Study on Thermal Decomposition of MnO₂ and Mn₂O₃ by Thermal Analysis

By Kiyoshi Terayama* and Masao Ikeda*

The present paper is concerned with the kinetics of thermal decomposition of manganese oxides and nonstoichiometric compounds formed in these reaction processes, studied by means of the thermal analyses (TG, DTA and DSC) and gas chromatography (GC).

The decomposition of MnO₂ to Mn₂O₃ proceeds at about 756 K, and the heat of reaction is 176±8 kJ/mol of O₂. For the decomposition of Mn₂O₃ to Mn₃O₄, the activation energy of about 163 kJ/mol of O₂ is obtained. The nonstoichiometric compounds, MnO₁.₆₁ and MnO₁.₄₂, seem to be formed in the thermal decomposition processes of MnO₂ and Mn₂O₃, respectively.

(Received April 2, 1983)

Keywords: thermal decomposition, manganese oxide, thermal analysis, gas chromatograph, nonstoichiometric compound

I. Introduction

In the Mn–O system, MnO₂, Mn₃O₄, Mn₃O₄ and MnO are known to exist as stable crystalline phases, and MnO₂ is continuously converted into lower oxides under a suitable condition of temperatures and oxygen partial pressures. Thermal decomposition of MnO₂ to Mn₂O₃ and that of Mn₂O₃ to Mn₃O₄ take place by heating, and Mn₃O₄ is easily formed up to about 1273 K. Further reduction of Mn₃O₄ to MnO can be achieved by CO or carbon.

In spite of many studies dealing with various aspects of the chemistry of manganese oxides, only a few studies(1)–(5) have been reported about the nonstoichiometry in the carbon thermic reduction of these oxides.

The present paper is concerned with the kinetics of thermal decomposition of MnO₂ and Mn₂O₃ and nonstoichiometric compounds formed in these reaction processes, studied by the simultaneous thermal analyses (TG, DTA and DSC) and gas chromatography (GC).

II. Experimental Procedure

1. Specimen

MnO₂ was prepared from a reagent of recrystallized manganese nitrate by heating at 473 K in air. Then it was heated at 873 K in an electrical resistance furnace under an Ar atmosphere for 43.2 ks. It was known by the X-ray diffraction method, that the oxide samples obtained had chemical formulas of MnO₂ and Mn₂O₃.

The sample quenched at a chosen condition was used for identifying phases present by means of the X-ray diffraction method using Fe-Kα radiation and the chemical analysis.

* Department of Metallurgy, Faculty of Engineering, Toyama University, Takaoka, Japan.
III. Results and Discussion

1. Simultaneous TG, DTA, DSC and GC

For the thermal decomposition of MnO₂, results obtained by simultaneous TG, DTA, DSC and GC under the same experimental conditions are presented in Fig. 1. A good agreement is found among results obtained by different methods: The oxygen evolution determined by GC and the weight loss of the sample are recognized, when the heat change is observed in DTA curve. The weight loss in TG curve occurs gradually at about 703 K. The weight loss, an endothermic peak in DTA curve, a clear peak in DSC curve and the oxygen evolution in GC curve occur at the same temperature of about 756 K. The maximum peak of the reaction is found at about 860 K. This reaction corresponds to the thermal decomposition of MnO₂ expressed by eq. (1):

\[ 4\text{MnO}_2 = 2\text{Mn}_2\text{O}_3 + \text{O}_2. \]  

The heat of reaction, 176±8 kJ/mol of \text{O}_2, calculated from the DSC curve agrees well with the value based on the thermochemical data\(^8\), 165 kJ/mol.

The heat of reaction (1) in the present study is in reasonable agreement with those of Wicks et al.\(^9\) and Kapustinsky et al.\(^10\), (164.0 and 132 kJ/mol of \text{O}_2) obtained by equilibrium and calorimetric measurements, respectively, while the result of the present study slightly differs from those obtained by the differential thermal analysis, 108\(^{11}\) and 102.2\(^{12}\) kJ/mol of \text{O}_2, and that obtained by equilibrium measurement, 241.8\(^{13}\) kJ/mol of \text{O}_2.

It is known that the heat of reaction can be quantitatively determined by DSC more accurately than by DTA, and the equilibrium measurement is thought to be a standard method by which it takes a considerable long time.

For the thermal decomposition of Mn₂O₃ to Mn₃O₄ expressed by eq. (2), TG, DTA and GC curves are shown in Fig. 2.

\[ 6\text{Mn}_2\text{O}_3 = 4\text{Mn}_3\text{O}_4 + \text{O}_2. \]  

The weight loss in TG curve, the endothermic reaction in DTA curve and the oxygen evolution in GC curve occur at about 923 K, and the peak temperature of the thermal decomposition is about 1072 K. In the present study, DSC technique can not be applicable because of the limitation of DSC apparatus (from room temperature to 1073 K).

The weight loss obtained by TG curve exactly equals that calculated for the reaction expressed by eq. (2).

2. Isothermal decomposition process

Typical effects of temperature on the thermal
decomposition of MnO₂ to Mn₂O₃ measured by EGA technique are shown in Fig. 3. At an earlier stage, the decomposition does not quickly proceed for some time and the sigmoidal curves are observed. The decomposition rate increases as the temperature increases from 805 to 880 K.

