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THERMAL DECOMPOSITION OF SILVER CARBONATE
1. DIFFERENTIAL THERMAL GAS ANALYSIS

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ABSTRACT

The thermal decomposition of silver carbonate (Ag_2CO_3) was studied using the following methods: gas analysis (differential thermal gas analysis) in helium, carbon dioxide and oxygen flows with and without a P_2O_5 or KOH trap, DTA–TG in a static air atmosphere and in a carbon dioxide flow and X-ray diffraction analysis of the specimens quenched from the DTA–TG apparatus.

The gas evolution at ~ 200 °C consisted of carbon dioxide. A simultaneous evolution of carbon dioxide and oxygen took place at ~ 400 °C. An endothermic phenomenon at ~ 194 °C without weight loss in a carbon dioxide atmosphere was estimated to be due to a phase transition of Ag_2CO_3 from the normal to the high-temperature form. An inhomogeneous decomposition mechanism was proposed.

INTRODUCTION

The thermal decomposition of silver carbonate (Ag_2CO_3) proceeds via multiple steps. The decomposition process is affected by the conditions of preparation of the silver carbonate [1, 2], by dopants (K [3], Cs [3], Ca [4], Sr [4], Ba [3, 5], Y [6,7] and Gd [7,8]) and by the decomposition atmosphere [7, 9–12]. Conflicting results have been reported by different workers. The decomposition steps are divided into two major groups (one group at ~ 200 °C (150–250 °C) and the other at ~ 400 °C (350–450 °C)), although

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a few exceptions may exist [2]. Many studies have been concerned with the decomposition at ~ 200 ° C; their aim has been the preparation of a so-called "active" catalyst for the oxidation of ethylene or a regenerative sorbent for carbon dioxide. Results of gas analysis at ~ 400 ° C have not been reported, although gas analysis is indispensable in the understanding of the decomposition mechanism at ~ 400 ° C where multiple DTA peaks are often observed. It is important to determine whether decarbonation occurs prior to the reduction at ~ 400 ° C or whether decarbonation and reduction occur simultaneously. In this study, the thermal decomposition of silver carbonate was investigated by differential thermal gas analysis (DTGA).

EXPERIMENTAL

Specimen

Reagent grade silver carbonate (Ag_2CO_3) (Wako Pure Chemical Co. Ltd., Japan) was used. The X-ray diffraction pattern showed Ag_2CO_3 (normal form [13]); no other phase was detected. The powder specimens (light green) were used for the thermal analyses without grinding.

Differential thermal gas analysis

The gases evolved from the heated specimen were determined using a differential thermal gas analysis (DTGA) system developed by Mizutani and Kato [14]. The apparatus is presented in Fig. 1. The evolution of gas from the specimen was determined by the change in the thermal conductivity of the carrier gas or the reactor gas (detectors, TCD-1 and TCD-2). The main constituents of the gas evolved from the specimen were assumed to be carbon dioxide, water vapour and oxygen. The arrangement presented in Fig. 1, i.e. (1) a helium gas flow with a P_2O_5 trap which removes water vapour, (2) a helium gas flow with a KOH ("Askarite") trap which removes both water vapour and carbon dioxide, (3) a carbon dioxide gas flow with a P_2O_5 trap, and (4) an oxygen gas flow with a KOH trap, was used to examine this assumption.

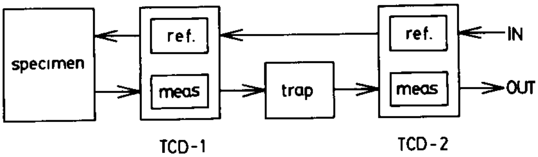

Fig. 1. Arrangement of DTGA system: TCD, thermal conductivity detector; ref., reference cell of TCD; meas., measurement cell of TCD; trap, P_2O_5 or KOH.

DTA–TG

A DTA–TG instrument (Rigaku-Denki Co. Ltd., Japan) was used in a static air atmosphere and in a carbon dioxide flow (50 ml min^{-1}) with a heating rate of ~ 10 °C/min^{-1}. The powder specimens were packed tightly into the platinum specimen containers (8 mm (ϕ) × 4 mm).

X-ray diffraction analysis

The decomposed specimens were quenched in the DTA–TG instrument. A Philips PW-1100 X-ray powder diffractometer with a copper target and a nickel filter was used for the analysis.

