Thermochimica Acta, 104 (1986) 101–109
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

INFLUENCE OF THE SELF-GENERATED AND CONTROLLED ATMOSPHERE ON THE THERMAL DECOMPOSITION OF BASIC NICKEL CARBONATE, $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$

HIROSHI HENMI, MITSUO MORI and TORU HIRAYAMA

Department of Industrial Chemistry, School of Engineering, Tokai University, 1117 Kitakaname, Hiratsuka, Kanagawa-pre, 259-12 (Japan)

NOBUYASU MIZUTANI * and MASANORI KATO

Department of Inorganic Materials, Faculty of Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152 (Japan)

(Received 26 December 1985)

ABSTRACT

Thermal decomposition of basic nickel carbonate, $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$, was studied by high pressure DTA using various types of sample holder under high pressure carbon dioxide and nitrogen (0–50 atm).

The decomposition proceeded in two steps. In the first step, the water of crystallization evolved to give an anhydride, and in the next step both H_2O and CO_2 evolved to give NiO. The decomposition temperature increased as the pressure of carbon dioxide and nitrogen increased. The DTA peaks were changed by using different sample holders. The relationship between the decomposition temperature and the formation of self-generated atmosphere is discussed.

INTRODUCTION

The basic carbonates were classified into three groups on the basis of the thermal decomposition mechanism by Kato and Mizutani [1]. The thermal decomposition of hydroxy magnesium carbonate [2], hydroxy lead carbonate [3] and basic copper carbonate [4] has already been reported.

Basic nickel carbonates (hydroxy nickel carbonates and oxy nickel carbonates) having different compositions have been reported, i.e., various hydrated normal nickel carbonates ($NiCO_3 \cdot H_2O$, $NiCO_3 \cdot 2H_2O$, $NiCO_3 \cdot 3H_2O$, $NiCO_3 \cdot 6H_2O$ [5], etc), hydroxy nickel carbonates ($NiCO_3 \cdot 4Ni(OH)_2 \cdot H_2O$ [6], $NiCO_3 \cdot 3Ni(OH)_2 \cdot 4H_2O$ [6], $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$ [6], $3NiCO_3 \cdot 4Ni(OH)_2 \cdot 12H_2O$ [6], $5NiCO_3 \cdot 2Ni(OH)_2 \cdot 7H_2O$ [6],

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* Author to whom all correspondence should be addressed.

0040-6031/86/$03.50

$4NiCO_3 \cdot Ni(OH)_2$ [6,7], $3NiCO_3 \cdot Ni(OH)_2$ [6,7], $3NiCO_3 \cdot 4Ni(OH)_2 \cdot 12H_2O$ [8], etc.) and oxy nickel carbonates [6] ($NiCO_3 \cdot 21NiO \cdot 18H_2O$, $NiCO_3 \cdot 20NiO$, $NiCO_3 \cdot 16NiO \cdot 21H_2O$, $NiCO_3 \cdot 15NiO \cdot 14H_2O$, $NiCO_3 \cdot 13NiO \cdot 16H_2O$).

The composition of these carbonates is influenced by the synthetic conditions such as pH, temperature, atmosphere, aging duration, etc.

Deren et al. [9] investigated, using TG, DTA and powder X-ray diffraction, the decomposition of $NiCO_3$ that was complete at 500°C, and the surface of NiO of the final product was covered with chemisorbed oxygen.

Topor et al. [10] reported that the decomposition of $NiCO_3$ in air took place within the temperature range from 300 to 420°C, and the DTG curve having a small bend, permitted the assumption that the decomposition of $NiCO_3$ proceeded in several steps in air.

Carthey et al. [11] reported that the thermal decomposition of $NiCO_3 \cdot 2Ni(OH)_2 \cdot 2H_2O$ which was heated to constant weight at 105°C showed the dehydration of two molecules of water of crystallization at about 290°C, as follows

$$NiCO_3 \cdot 2Ni(OH)_2 \cdot 2H_2O \rightarrow NiCO_3 \cdot 2Ni(OH)_2 + 2H_2O$$

Mallaya et al. [12] reported on the thermal decomposition of various basic nickel carbonates and found that the weight loss occurred in two steps for all samples heated at 2°C min^{-1}. The evolution of H_2O only and of H_2O and CO_2 occurred from 90 to 200°C and from 270 to 420°C, respectively, but with rapid heating rate, two steps overlapped into one step. Table 1 shows the thermal decomposition behaviors of various basic nickel carbonates.

However, in addition to the anticipation of the decomposition process from the weight loss as mentioned above, it is important to ensure the decomposition process by analyzing the gases evolved from the sample.

