The Thermal Decomposition of Manganese(III) Phosphate Monohydrate

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(Received February 16, 1983)

Synopsis. Manganese(III) phosphate monohydrate begins to decompose at 200 °C by the dehydration accompanying the reduction of manganese(III) and changes completely to manganese(II) pyrophosphate at 500 °C. The reaction order and activation energy for the reduction process are 1.3 and 176.8 kJ mol^{-1}, respectively.

Manganese(III) phosphate monohydrate was just synthesized by Christensen[1] and is prepared conveniently by the reaction of manganese(III) acetate with phosphoric acid or by the oxidation of manganese(II) nitrate with nitric acid in the presence of phosphoric acid.[1,2] Although manganese(III) phosphate monohydrate is one of the few manganese(III) salts, no information is at present available concerning its properties. It has been reported that manganese(III) phosphate monohydrate loses water of crystallization slowly at 300 to 400 °C and rapidly at a red-heat with the simultaneous loss of oxygen.[2,3] However, this is doubtful. The present authors have shown that manganese(III) phosphate monohydrate precipitates *via.* $[Mn(PO_4)_2]^{3-}$ complex ion by the reduction of manganate(VII) ion in the presence of phosphoric acid and changes to manganese(II) pyrophosphate at 500 °C.[4]

In this study the thermal decomposition of manganese(III) phosphate monohydrate has been investigated by TG and DTA techniques.

Experimental

Material.[1] To a warm solution of 34.2 g of manganese(II) chloride tetrahydrate in 50 cm^3 of water, 30 g of concentrated phosphoric acid (87%) and 10 g of concentrated nitric acid (61%) were added. On concentrating slowly to near dryness, this mixture deposited a green-grey precipitate. After cooling, water was added and the precipitate filtered off, washed and dried overnight in an electric oven in air at 110 °C. According to chemical analyses,[4] the composition of the precipitate was: $Mn^{3+}:PO_4^{3-}:H_2O = 1:1.03:1.13$.

Decomposition Procedure. The thermal decomposition of manganese(III) phosphate monohydrate (32—36 mg) was carried out using a Rigaku Denki Thermoflex high temperature type TG-DTA instrument in air. Ignited α-Al_2O_3 was used as a reference material in the DTA sample block. The heating rate of the furnace was 5—20 deg/min.

Measurement. The X-ray diffraction patterns of the heated products were obtained using a Rigaku Denki Geigerflex 2013 with Ni filtered Cu $K\alpha$ radiation, with 30 kV and 10 mA. The IR absorption spectra were obtained using a Shimadzu I-430 spectrometer with the KBr pellet technique.

Results and Discussion

Thermal Decomposition Process. The TG and DTA curves for manganese(III) phosphate monohydrate are shown in Fig. 1. The weight loss in the heating process was indicated on the TG curve in three steps which corresponded to the endothermic peaks of the DTA curve at 263, 377, and 476 °C, respectively. The X-ray diffraction patterns of four samples obtained at A(110 °C), B(320 °C), C(420 °C), and D(520 °C) in Fig. 1 are shown in Fig. 2. Sample A was typical manganese(III) phosphate monohydrate. Although the pattern of sample B, which was obtained just after the first weight loss, indicated the partial disintegration of the crystal structure and the formation of a small amount of manganese(II) pyrophosphate,[5] it still was similar to that of sample A. Sample C obtained just after the second weight loss was manganese(II) pyrophosphate. The IR spectrum also indicated that it had lost the PO_4^{3-} structure and still contained a large amount of water. In spite of the largest third weight loss, the pattern of sample D was hardly changed in comparison with that of

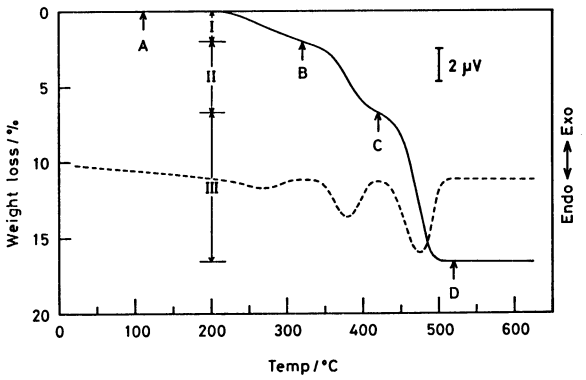

Fig. 1. TG and DTA curves of manganese(III) phosphate monohydrate under an air atmosphere. Heating rate of furnace: 10 (deg/min), sample weight: 32.6 (mg), ——: TG, ----: DTA.

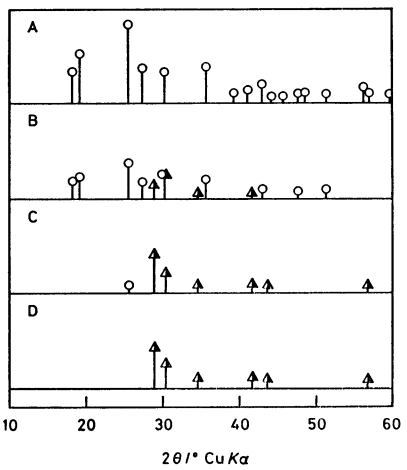

Fig. 2. X-Ray diffraction patterns of the heating products of manganese(III) phosphate monohyrate. A: 110 °C, B: 320 °C, C: 420 °C, D: 520 °C, ○; $MnPO_4 \cdot H_2O$, △: $Mn_2P_2O_7$.