RESULTS

DTA–TG

The decomposition process was examined by DTA–TG prior to DTGA. The decomposition apparently proceeds via two steps in a static air atmosphere (Fig. 2A). The total weight loss from TG (21.5%) agrees with the theoretical value (21.8%) of silver carbonate to metallic silver.

Four endothermic peaks are observed during the decomposition in a carbon dioxide flow (Fig. 2B). The first (194 °C) is not accompanied by a weight loss. When the specimen is cooled from ~ 220 °C, an exothermic peak is observed at 180 °C. The endothermic and exothermic peaks are repeatedly observed during cyclic heating and cooling between 160 and

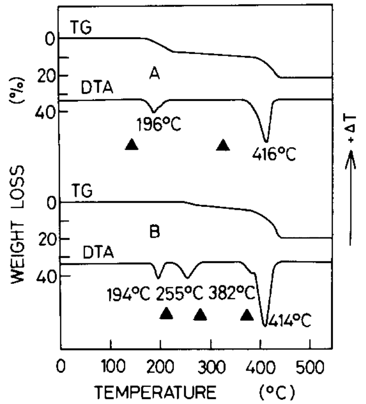

Fig. 2. DTA–TG for the thermal decomposition of Ag_2CO_3: A, in a static air atmosphere; B, in a carbon dioxide flow; Δ, temperature of quenching for X-ray diffraction analysis.

220 °C, although the peak intensities decrease gradually during repeated cycling.

The second endothermic peak (255 °C) in a carbon dioxide flow (Fig. 2B) is accompanied by a small amount of weight loss in TG.

The decomposition at ~ 400 °C in a carbon dioxide flow (Fig. 2B) seems complicated; a strong endothermic peak at 414 °C accompanies a small peak (382 °C). In a static air atmosphere (Fig. 2A), a single peak is observed at ~ 416 °C.

Differential thermal gas analysis

The results of the differential thermal gas analysis are shown in Fig. 3. In a helium gas flow (Fig. 3A), the result without a trap (full line) shows multiple steps of gas evolution; the thermal conductivities of the gases evolved are lower than that of helium. Water vapour is not detected since the result with a P_2O_5 trap (not shown in Fig. 3A) is the same as that without a trap. The result with a KOH trap is shown by the broken line in Fig. 3A. The KOH trap absorbs the gas corresponding to the peak at ~ 200 °C. This supports the hypothesis that the gas evolution at ~ 200 °C consists of carbon dioxide. Two small peaks are observed at ~ 400 °C after passing through a KOH trap. This supports the simultaneous decarbonation and reduction. The small peak heights are explained qualitatively by the thermal conductivity of oxygen which is between that of helium and carbon dioxide.

The result in a carbon dioxide flow (without a trap) is shown in Fig. 3B. No gas evolution is detected until ~ 300 °C. This supports the hypothesis that decarbonation occurs at ~ 200 °C. Two peaks are detected at ~ 400 °C.

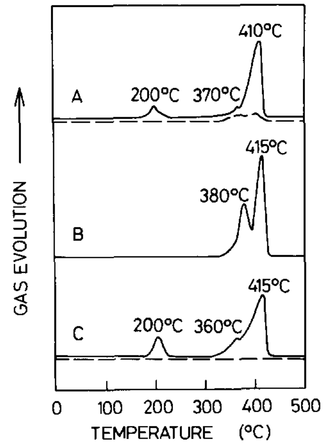

Fig. 3. DTGA for the thermal decomposition of Ag_2CO_3: A, in a helium flow; B, in a carbon dioxide flow; C, in an oxygen flow. Full line, without a trap (detected by TCD-1); broken line, with a KOH trap (detected by TCD-2); heating rate, ~ 10 °C/min^{-1}.

The thermal conductivity of the gas evolved is higher than that of carbon dioxide, so that the evolution of oxygen (two peaks) is obvious. The same result is obtained with a P_2O_5 trap (not shown in Fig. 3B).

The results in an oxygen flow are shown in Fig. 3C. The result without a trap (full line) is similar to that in a helium flow (Fig. 3A). The thermal conductivity of the gas evolved is lower than that of oxygen. No gas evolution is detected after the KOH trap (broken line). This shows that the gas evolved from the specimen consists of carbon dioxide apart from oxygen.

