Discontinuous Change of the Surface of Natural Manganese Dioxide Catalyst

Masayoshi KOBAYASHI, Masakatsu HATANO and Haruo KOBAYASHI

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The oxidation kinetics of carbon monoxide on natural manganese dioxide of β-type crystal structure was studied in a temperature range of 140 to 155°C. The oxidation rates are proportional to the partial pressure of carbon monoxide, however they change discontinuously at partial pressures of carbon monoxide above 0.08 atm regardless of the concentration of oxygen and the temperature. Kinetic analysis of the rate data obtained below and above this critical partial pressure of carbon monoxide gave the same activation energy, 16.5 kcal/mole and also the same heat of adsorption of oxygen, 22 kcal/mole. It is concluded from these results that the change of reaction rates can be attributed solely to the change of the number of active sites on the surface of manganese dioxide.

1. Introduction

As well known, manganese dioxide is not a stable oxide as other transition metal oxides. Mathieu[1] observed that MnO_2 was reversibly reduced to Mn_2O_3 by CO at temperatures above 100°C. Bussiere, Zhabrova and Shibanova[2] found the phase transition γ'-$MnO_2 \cdot xH_2O \longrightarrow \beta$-$MnO_x$ in an atmosphere of inert gases in a temperature range of 200–350°C. In our previous papers[3,4] it was found that the surface structure of electrolytic manganese dioxide changes to manganese sesquioxide at certain partial pressure of carbon monoxide with an accompanying discontinuous change in the catalytic activity. In addition, it was shown that this modification of the catalyst surface affects the reaction rate through the change of the amount of surface oxygen species, which played an important role as active sites. In this study, the modification of the catalyst activity owing to the change in concentration of carbon monoxide is further studied on different manganese dioxide, natural manganese dioxide ore.

2. Experimental

A natural manganese dioxide ore (0.36 wt.% Fe, 0.013 wt.% Cu, and 0.013 wt.% Ni) from Indonesia was used as the catalyst. An X-ray analysis of this oxide showed the crystal structure of β-manganese dioxide. The composition of the catalyst was $MnO_{1.95}$ and BET surface area with nitrogen was 74 m^2/g. The catalyst in 20–48 mesh particle size was dried by heating in a flowing gas mixture of 20 vol.% oxygen and 80 vol.% nitrogen at 180°C for 24 hrs. The purification of the reaction gas and the experimental system were exactly the same as that described in the previous paper.[3] The catalyst (3 g) was packed in a reactor consisting of a pyrex glass tube immersed in a fluidized bed. The total flow rate of the gas was kept constant at 50 ml/min and the concentrations of carbon monoxide and

Department of Chemical Process Engineering Hokkaido University Sapporo Japan

oxygen were varied by changing the concentration of nitrogen as a diluent. The intraparticle diffusion resistance of the catalyst was found to be negligible as a result of examining the rate data for catalysts of different sizes, namely 60–80 and 20–48 mesh at 150°C. The reaction conditions were chosen in such a way that the total conversion did not exceed 6%.

3. Results and Discussion

The rate of carbon monoxide oxidation on natural manganese dioxide ore is proportional to the partial pressure of carbon monoxide as shown in Fig. 1, however the reaction rates change anomalously at about 0.08 atm of carbon monoxide without depending on the reaction temperature and the partial pressure of oxygen. As presented in the previous paper[3] we have designated two regions 1 and 2 respectively, as shown in Fig. 1.

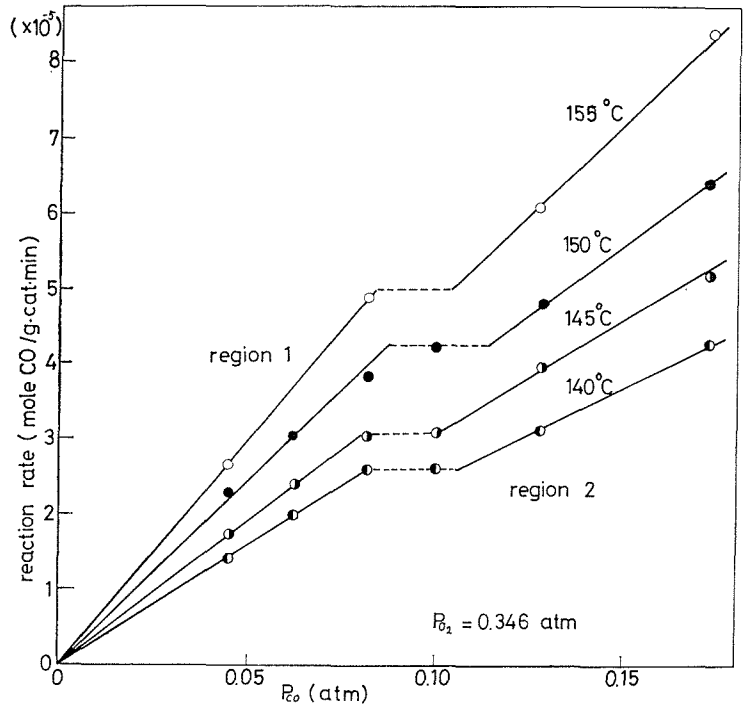

Fig. 1 The reaction rate as a function of P_{CO} and temperature.

