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Kinetics and Mechanism of the Oxidation of Carbon Monoxide on Cd-Doped α-Fe_2O_3

INTRODUCTION

Oxygen deficiency in ZnO (n-type) is due to excess Zn. This excess Zn can be dissolved in the interstitial sites of ZnO (*1–5*). Choi and Kim (*6*) reported the catalytic activity of ZnO in terms of the amount of excess Zn in ZnO. Interstitial Zn can easily be oxidized at the low temperature of 261°C and oxidized Zn_i^+ is the site involved in covalent adsorption of CO molecule.

Amigues and Teichner (*7*) reported that the adsorption of oxygen on ZnO reduces electrical conductivity of ZnO, since electron transport occurs from ZnO to the adsorbed oxygen. Choi *et al.* (*8*) reported that sulfur dioxide is adsorbed on an oxygen vacancy at temperature of 240–330°C for a n-type TiO_2 catalyst, and interpreted the kinetic data as indicating competitive adsorption of SO_2 and O_2 on an oxygen vacancy. Tascon *et al.* (*9*) assumed that a CO_3^{-2} formation step is rate determining on perovskite-type oxide, $LaCoO_3$. Kim and co-workers (*10*) reported CO adsorption step is rate controlling on α-Fe_2O_3. On a Cd-doped α-Fe_2O_3, however, the present kinetic data for the CO oxidation and conductivity data of Cd-doped α-Fe_2O_3 under various P_{CO} and P_{O_2} show that O_2 oxidizes the catalyst by adsorption on an oxygen vacancy, while CO reduces catalyst by adsorption on a lattice oxygen.

EXPERIMENTAL

Preparation of materials. Cd-doped α-Fe_2O_3 (8 mol%) powder was prepared by following steps:

$$Cd(OH)_2 + 2\gamma\text{-}FeO(OH) \xrightarrow[300^\circ C]{} CdO\text{–}\gamma\text{-}Fe_2O_3 + 2H_2O \xrightarrow[1000^\circ C]{} 2H_2O + CdO\text{–}\alpha\text{-}Fe_2O_3$$

The prepared materials were identified by X-ray diffraction and resulting CdO–α-Fe_2O_3 was annealed at 500°C under 1×10^{-3} Torr in a quartz chamber for 2 h, and then slowly cooled to room temperature. Catalyst was mechanically stirred for 15 h in ethanol solution, and then dried at 150°C in an oven.

Kinetic and conductivity measurements. Details of the experimental apparatus and the procedures of kinetic and conductivity measurements are similar to those described in previous works (*8, 10*). In this study the total volume of a reaction chamber was 140 ml and the grain size of the powder was 100–160 mesh. The fixed amount of catalyst was 0.5 g. The total initial pressure of stoichiometric reactant mixtures ($2\ CO + O_2$) was 180 Torr. The catalyst was etched by dilute HNO_3 and $(NH_4)_2S_2O_8$, washed with ethanol, dried in an oven, and sintered at 500°C under 1×10^{-5} Torr for 2 h.

RESULTS

The reaction rates of CO oxidation on Cd-doped α-Fe_2O_3 are found to closely obey the equation of $-dP/dt = K\,P^{1.5}_{(CO+O_2)}$ with respect to the total pressure ($P_{CO} + P_{O_2} = 180$ mm Hg) in the reaction temperature range of 300 to 460°C. Figure 1 shows $(P^{-0.5} - P_o^{-0.5}) \times 2$ plotted against time at various temperatures and the linearity confirming the 1.5-order kinetics. From the Ar-

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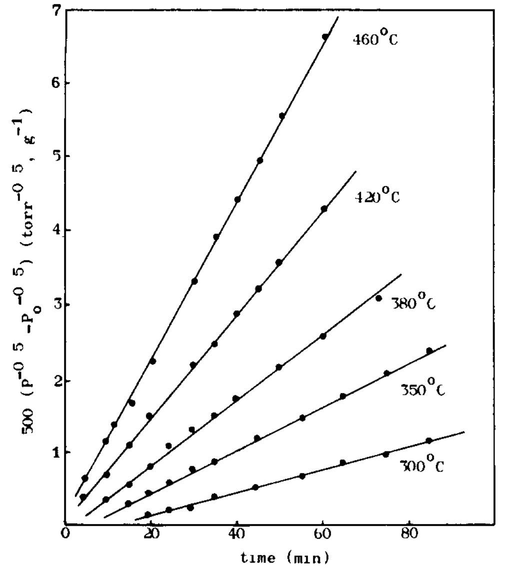

FIG 1 Oxidation rates of CO on 8 mol% Cd-doped α-Fe_2O_3 at temperatures from 300 to 460°C P_{CO} = 120 Torr, P_{O_2} = 60 Torr, P = total pressure P_O = total initial pressure

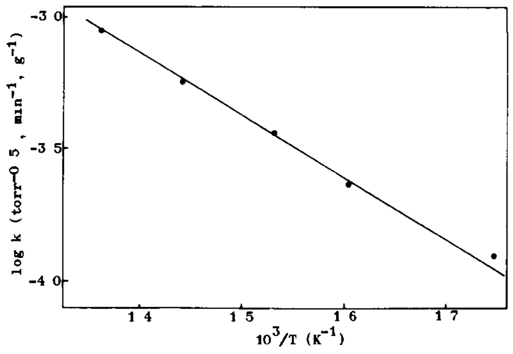

FIG 2 Arrhenius plot for the oxidation of CO on 8 mol% Cd-doped α-Fe_2O_3

rhenius plot, the activation energy is found to be 10 8 kcal/mol for Cd-doped α-Fe_2O_3 catalyst Table 1 represents the influence of partial pressures of CO and O_2 on the oxidation of CO at the same reaction temperature range From Table 1, the partial orders of CO and O_2 are found to be 1 and 0 5 on Cd-doped α-Fe_2O_3 The equation which represents the experimental data for Cd-doped α-Fe_2O_3 in the reaction temperature range 300–460°C is given by $-dP/dt = K P_{CO} P_{O_2}^{0 5}$