In the present study, a He flow rate of 1.17 × 10⁻⁶ m³/s controlled by a gas flow equipment is sufficient for neglecting the effect of the transport of the product gas from the outer surface of the sample to the bulk gas.

It has been mentioned in the previous paper that the rate determining step of the reaction expressed by eq. (1) is an interfacial reaction and the rate equation in the form of

\[ 1 - (1 - \alpha_1)^{1/3} = kt \]  \hspace{1cm} (3)

is applied, \( k \) being an apparent velocity constant. In the following discussion, \( \alpha_1 \) and \( \alpha_2 \) are fractions of the thermal decomposition in converting MnO₂ to Mn₂O₃ and Mn₂O₃ to Mn₃O₄, respectively.

The plots of \[ 1 - (1 - \alpha_1)^{1/3} \] vs \( t \) are shown in Fig. 4. It can be seen that they are linear in the \( \alpha_1 \) range from about 0.2 to 0.8, but this relationship holds no longer at the later steps, where mixed kinetics of interfacial reaction and diffusion are to be considered.

The activation energy, about 163 kJ/mol of O₂, is determined from an Arrhenius-type plot shown in Fig. 5, and this value is in good agreement with the values reported in the literatures.

The effects of temperature on the thermal decomposition of Mn₂O₃ to Mn₃O₄, measured by EGA technique, are shown in Fig. 6. As shown here, the decomposition rate increases at higher temperatures and approaches unity in the first period of about 0.7 ks. The relation between \[ 1 - (1 - \alpha_2)^{1/3} \] and \( t \) is shown in Fig. 7. From the slope of these straight lines at earlier stages, the activation energy of this reaction expressed by eq. (2) is estimated to be about 226 kJ/mol of O₂, nearly equal to those of Siemonsen and Hahn et al. (210.0,
Study on Thermal Decomposition of MnO₂ and Mn₂O₃ by Thermal Analysis

Fig. 6 Effect of temperature on the thermal decomposition of Mn₂O₃.

Fig. 7 Relation between time and 1−(1−x)₁/₃ for the thermal decomposition of Mn₂O₃.

These activation energies obtained in the present study are thought to be accurate, because of the adoption of simultaneous measurements of thermal analyses (TG, DTA and DSC) and gas analyses (GC, EGA). The gas analysis method, which is sensitive and troubleless compared with other methods in thermal analysis(6), can be applicable to studying the carbon reductions of oxides having high vapour pressures, such as manganese oxides(4)(7).

3. Formation of nonstoichiometric compound

During the thermal decomposition of MnO₂ and Mn₂O₃, the reaction rates increase at 833 and 1053 K in the DTA curves illustrated in Fig. 1 and Fig. 2, respectively. The decomposition rate (dα₁/dt), α and x are calculated from the EGA curves at temperature from 823 to 843 K for MnO₂ and from 1043 to 1063 K for Mn₂O₃, where the decimal notation, x, in MnOₓ is used to specify a certain composition of manganese oxide.

A procedure similar to that described in the previous paper(4) for determining the nonstoichiometric compound can be applicable to the thermal decomposition of MnO₂. The relation between dα₁/dt, α₁ and x is illustrated in Fig. 8. The value of α₁, at which the decomposition rate becomes slower, is obtained by calculating the intersection of the lines tangent to the dα₁/dt−α₁ curve(4) at 833 K illustrated graphically in Fig. 8. The calculated value of α₁ is 0.78 which corresponds to the nonstoichiometric compound, MnO₁.₆₁(5), and this compound has also been presented by Amirova et al. (1) based on the oxidation of MnO in an oxygen atmosphere.

A similar procedure of plotting dα₂/dt−α₂, x can be applicable to the thermal decomposition of Mn₂O₃, as shown in Fig. 9. The value of α₂,
Fig. 9 Relation between $\frac{d\alpha_2}{dt}$ and $\alpha_2$ obtained from EGA curve for the thermal decomposition of $\text{Mn}_2\text{O}_3$.

0.48, which corresponds to the nonstoichiometric compound, $\text{MnO}_{1.42}$, is obtained at 1053 K, and this compound is also formed in the reduction process of $\text{Mn}_2\text{O}_3$\(^\text{14}\).

These nonstoichiometric compounds obtained in the present study are in good agreement with those determined by a study for the Mn–O system in CO\(_2\)–H\(_2\) mixtures\(^\text{5}\).

IV. Summary

The thermal decomposition of MnO\(_2\) and Mn\(_2\)O\(_3\) is studied in order to clarify the kinetics of these reactions as well as the nonstoichiometric compound by the simultaneous application of TG, DTA, DSC and GC. The results may be summarized as follows:

1. The decomposition of MnO\(_2\) to Mn\(_2\)O\(_3\) proceeds at about 756 K. The heat of reaction, 176 ± 8 kJ/mol of O\(_2\), is obtained.

2. For the decomposition of Mn\(_2\)O\(_3\) to Mn\(_3\)O\(_4\) which occurs at about 923 K, the activation energy, about 163 kJ/mol of O\(_2\), is obtained.

3. The nonstoichiometric compounds of MnO\(_{1.61}\) and MnO\(_{1.42}\) seem to be formed in the thermal decomposition processes of MnO\(_2\) and Mn\(_2\)O\(_3\) at 833 and 1053 K, respectively.

REFERENCES

(3) H. B. Hien and D. I. Rijonkov: ibid., 3 (1972), 1074.