sample C. On the basis of these results, manganese(III) phosphate monohydrate appears to decompose in three steps as follows:

$$MnPO_4 \cdot H_2O \longrightarrow MnPO_4 \cdot (1-x)H_2O + xH_2O\uparrow \quad \text{(Step I)}$$

$$2[MnPO_4 \cdot (1-x)H_2O] \longrightarrow Mn_2P_2O_7 \cdot 2(1-x)H_2O + 1/2\,O_2\uparrow \quad \text{(Step II)}$$

$$Mn_2P_2O_7 \cdot 2(1-x)H_2O \longrightarrow Mn_2P_2O_7 + 2(1-x)H_2O\uparrow. \quad \text{(Step III)}$$

The value of x was 0.25 from the TG curve in Fig. 1. The important feature in this process is that the reduction of manganese(III) phosphate monohydrate occurred even at 400 °C.

Kinetics. On the second weight loss (Step II), *i.e.*, the reduction of manganese(III) to manganese(II), the methods of Freeman-Carroll,[6] Coats-Redfern,[7] and Kissinger[8] were used to study the kinetics. The methods are generally used only when the reaction is a single elementary reaction.

The formula of the Freeman-Carroll method is written as

$$\Delta\log(dW/dt)/\Delta\log Wr = n - E\Delta(1/T)/2.303R(\Delta\log Wr), \quad (1)$$

where dW/dt is the weight change in mg per minute, n the order of the reaction, T the absolute temperature and $Wr = W - Wc$, where W is the weight(mg) at time t and Wc the weight(mg) of the sample at the end of the reaction, E the energy of activation. If the plot of the ratio $\Delta\log(dW/dt)/\Delta\log Wr$ values *vs.* $\Delta(1/T)/\Delta\log Wr$ lie on a straight line, the activation energy and the reaction order will be given by its slope and intercept, respectively. This is illustrated in Fig. 3. As given in Table 1, the reaction order and activation energy obtained by the Freeman-Carroll method were 1.3 and 184.9 kJ mol^{-1}, respectively.

When the reaction order is not 1.0, the formula of the Coats-Redfern method is written as

$$\log\{1-(1-x)^{1-n}/(1-n)T^2\} = \log(AR/\phi E)(1 - 2RT/E) - E/2.303RT, \quad (2)$$

where x is the fraction of reaction, ϕ the heating rate of furnace and A the frequency factor. Graphic representation of the $\log\{1-(1-x)^{1-n}/(1-n)T^2\}$ values as a function of $1/T$ gives a straight line of slope $-E/2.303R$ for the correct value of n. As also illustrated in Fig. 3, a good linear relationship was obtained when the value of n was postulated as 1.3. The activation energy was calculated as 169.4 kJ mol^{-1}.

According to the Kissinger method, the activation energy of the reaction is obtained from the change in peak temperature on the DTA curve when the heating rate of furnace, ϕ, was altered. The formula of the Kissinger method is written as

$$d\{\log(\phi/T_m^2)/d(1/T_m)\} = -E/2.303R, \quad (3)$$

where T_m is the sample temperature, $T_m = T_p - T_h$, where T_p is the absolute temperature of peak, T_h the height of peak(deg). Graphic representation of $\log(\phi/T_m^2)$ as a function of $1/T_m$ gives a straight line of slope $-E/2.303R$. In this experiment ϕ was altered as 5, 10, and 20 °C/min. A straight line of slope 9.20 was obtained and the activation energy was calculated as 176.1 kJ mol^{-1}.

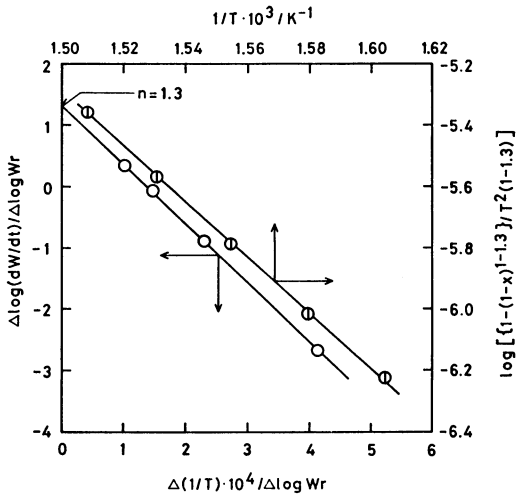

Fig. 3. Freeman-Carroll and Coats-Redfern straight lines for the thermal decomposition (reduction: Step II) of manganese(III) phosphate monohydrate.
○: Freeman-Carroll plots, ①: Coats-Redfern plots.

Table 1. Reaction order and activation energy of the thermal decomposition (reduction: Step II) of manganese(III) phosphate monohydrate

Method	Activation energy / kJ mol^{-1}	Reaction order
Freeman-Carroll (TG)	184.9	1.3
Coats-Redfern (TG)	169.4	1.3
Kissinger (DTA)	176.1	—
Average	176.8	1.3

As can be seen in Table 1, the kinetics parameters obtained by the three methods agreed well with each other and the average reaction order and activation energy were 1.3 and 176.8 kJ mol^{-1}, respectively. On the first and third weight losses (Steps I and III), *i.e.*, the dehydration, the above analytical methods could not be used. However, it was found that a large part of the water of crystallization was lost after the reduction of manganese(III) to manganese(II) and the dehydration was completed at about 500 °C.

References

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