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The pyrolysis of basic magnesium carbonate trihydrate

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Abstract

The pyrolysis of $(MgCO_3)_3 \cdot Mg(OH)_2 \cdot 3H_2O$ was investigated using a combined TG–DTA–DTG technique in a flow of nitrogen gas. The TG–DTG curves showed three mass-loss steps corresponding to three endothermic peaks in the DTA curve, indicating the existence of $(MgCO_3)_3 \cdot Mg(OH)_2$, $MgCO_3 \cdot 3MgO$ and MgO in the respective steps.

INTRODUCTION

The reactions of various carbonates and basic carbonates with molten $K_2S_2O_7$ were reported previously [1]. For the interpretation of the reactions, it was necessary to carry out initially the pyrolysis of the carbonates and basic carbonates. The investigation of the pyrolysis of $(MgCO_3)_3 \cdot Mg(OH)_2 \cdot 3H_2O$ indicated that our results were at variance with the previously reported results [2, 3]. We now present a paper to point out the differences.

EXPERIMENTAL

Material

Basic magnesium carbonate (Hopkins and Williams, GPR) labelled as $(MgCO_3)_3 \cdot Mg(OH)_2 \cdot 3H_2O$ was used as received.

Procedure and physical measurement

Thermogravimetry (TG), derivative thermogravimetry (DTG) and differential thermal analysis (DTA) were carried out on a Rigaku-Denki Thermoflex modular thermal analysis instrument capable of measuring TG, DTG and DTA simultaneously. Samples and alumina (used as inert reference material), of masses approximately 10 mg each, were weighed in

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platinum crucibles which were mounted on the sample holder of the instrument. A silica glass envelope and a gas sleeve were put around the furnace which was heated at a rate of 10°C min^{-1} under a constant nitrogen flow of 0.2 l min^{-1}. Sensitivity of 25 μV and a chart speed of 2.5 cm min^{-1} were used in order to obtain sharp DTA peaks.

An X-ray powder diffraction (XRD) was obtained using a Siemens-Philips PW1009 diffractometer and Philips PW 1840 X-ray generators. Samples were exposed to a nickel filtered Cu Kα beam of X-rays. During the exposure, the accelerating potential was maintained at 40 kV and the filament current at 20 mA.

RESULTS AND DISCUSSION

The TG–DTA–DTG curves for the pyrolysis of $(MgCO_3)_3 \cdot Mg(OH)_2 \cdot 3H_2O$ are shown in Fig. 1. Both the TG–DTG curves indicate three steps in the decomposition. The three mass-loss steps are more pronounced in the DTG curve than in the TG curve. The DTA curve also shows three endotherms corresponding to the mass losses in the same temperature ranges. The first step occurs between 206 and 316°C with a mass loss of 14.1 ± 0.6% which compares with 14.8% for the loss of three moles of water of crystallisation

$$(MgCO_3)_3 \cdot Mg(OH)_2 \cdot 3H_2O \rightarrow (MgCO_3)_3 \cdot Mg(OH)_2 + 3H_2O \qquad (1)$$

The second step occurs between 340 and 488°C with an accumulative mass loss of 44.0 ± 1.0% compared to 43.8% for the loss of further one

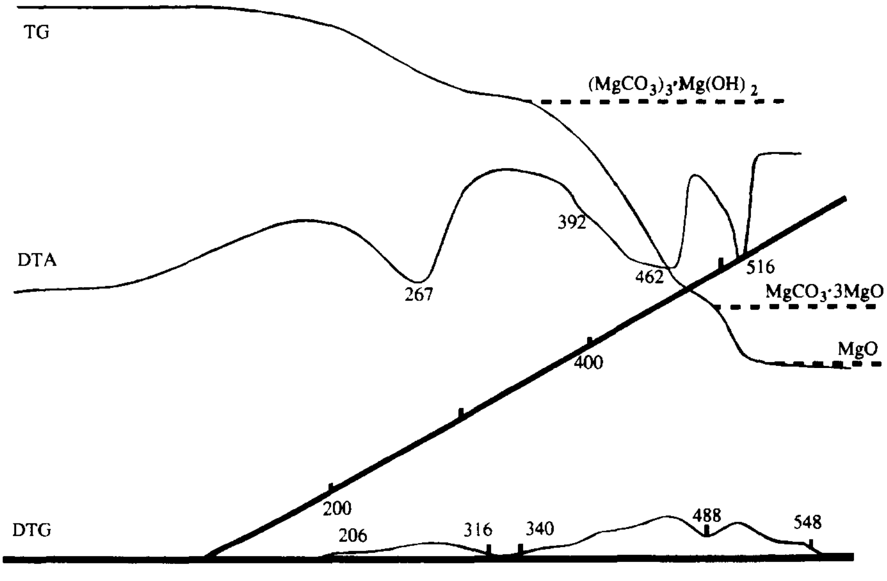

Fig. 1. TG–DTA–DTG curves for the pyrolysis of $(MgCO_3)_3 \cdot Mg(OH)_2 \cdot 3H_2O$.