Furthermore, when the relationship between the dehydration or the decomposition temperature and partial pressure is considered, it is not possible

TABLE 1

Thermal decomposition behaviors of various basic nickel carbonates [12]

Initial	Intermediate	Final
$2NiO \cdot CO_2 \cdot 5H_2O$	$\rightarrow 2NiO \cdot CO_2 \cdot H_2O$	
$2NiO \cdot CO_2 \cdot 3H_2O$	$\rightarrow 2NiO \cdot CO_2 \cdot H_2O$	
$3NiO \cdot CO_2 \cdot 6H_2O$	$\rightarrow 3NiO \cdot CO_2 \cdot H_2O$	
$4NiO \cdot CO_2 \cdot 7H_2O$	$\rightarrow 4NiO \cdot CO_2 \cdot 3H_2O$	
$4NiO \cdot CO_2 \cdot 5H_2O$	$\rightarrow 4NiO \cdot CO_2 \cdot 3H_2O$	$\rightarrow NiO$
$14NiO \cdot CO_2 \cdot 16H_2O$	$\rightarrow 14NiO \cdot CO_2 \cdot 11H_2O$	
$16NiO \cdot CO_2 \cdot 14H_2O$	$\rightarrow 16NiO \cdot CO_2 \cdot 9H_2O$	
$17NiO \cdot CO_2 \cdot 21H_2O$	$\rightarrow 17NiO \cdot CO_2 \cdot 15H_2O$	
$22NiO \cdot CO_2 \cdot 18H_2O$	$\rightarrow 22NiO \cdot CO_2 \cdot 12H_2O$	

to ignore the problem of the self-generated atmosphere caused by the gas evolved from the sample. It is necessary to make clear these relationships for the elucidation of the correct mechanism of the decomposition.

The decomposition of $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$ was studied on the basis of the influence of the controlled atmosphere and the self-generated atmosphere on dehydration and decomposition temperatures and the analysis of evolved gas on heating.

The experiment was carried out using the open sample holder (without cover) and the closed one (with double covers) over a wide pressure range of N_2 and CO_2 (0–50 atm).

EXPERIMENTAL

Samples

Reagent grade basic nickel carbonate (Kanto Chemical Co., Japan) was used as the sample. The $NiO : CO_2 : H_2O$ molar ratio (1.00 : 0.27 : 2.32) was determined by chemical analysis, and was almost equal to the ideal composition $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$(1.00 : 0.33 : 2.00).

Differential thermal analysis and thermogravimetry

The DTA–TG apparatus (Type M8076, Rigaku Denki Co., Japan) was used.

The high-pressure DTA apparatus [2] was designed and constructed by authors. The sample was heated under various CO_2 and N_2 pressures at a heating rate of 15°C min^{-1} up to 500°C. The atmosphere in the DTA chamber was changed from air to CO_2 or N_2 by filling with pure CO_2 or N_2 up to 5 kg cm^{-2} and discharging three times before heating. The CO_2 or N_2 was then passed through this chamber (about 10 ml min^{-1}) to remove rapidly the gases evolved on thermal decomposition.

Evolved gas analysis

The differential thermal gas analysis (DTGA) developed by Mizutani and Kato [13] was used. The gas evolved from the sample was determined by detecting the change of the thermal conductivity of the carrier gas. He and CO_2 gases were used as the carrier gas. The flow rate of a carrier gas was about 40 ml min^{-1}. The trap of P_2O_5 or Ascarite was inserted before the thermal conductivity detector (TCD) in the gas flow system to identify the evolved gas.

X-ray powder diffraction

The sample was identified using X-ray diffractometer (Type 2171, Rigaku Denki Co., Japan) with Cu target and monochromator.

RESULTS AND DISCUSSION

Decomposition process

Figure 1 shows the typical curves of DTA–TG. The $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$ decomposed to give NiO as the final product (heating rate, 10°C min^{-1}; sample weight, 9.8 mg; in air; open sample holder). DTA showed two broad endothermic peaks. The TG curve suggested two steps lie in the decomposition process. The first weight loss was due to evolution of water of crystallization, and the second to both dehydration and decarbonation.

Figure 2 shows the results of thermogravimetry (TG) using the closed sample holder (double covers) at various heating rates (0.625, 2.5, 5, 10°C min^{-1}). The shapes of TG curves are at various heating rates mutually similar. These curves have two sharp bends about 200 and 200–350°C, which indicate that the decomposition proceeds by two steps.

From Figs. 1 and 2, the weight loss of the first step (about 20%) is almost the same as the weight of $4H_2O$ (about 19.9%) dehydrated from $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$.

