Science, Ann Arbor, 1977, pp. 27–31.
[11] L. Reich and S.S. Stivala, Thermochim. Acta, 62 (1983) 129.
[12] J.E. House, Jr. and L.A. Marquardt, J. Solid State Chem., 89 (1990) 153.
[13] J.E. House, Jr. and L.A. Marquardt, Transition Met. Chem., 18 (1993) 548.
[14] J.E. House, Jr. and R.P. Ralston, Thermochim. Acta, 214 (1993) 255.
[15] J.E. House, Jr. and R.W. Eveland, J. Solid State Chem., 105 (1993) 136.