mole of water of constitution and two moles of carbon dioxide

$$(MgCO_3)_3 \cdot Mg(OH)_2 \rightarrow MgCO_3 \cdot 3MgO + 2CO_2 + H_2O \qquad (2)$$

The third step occurs between 488 and 548°C with a total mass loss of 55.2 ± 2.8% compared to 55.8% calculated for the loss of further one mole of carbon dioxide

$$MgCO_3 \cdot 3MgO \rightarrow 4MgO + CO_2 \qquad (3)$$

The final product was identified by the XRD method which gave "d" values of 1.49(m), 2.10(s), and 2.42(w) compared to the first three most intense A.S.T.M. values of 1.49(52), 2.11(100) and 2.43(10) for MgO.

The DTA curve shows three endotherms with peak temperatures at 267, 462 (with a shoulder on the lower side of the peak temperature), and at 516°C corresponding to the above three steps for the decomposition of the basic carbonate, respectively.

Equation (4) represents the sum of the eqns. (1)–(3) to indicate the overall decomposition reaction of the basic carbonate.

$$(MgCO_3)_3 \cdot Mg(OH)_2 \cdot 3H_2O \rightarrow 4MgO + 3CO_2 + 4H_2O \qquad (4)$$

As indicated, the pyrolysis of basic magnesium carbonate has been reported previously in two different studies [2, 3] indicating three decomposition steps with the formation of $(MgCO_3)_3 \cdot Mg(OH)_2$, $(MgCO_3)_3 \cdot MgO$ and MgO in each respective step. The present study supports the formation of anhydrous basic carbonate in the first mass-loss step as well as MgO as the final product. However, it does not agree with the existence of $(MgCO_3)_3 \cdot MgO$ in the second step, as the calculated mass loss in the formaton of this intermediate is 19.70% compared to the present TG–DTG results which give a value of 44.0 ± 1.0% suggesting the existence of $MgCO_3 \cdot 3MgO$ in the second step, as discussed above. The DTA curve, indeed, shows a slight inflection at about 392°C. The value of the mass loss corresponding to this inflection is about 19% indicating that the loss of one mole of water does occur at this point. However, after the evolution of water, both the TG and DTG curves show a continuous mass loss until a pronounced inflection appears in the TG curve and a minimum is shown in the DTG curve as well as the second broad endotherm corresponding to the mass loss is completed in the DTA curve. Thus, the process of the second mass loss, as shown by the TG, DTG and DTA curves, begins with the loss of one mole of the constitution water and continues with the evolution of two moles of CO_2, and on completion the total value of mass loss indicates the formation of $MgCO_3 \cdot 3MgO$.

The existence of $MgCO_3 \cdot 3MgO$ rather than the previously reported intermediate $(MgCO_3)_3 \cdot MgO$ may also be supported by the consideration of the areas and the shapes of the second and third DTG peaks. Thus, for example, the DTG peak in the second step is larger than that of the third step and it is also distinctly separate from it, indicating a higher mass loss in the second step. The shape of the second DTG peak is also much less symmetrical than that of the third step. In addition to the rate of mass loss, the asymmetric shape of the second endothermic peak may be taken to indicate the loss of two different moieties in the former step, i.e. H_2O and CO_2, and the loss of CO_2 in the latter step.

Because of the difference in the nature of the second product between the present work and the two published reports [2, 3], the pyrolysis of $(MgCO_3)_3 \cdot Mg(OH)_2 \cdot 3H_2O$ was repeated a number of times carefully selecting the same heating rate and atmosphere as mentioned in the reports, but consistent results were obtained in the present study indicating the formation of $MgCO_3 \cdot 3MgO$ rather than $(MgCO_3)_3 \cdot MgO$ in the second step. The DTG peaks may be affected by the experimental method employed, i.e. heating rate, nature and pressure of the surrounding atmosphere, nature of the container material, particle size of the basic carbonate, etc. However, whatever may be the reason, the present results do not support the existence of $(MgCO_3)_3 \cdot MgO$ as the second intermediate in the pyrolysis of the basic carbonate.

The intermediate species was also examined by the XRD method but unfortunately it showed diffuse lines indicating the amorphous nature of the product. As the amount of carbonate in the intermediate is different, the only other method which could be used to confirm its formulation was to carry out its reaction with molten $K_2S_2O_7$ on a thermobalance in order to determine the amount of carbonate present from the amount of CO_2 evolved during the reaction. The calculated values for the evolution of CO_2 from $(MgCO_3)_3 \cdot MgO$ and $MgCO_3 \cdot 3MgO$ are 44.99 and 21.42% respectively. When the intermediate species was heated with $K_2S_2O_7$, a value of 21.80% was obtained, supporting the formation of the moiety proposed in the present work.

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