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Direct Participation of Lattice Oxygen Atoms in Catalytic Oxidation of Carbon Monoxide over Praseodymium Oxides

There is substantial evidence which supports the concept that lattice oxygen atoms of a reducible metal oxide could serve as a useful oxidizing agent for hydrocarbons and other compounds (*1*). Thus, catalytic oxidation of hydrocarbons or other catalytic oxidation reactions over metal oxides is generally believed to proceed via the reduction and oxidation cycles of the catalysts (redox mechanism).

Takasu *et al.* (*2, 3*) have investigated thermal behavior and catalytic reactivity of the lattice oxygen atoms in praseodymium oxides by temperature-programmed desorption (TPD) and ^{18}O-tracer techniques to the oxidation of carbon monoxide. They suggested that the lattice oxygen atoms of the praseodymium oxides play an important role in the catalytic oxidation of carbon monoxide. In this report, we demonstrate the direct contribution of lattice oxygen atoms of praseodymium oxides to the catalytic oxidation of CO by measuring the kinetics for oxidation of CO by the lattice oxygen of the catalyst and for oxidation in the presence of oxygen in the gas phase.

The praseodymium oxides form a homologous series of intermediate phases of the formula Pr_nO_{2n-2}(n = 4, 7, 9, 10, 11, 12), based on ordering of the oxygen vacancies in the oxygen-deficient fluorite structure at low temperatures (*4, 5*). The existence of the phase $Pr_{16}O_{30}$($PrO_{1.875}$) has been shown by us (*6*). Reduction and oxidation of praseodymium oxides proceed via the phase transition between these phases (*6*).

The praseodymium oxide used was a reagent-grade powder (purity > 99.9%) obtained from Asahi Chemical Industry Co. The BET surface area of the sample was 11.9 $m^2\ g^{-1}$ and did not change after repeated reduction–oxidation cycles. CO and O_2 were purified by trap-to-trap distillation in a vacuum apparatus.

Kinetic measurements for the oxidation of CO by praseodymium oxides and for oxidation in the presence of oxygen in the gas phase were carried out in a conventional gas-circulation apparatus of ca. 420 ml. Before each experiment, the sample praseodymium oxide was treated for 1 h in an atmosphere of oxygen (8.0 kPa) at 973 K. Then, the oxide was degassed for 30 min in vacuo at the same temperature. During both reactions the CO_2 formed was always condensed in a trap which was placed in the gas-circulation line and cooled at 77 K. The changes in the O/Pr ratio with time during oxidation of CO with praseodymium oxides were calculated on the basis of the quantity of CO consumed as the reaction progressed. The method for the determination of the initial O/Pr ratio has been described elsewhere (*7*). The experimental error for the O/Pr ratio determined in this work was ±0.005.

Reduction of Praseodymium Oxide by CO

Figure 1 shows some typical examples of the kinetic curves of reduction of PrO_x(x = O/Pr ratio of the sample oxide) at different temperatures and different pressures of CO. The values of n for a stoichiometric phase Pr_nO_{2n-2} are also indicated at the corresponding x values by arrows. The initial compositions of PrO_x had been adjusted by adsorption of oxygen at an appropriate pressure and temperature. The kinetic curves observed at <530 K show several breaks and steps. When the O/Pr ratio is less than 1.875, the steps appear at the compositions of the intermediate phases

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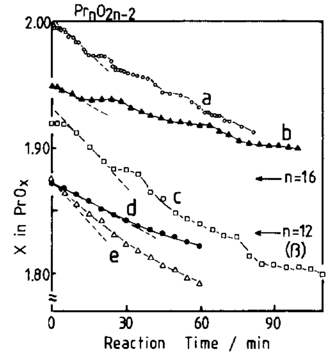

FIG. 1. Some examples of kinetic curves for reduction of praseodymium oxides at different temperatures and CO pressures. Temperatures and initial CO pressures: (a) 513 K and 21.3 kPa; (b) 493 K and 13.3 kPa; (c) 513 K and 20.0 kPa; (d) 543 K and 6.7 kPa; and (e) 573 K and 5.3 kPa.

Pr_nO_{2n-2}(n = 16, 12, and 10), indicating that the reduction of the oxide proceeds stepwise through these intermediate phases. However, the steps and breaks on the kinetic curves observed for the oxygen compositions greater than $Pr_{16}O_{30}$ could not be ascribed to the formation of the intermediate stoichiometric phases (Pr_nO_{2n-2}, n > 16), because the XRD analysis indicated that there was no single phase oxides between the compositions $Pr_{16}O_{30}$ and PrO_2 (*6*). Hysteresis in the phase transition from PrO_2 to $Pr_{16}O_{30}$ for domains of PrO_2 crystals may explain the steps and breaks on the kinetic curves for the sample with O/Pr ratio greater than 1.875 (*6*). On the other hand, the kinetic curves observed at temperatures higher than 543 K show neither steps nor breaks.