Figures 3 and 4 show the DTGA curves of $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$ in He and CO_2 flows, respectively, as a carrier gas using the P_2O_5 and Ascarite traps. P_2O_5 can absorb water but not CO_2 and Ascarite trap containing

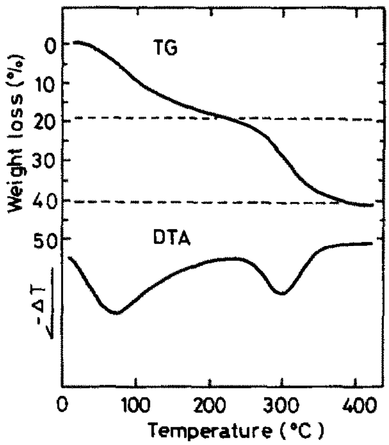

Fig. 1. Typical curves of DTA–TG in air (heating rate, 10°C min^{-1}; sample weight, 9.8 mg).

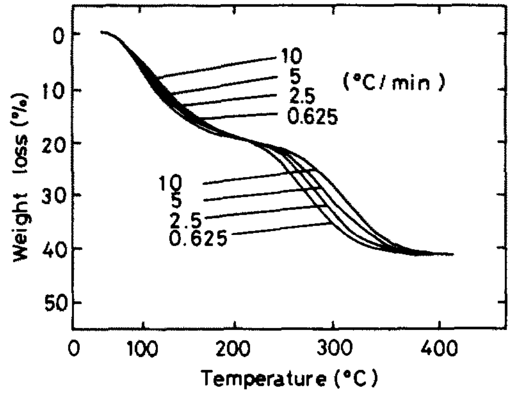

Fig. 2. TG curves using the closed sample holder (heating rate, 0.625, 2.5, 5 and 10°C min^{-1}; sample weight, 10 mg).

KOH can absorb both water and CO_2. In DTGA, the same evolved gas with the carrier gas is not detected, for example, evolved CO_2 gas in CO_2 carrier gas. By using these techniques we can not only detect the evolved gas but also identify the species of these gases in relative simple reactions.

In Fig. 3, the gas evolved from the sample at about 100°C, was absorbed with P_2O_5 and Ascarite traps. Therefore, the first peak is due to dehydration. While, the gas evolved at 200–350°C, was absorbed perfectly with the Ascarite trap, but only partially with P_2O_5 trap, compared with the peak area of the second peak of (a) and (b).

In Fig. 4(a), two evolution peaks appeared without a trap in CO_2. This supposes that the second peak is due to evolution of H_2O. While, in Figure 4(b), no peak appeared with a P_2O_5 trap in CO_2. But, in Fig. 3, the second peak appeared with a P_2O_5 trap in He. This supposes the evolution of some other gas except water, probably CO_2. These observations suggest that the second peak is due to the simultaneous evolution of both water and CO_2.

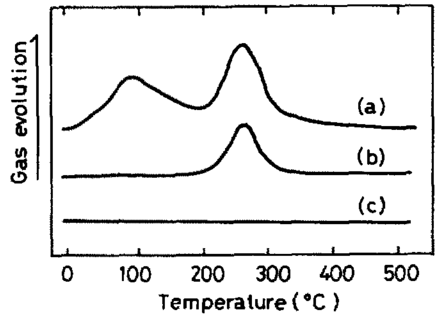

Fig. 3. Differential thermal gas analysis curves in He [heating rate, 10°C min^{-1}; sample weight, 5 mg; (a) no trap; (b) P_2O_5 trap; (c) Ascarite trap; carrier gas, He 40 ml min^{-1}].

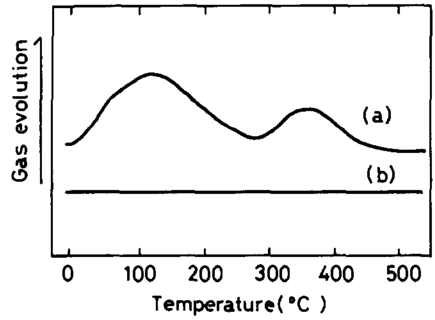

Fig. 4. Differential thermal gas analysis in CO_2 [heating rate, 10°C min^{-1}; sample weight, 30 mg; (a) no trap; (b) P_2O_5 trap; carrier gas, CO_2 40 ml min^{-1}].

The ratio of evolution of H_2O at the first step to that in the second step was about 2 : 1, i.e., the evolution of $4H_2O$ in the first step and that of $2H_2O$ in the second step occurred, respectively.

From the above-mentioned, the thermal decomposition of $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$ proceeds in two steps.

In the first step the dehydration of water of crystallization occurs, and in the second step, the decomposition of anhydride [$NiCO_3 \cdot 2Ni(OH)_2$] occurs. That is, the thermal decomposition mechanism is presented as follow

$$NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O \rightarrow NiCO_3 \cdot 2Ni(OH)_2 + 4H_2O \text{ (1st step)} \quad (1)$$

$$NiCO_3 \cdot 2Ni(OH)_2 \rightarrow 3NiO + CO_2 + 2H_2O \text{ (2nd step)} \quad (2)$$

Effect of atmosphere on decomposition

Typical DTA curves using the open sample holder at various CO_2 pressure are shown in Fig. 5. Figure 6 shows the relationship between CO_2 and N_2 pressures and peak temperatures, which were obtained from DTA curves used the open sample holder (without cover) and the closed one (with double covers).