X-ray diffraction analysis

The temperatures from which the specimens were quenched in the DTA–TG instruments for X-ray diffraction analysis are shown by the triangles in Fig. 2. The diffraction pattern of Ag_2CO_3 [13] was observed for all the specimens in the present experiments with the exception of that quenched (500 °C) after the completion of decomposition. X-ray analysis (powder method) was abandoned for this exceptional specimen (a white sintered pellet) since grinding was impossible.

The X-ray diffraction patterns of the specimens quenched in a carbon dioxide flow are shown in Fig. 4. The specimens (light grey or light brown) quenched from 230 °C show only the diffraction pattern of Ag_2CO_3 [13]. The specimen (brown) quenched from 290 °C shows the (111) diffraction peak of Ag_2O ($2\theta = \sim 32.8°$) [15] as a shoulder on the ($\bar{1}01$) diffraction peak of Ag_2CO_3 (32.6°). The specimen quenched from 400 °C forms a

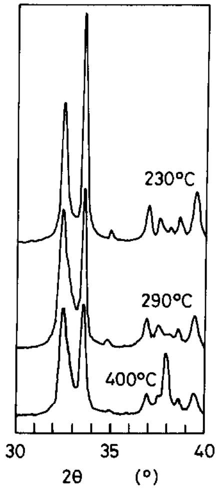

Fig. 4. X-ray diffraction patterns for the quenched specimens decomposed in a carbon dioxide flow.

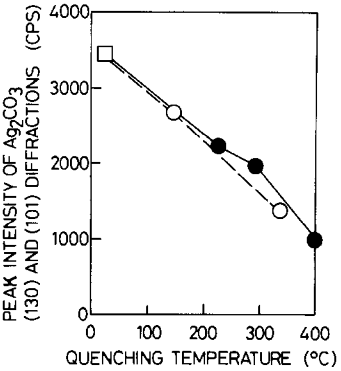

Fig. 5. Intensities of the X-ray diffraction peaks of Ag_2CO_3 for the specimens quenched from various temperatures during the decomposition: □, untreated; ○, heated in a static air atmosphere (quenched from the temperatures indicated by the triangles in Fig. 2A); ●, heated in a carbon dioxide flow (quenched from the temperatures indicated by the triangles in Fig. 2B).

slightly sintered pellet whose outer surface is white and whose inside is brown. These results show that the thermal change occurs inhomogeneously in the pellet. This specimen clearly shows the (200) diffraction peak ($2\theta =$ 38.0 °) of Ag_2O; the $(\underline{1}01)$ diffraction peak of Ag_2O (~ 32.8 °) is observed as a shoulder on the $(\underline{1}01)$ diffraction peak of Ag_2CO_3 (32.6 °). Ag_2O is not observed in the specimen (brown) quenched from 335 °C in a static air atmosphere.

The intensities of the diffration peaks of Ag_2CO_3 (33.6 °, (130) and (101)) for the specimens quenched during thermal decomposition in a static air atmosphere and in a carbon dioxide flow are shown in Fig. 5. The intensity decreases with the progress of decomposition. No distinct difference is observed between the decomposition atmospheres.

DISCUSSION

Phase transition of Ag_2CO_3

The first endothermic peak (194 °C) in a carbon dioxide flow (Fig. 2B) cannot be attributed to decomposition. A reversible endothermic phenomenon has been reported by many workers [2, 9]. This endothermic phenomenon can be attributed to the phase transition of silver carbonate from the normal to the high-temperature form, probably the α phase reported by van Hattum et al. in ref. 12.

The high-temperature form of Ag_2CO_3 (α [12] and β [7, 11]) was not detected in the quenched specimens. Phase transition from the high-temperature to the normal form is expected to occur during quenching.

The decrease in the DTA peak intensity on cyclic heating and cooling between 160 and 220 °C can be explained by a slight decomposition at ~ 200 °C.

In the static air atmosphere (Fig. 2A), two endothermic phenomena (which are supposed to be the phase transition and the decomposition) are thought to occur at ~ 200 °C almost simultaneously; a shoulder (~ 200 °C) on the endothermic peak (~ 196 °C) supports this hypothesis.

The decrease in diffraction intensity is observed in Fig. 5 even for the specimen quenched before the decomposition; this specimen (light grey) was quenched from 147 °C in static air. This can be attributed to a decrease in crystallinity which is a precursory phenomenon of the phase transition.