Catalytic Oxidation of CO with O_2

Pressure effects on the rate of oxidation of CO over PrO_x in the presence of O_2 in the gas phase have been examined at 493, 513, 523, 543, 573, 603, and 633 K and at CO pressures of 4.0 to 26.6 kPa. Before the experiment, the sample PrO_x was equilibrated with oxygen at 8.0 kPa. Oxidation of CO was initiated by adding CO to this equilibrated system. Thus, the initial pressure of O_2 was 8.0 kPa. Figure 2 shows the correlation between the inverse of the initial rate of CO oxidation (R_0) and the inverse of CO pressure. The very good linear correlation between $1/R_0$ and $1/P_{CO}$ observed at all temperatures in Fig. 2 shows that the rate equation for CO oxidation in the presence of O_2 can be expressed as

$$R_0 = k \cdot \frac{KP_{CO}}{1 + KP_{CO}}, \qquad (1)$$

where k and K are the constants at a fixed temperature.

The effects of pressure of oxygen on the rate of oxidation of CO were examined at 513, 573, and 633 K. The rate of oxidation of CO did not depend on the pressure of oxygen at any of these temperatures.

Kinetic Studies on the Rate of Oxidation of CO by PrO_x

The effects of pressure of CO on the initial rate of oxidation of CO by lattice oxygen atoms (referred to as R_r) were examined at 493, 513, 543, 573, and 603 K and at the pressure range from 4.0 to 26.6 kPa. Before the experiments, the catalyst was pretreated as follows: After gas–solid equilibrium was established between O_2 and PrO_x at the same temperature as that applied for the CO oxidation by PrO_x, the oxygen in the gas phase was outgassed within

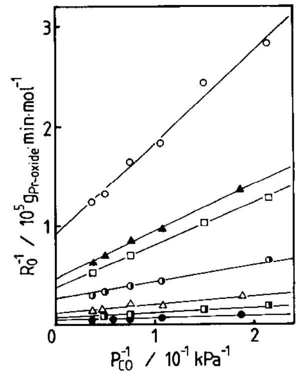

FIG. 2. $1/R_0$ vs $1/P_{CO}$. Reaction temperatures: (○) 493 K; (▲) 513 K; (□) 523 K; (◑) 543 K; (△) 573 K; (◨) 603 K; and (●) 633 K.

2 min. The amount of oxygen desorbed during this evacuation could be neglected. Then, the oxidation of CO by the lattice oxygen atoms was commenced by introducing and circulating CO. During the reaction, there was no oxygen evolved from the oxide. The initial rates of oxidation of CO by PrO_x were calculated from the slopes of kinetic curves at $t = 0$ for the reactions at >530 K. However, for the reactions at temperatures lower than 530 K, the rates were estimated from the maximum slopes for each kinetic curve (for example, the dotted slopes in Fig. 1) at the early stage of the reaction.

A good linear correlation between the inverse of the rate of CO oxidation and inverse of CO pressure was observed at the temperatures tested. The results show that the rate equation for the CO oxidation by PrO_x can be written by the following equation, similar to Eq. (1),

$$R_r = k' \cdot \frac{K'P_{CO}}{1 + K'P_{CO}}, \qquad (2)$$

where k' and K' are the constants which depend on temperature. R_0 and R_r were comparable to each other at the same temperatures and CO pressures. Although R_0 values were somewhat greater than R_r, the discrepancies between them were less than 50%.

Reaction Mechanism

The observation that the rates of oxidation of CO in the presence and absence of oxygen in the gas phase were comparable to each other at the same temperature and pressure of CO suggests that the rate-determining step in oxidation of CO is the reaction between CO and lattice oxygen atoms of PrO_x. Zero-order dependence of the rate on the oxygen pressure supports this idea. The similar rates observed in Eqs. (1) and (2) in the presence and absence of oxygen, respectively, also support the idea that the catalytic oxidation of CO is determined by the reaction between the adsorbed CO and the surface lattice oxygens. The experimental rates of Eqs. (1) and (2) can be explained by means of a simple Langmuir–Hinshelwood type reaction mechanism as

$$CO(g) \overset{K_{CO}}{\rightleftharpoons} CO(a) \qquad (i)$$

$$\tfrac{1}{2}O_2 \rightleftharpoons O_s \rightleftharpoons O_l \qquad (ii)$$

$$CO(a) + O_s \xrightarrow{k_{iii}} CO_2(a) \qquad (iii)$$

$$CO_2(a) \rightarrow CO_2(g)\ (\text{trapped}) \qquad (iv)$$

where CO(a) and CO_2(a) are the adsorbed CO and CO_2, respectively. O_s and O_l indicate the lattice oxygen atoms on the surface and in the bulk, respectively. The desorption of O_s was very slow, as described earlier. The reaction between the adsorbed CO and the surface lattice oxygen is the rate-determining step. When we assume that the adsorption isotherm of CO is expressed by the Langmuir equation, the rate equation can be written as