In Fig. 6, the decomposition temperature of anhydride ($NiCO_3 \cdot 2Ni(OH)_2$) in CO_2 increases as the pressure increases and becomes constant above 30–40 atm for both sample holders. The two curves of (a) and (b) are similar because the evolved gas is the same as the gas of the atmosphere. But the small differences in the two curves in the lower pressure range may be due to the effect of slightly increasing the pressure of CO_2 and H_2O by using the closed sample holder compared with the open one. In N_2 atmosphere, the decomposition temperature [(e) and (f)] also increases with the pressure, but is lower than in CO_2 atmosphere. But, the large difference between the open and closed sample holder is due to the self-generated atmosphere in the closed one. The decomposition temperature for the closed sample holder

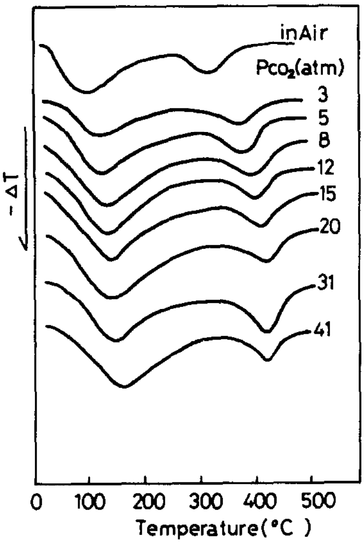

Fig. 5. Typical DTA diagrams using the open sample holder at various CO_2 pressures (heating rate, 15°C min^{-1}; sample weight, 10 mg).

above about 25 atm seems to be constant, but lower than in CO_2 atmosphere.

The dehydration temperature of water of crystallization [(c), (d), (g) and (h)] in CO_2 and N_2 also increases as the pressure increases and seems to be

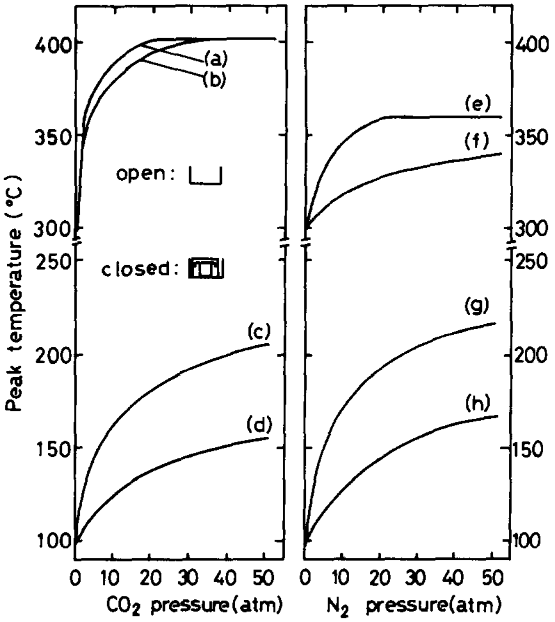

Fig. 6. Relationship between CO_2 and N_2 pressures and peak temperatures. (a), (c), (e), (g) closed sample holder; (b), (d), (f), (h) open one.

influenced only by the H_2O pressure. The dehydration temperature of (c) and (g) is higher than that of (d) and (h), and the temperature difference is about 50°C. This indicates that the H_2O pressure in the closed sample holder is considerably higher than that in the open one.

If the decomposition proceeds under the perfectly closed system, the decomposition of 10 mg of $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$ products the H_2O of 1.1×10^{-4} mole in the first step, and the H_2O of 5×10^{-5} mole and CO_2 of 2.7×10^{-5} mole in the second step. When these values are converted into the volume, the volume of H_2O in the first step should be 2.4 cm^3, and in the second step those of H_2O and CO_2 should be 1.1 and 0.6 cm^3, respectively. The volume of the sample holder used is 0.015 cm^3 (here, the volume of sample is ignored). In the first step, the sample holder is filled up sufficiently with only about 0.6% of water of crystallization. When the water of crystallization fully evolves, the H_2O should become 160 times greater than the volume of the sample holder. However, it is considered that such a value is not truly able to be achieved because the sample holder is not a perfectly closed system. In the case of the second step, a similar calculation may be carried out.

In conclusion, a self-generated atmosphere can be realized in a high pressure DTA as in a conventional one, but has no influence on DTA curves when a self-generated atmosphere is the same gas species as the controlled atmosphere.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the technical suggestion of Mr. O. Sakurai for high pressure DTA, and the assistance of Mr. K. Adachi and Mr. K. Miyazawa for examination.

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