Influence of partial pressure

The decarbonation temperature (endothermic peak at 196 °C in Fig. 2A) in a static air atmosphere is lower than that (255 °C in Fig. 2B) in a carbon dioxide flow. This difference can be explained by the influence of the partial pressure of carbon dioxide.

One endothermic peak is observed at 416 °C in a static air atmosphere (Fig. 2A), whereas two endothermic peaks (382 and 414 °C) are observed in a carbon dioxide flow (Fig. 2B). This difference can be attributed to the influence of the partial pressure of carbon dioxide or oxygen. Peak splitting at ~ 400 °C is observed in the present DTGA results (Fig. 3). Peak splitting in a helium flow (Fig. 3A) can be explained by the influence of the self-generated atmosphere of carbon dioxide or oxygen, since the amount of specimen (165–195 mg) used for DTGA is much greater than that used for DTA–TG (35–70 mg).

Decomposition mechanisms

Decomposition mechanisms can be tentatively proposed on the assumption that the type of decomposition is determined only by the partial pressure of carbon dioxide. The decomposition is assumed to proceed inhomogeneously from the surface portion to the inner portion of the powder specimen. The thickness of the surface portion (layer) depends on the various conditions such as heating. The size and shape of the specimen container may also be important since the ventilation of the evolved gases affects the self-generated atmospheres.

Type I: relatively low partial pressure of carbon dioxide

Surface portion and inner portion

$$Ag_2CO_3\ (\text{normal}) \xrightarrow[194°\text{C}]{\text{phase transition}} Ag_2CO_3\ (\text{high}) \quad (1)$$

Surface portion

$$Ag_2CO_3\ (\text{high}) \xrightarrow[\sim 200°\text{C}]{-CO_2} Ag_2O\ (\text{amorphous}) \quad (2)$$

$$Ag_2O\ (\text{amorphous}) \xrightarrow[\sim 416°\text{C}]{-O_2} Ag \quad (3)$$

Inner portion

$$Ag_2CO_3\ (\text{high}) \xrightarrow[\sim 416°\text{C}]{-CO_2 \text{ and } -O_2} Ag \quad (4)$$

Equations (3) and (4) are assumed to occur simultaneously producing the single DTA peak in Fig. 2A.

Type II: relatively high partial pressure of carbon dioxide

Surface portion and inner portion

$$Ag_2CO_3\ (\text{normal}) \xrightarrow[194°\text{C}]{\text{phase transition}} Ag_2CO_3\ (\text{high}) \quad (5)$$

Surface portion

$$Ag_2CO_3\ (\text{high}) \xrightarrow[\sim 200\text{–}255°\text{C}]{-CO_2} Ag_2O\ (\text{crystalline}) \quad (6)$$

$$Ag_2O\ (\text{crystalline}) \xrightarrow[\sim 350\text{–}450°\text{C}]{-O_2} Ag \quad (7)$$

Inner portion

$$Ag_2CO_3\ (\text{high}) \xrightarrow[\sim 350\text{–}450°\text{C}]{-CO_2 \text{ and } -O_2} Ag \quad (8)$$

This type of decomposition is assumed to occur in a carbon dioxide flow (Figs. 2B and 3B). This mechanism is also expected to occur when a carbon dioxide atmosphere is self-generated by heating a large amount of specimen in a helium flow (Fig. 3A) or in an oxygen flow (Fig. 3C).

The temperature for the reaction indicated by eqn. (6) depends largely on the partial pressure of carbon dioxide.

Equations (7) and (8) are assumed to occur simultaneously via two steps (two DTGA peaks) each of which consists of both decarbonation and reduction. We cannot explain why two steps occur.

The influence of the partial pressures of carbon dioxide and oxygen must be investigated further to establish the mechanism which explains the decomposition process completely.

CONCLUSIONS

The thermal decomposition of silver carbonate was investigated by DTGA, DTA–TG and X-ray diffraction analysis.

The gases evolved were carbon dioxide and oxygen. Water vapour was not detected. Carbon dioxide was evolved at ~ 200 ° C. Carbon dioxide and oxygen were evolved simultaneously at ~ 400 ° C.

The X-ray diffraction patterns of Ag_2CO_3 (normal form) and Ag_2O were detected for the specimens quenched from the heating process (~ 10 ° C min^{-1}) in a carbon dioxide flow. An endothermic phenomenon at ~ 194 ° C with no weight loss was estimated to be a phase transition of silver carbonate from the normal to the high-temperature form.

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