On the basis of other experimental findings obtained by a transient response method[5] it may be stated that carbon monoxide was not adsorbed on to the surface and the reaction rate was not affected by the adsorption of carbon dioxide and the following rate equation for the oxidation of carbon monoxide on natural manganese dioxide ore may be expressed as

$$r=\frac{kK^{1/2}P_{O_2}^{1/2}}{1+K^{1/2}P_{O_2}^{1/2}}P_{CO}.$$

According to this equation a plot of (P_{CO}/r) versus $P_{O_2}^{-1/2}$ in each region should be on a straight line without depending on the partial pressure of carbon monoxide when experimental rate data taken at constant temperatures are used. Such plots in both regions were presented in Fig. 2. A fairly straight line can be drawn through the experimental points in each respective region.

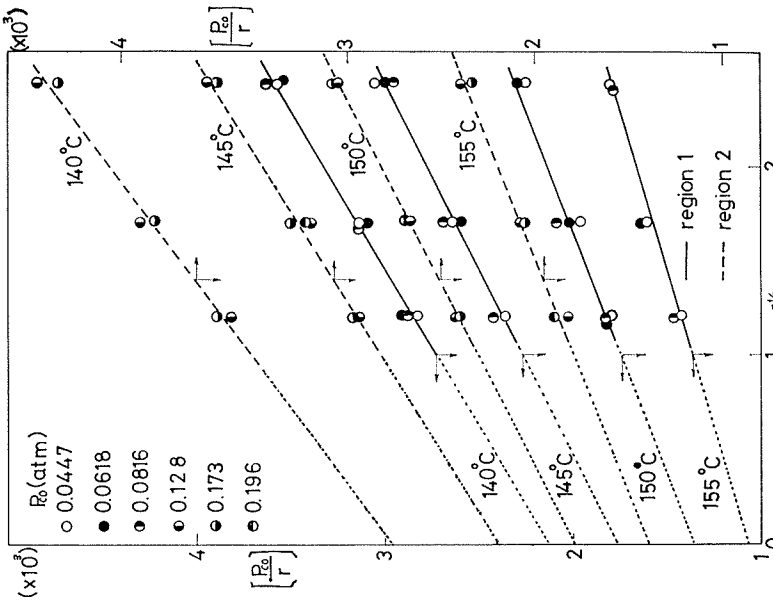

Fig. 2 Plots of (P_{eo}/r) vs. $P_{O_2}^{-1/2}$ (atm) at various P_{eo} and temperatures

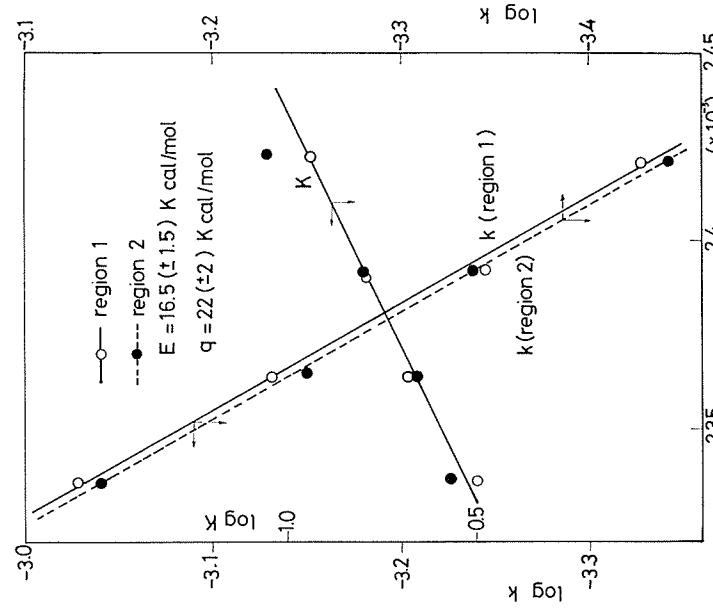

Fig. 3 Plots of $\log k$ and $\log K$ vs. $1/T$.

The activation energies (E) and the heat of adsorption of oxygen on the active sites (q) in both regions were obtained by plotting the logarithms of the rate constant, k, and the adsorption equilibrium constant of oxygen, K, obtained from Fig. 2, against the reciprocal of temperatures. These values in both regions are exactly the same,i. e. E (region 1 and 2)$=16.5$ (± 1.5) kcal/mol and q (region 1 and 2)$=22(\pm 2)$ kcal/mol respectively, as shown in Fig. 3. However, the rate constant in region 1 is larger than that in region 2. This result clearly shows that the number of active sites on the surface of region 1 is larger than that in region 2. Hence, it may be reasonable to conclude, in a similar manner to the case of the electrolytic manganese dioxide, that the modification of the catalyst surface owing to the change in gas composition affects the catalytic activity through the change of the number of active sites.

4. References

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