$$\begin{aligned} R &= k_{iii}[CO(a)][O_s] \\ &= k_{iii}n \frac{K_{CO}P_{CO}}{1 + K_{CO}P_{CO}} [O_s] \\ &= k_0 \frac{K_{CO}P_{CO}}{1 + K_{CO}P_{CO}} \ (k_0 = k_{iii}n[O_s]), \qquad (3) \end{aligned}$$

where $[O_s]$ and n are the numbers of surface lattice oxygen atoms and adsorption sites for CO per gram PrO_x, respectively, and K_{CO} is the equilibrium constant for CO adsorption. We can assume that $k_{iii}n[O_s]$ ($=k_0$) is constant at a fixed temperature and composition of PrO_x. The initial compositions of PrO_x were the same in the experiments examining the pressure effect of CO at a fixed reaction temperature because the catalyst had been equilibrated with oxygen at 8.0 kPa before the experiments. The reaction mechanism described above, as well as Eq. (3), well explain the rates in Eqs. (1) and (2) observed experimentally.

Temperature Effects on k_o and K_{CO}

We can evaluate k_0 and K_{CO} in Eq. (3) from the slopes and intercepts in Fig. 2 for each experimental temperature. This is true for the kinetic parameters (k_0 and K_{CO}) in

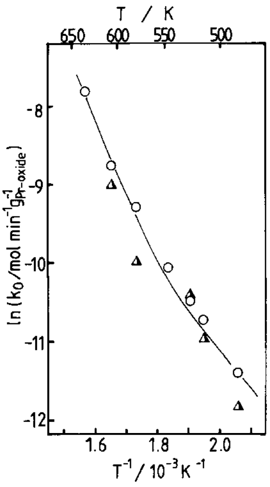

FIG. 3. $\ln k_0$ vs $1/T$ (○) from Fig. 2; and (▲) from the reaction with lattice oxygen atoms.

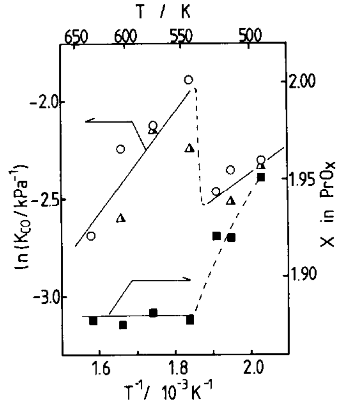

FIG. 4. Effects of temperature on $\ln K_{CO}$ and x in PrO_x. (○) K_{CO} from Fig. 2; (▲) K_{CO} from the reaction with lattice oxygen atoms; and (■) x in PrO_x.

the case of the reaction between CO and lattice oxygen atoms. Temperature dependences of k_0 and K_{CO} are shown in Figs. 3 and 4, respectively. The circles in both figures are the values calculated from the straight lines in Fig. 3 (CO oxidation in the presence of O_2). The triangles are the values obtained for the reaction between CO and lattice oxygen atoms. The kinetic parameters for oxidation of CO with and without gaseous oxygen coincide well with each other, as can be seen in Figs. 3 and 4.

It is to be noted that the line for the $\ln k_0$ vs $1/T$ plot in Fig. 3 is curved at temperatures around 530 K. An unusual transition of the linear lines for the $\ln K_{CO}$ vs 1/T plot in Fig. 4 also occurs around this temperature. The filled squares plotted in Fig. 4 indicate the initial O/Pr ratio ($=x$) of the PrO_x samples used for the experiments in Figs. 3 and 4. As described earlier, the compositions of PrO_x were determined on the basis of the amount of oxygen absorbed under the gas–solid equilibrium at the oxygen pressure of 8.0 kPa just before the initiation of CO oxidation. The squares in Fig. 4 indicate that the composition of PrO_x is constant ($x = 1.875 \pm 0.005$) at temperatures above 530 K, but x increases sharply as temperatures fall below 530 K. The composition of $PrO_{1.875}(=Pr_{16}O_{30})$ did not change with oxygen pressures of 2.7 to 16.0 kPa at temperatures above 530 K. Thus, the catalytic oxidation of CO must proceed over the intermediate phase $Pr_{16}O_{30}$ at above 530 K. However, at temperatures lower than 530 K, x in PrO_x was between 1.89 and 2.00 depending on the oxygen pressure. Since there exists no single phase oxide between the compositions of $Pr_{16}O_{30}$ and PrO_2 (*6*), the catalytic oxidation of CO below 530 K should be considered to proceed over the mixtures of $Pr_{16}O_{30}$ and PrO_2. However, it is natural to consider that the ability to oxidize CO is much stronger for PrO_2 than $Pr_{16}O_{30}$. Thus, the catalytic oxidation of CO at <530 K must proceed on the PrO_2 phase. The transition in the kinetic parameters (k_0 and K_{CO}) observed between the two temperature ranges (below and above 530 K) can be ascribed to the difference in the phases of PrO_x working in catalytic oxidation of CO under the experimental conditions.

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