The conductivity data for Cd-doped α-Fe_2O_3 are shown in Figs 3–5 Figure 5 shows the variations of conductivity with CO and after the introduction of O_2 The conductivities increase with CO and decrease with O_2

TABLE 1

Reaction Rate Effect of P_{CO} and P_{O_2} for the CO Oxidation on Cd-Doped α-Fe_2O_3

T(°C)	P_{O_2}	P_{CO}	3V (Torr, g^{-1}, min^{-1})
380	59	120	1 150
380	30	60	0 405
380	30	120	0 801
460	61	120	3 640
460	29	57	1 170
460	30	118	2 600

DISCUSSION

As shown in Fig 1, Cd-doped α-Fe_2O_3 has catalytic activity above 300°C in the oxidation of CO The activation energy of 10 8 kcal/mol indicates that the catalytic reaction appears to include chemisorption From the data in Table 1, oxidation rates of carbon monoxide depend on the partial pressures of CO and O_2 This result means that carbon monoxide and oxygen adsorb possibly on the same site of the Cd-doped

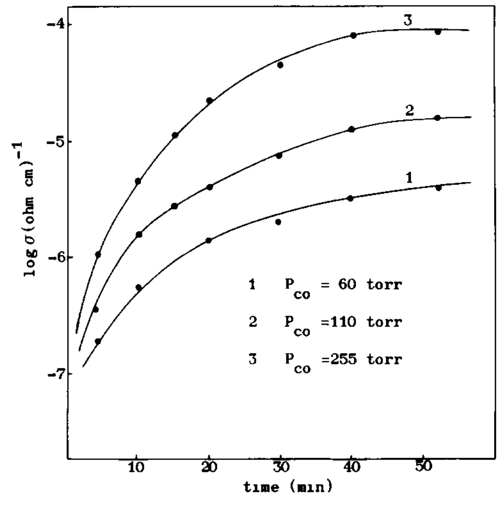

FIG 3 Conductivities of 8 mol% Cd-doped α-Fe_2O_3 with CO as a function of time at 400°C

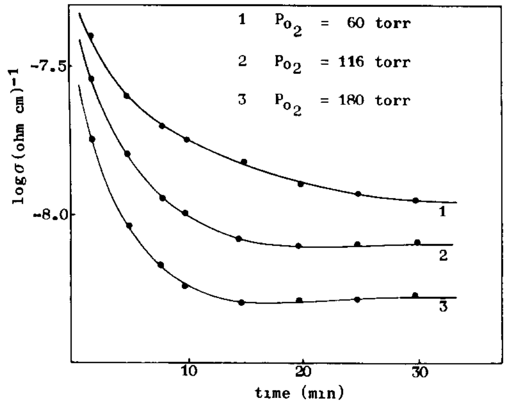

FIG 4 Conductivities of 8 mol% Cd-doped α-Fe_2O_3 with O_2 as a function of time at 400°C

α-Fe_2O_3 surface, the possible sites involved in the chemisorption of CO and O_2 are oxygen vacancy, interstitial iron, and lattice oxygen etc in *n*-type Cd-doped α-Fe_2O_3 catalyst

The conductivities increased along with time as shown in Fig 3 This indicates that the chemisorption of CO on above possible site of lattice oxygen, not oxygen vacancy, produces the conduction electron, and CO_2 was not observed by gas chromatograph

$$CO(g) + O^{2-}(latt) \overset{K_1}{\rightleftharpoons} CO_2^{-}(ads) + e^{-} \quad (1)$$

where O^{2-}(latt) is lattice oxygen and CO_2^-(ads) represents chemisorbed carbon monoxide on lattice oxygen, and e^- is conduction electron

The conductivity data shown in Fig 4, on the other hand, indicate that O_2 does not adsorb on a lattice oxygen, since the conductivities decreased along with time, the chemisorption of O_2 consumes the conduction electron, i e , probably produced in donor site due to the incorporation of cadmium into Fe_2O_3 lattice Moreover, the 0 5-order with respect to oxygen molecule suggests that O_2 may adsorb on an oxygen vacancy and then dissociate into two species, i e , $2O^-$(ads), first the oxygen molecule adsorbs on oxygen vacancy and the oxygen vacancy containing two trapped electrons ($O_0 \rightleftharpoons 2e^- + V_0^{2+} + \frac{1}{2} O_2(g)$) donates two electrons into the weakly adsorbed oxygen π^*_{2p} orbital, reducing the O—O bond order from double bond to single bond As a result of this reduction of the bond order, the weakly adsorbed species has a primary vibrational frequency characteristic of a peroxo O_2^{2-}(ads) species indicating an oxygen–oxygen single bond Secondly the conductivity data indicate that the peroxo O_2^{2-}(ads) can exist in the adsorbed state, since the π_g orbitals of molecular oxygen accept the conduction electrons trapped at oxygen vacancies However, this peroxo O_2^{2-}(ads) does not agree with the kinetic data, the 0 5-order with respect to oxygen One can agree with O^-(ads), satisfying the conductivity and kinetic data

The following equilibrium is included in the oxidation of CO,

$$O_2(g) + 2e^- \overset{K_2}{\rightleftharpoons} 2O^-(ads) \quad (2)$$

where O^-(ads) is adsorbed oxygen atom on oxygen vacancy The kinetic data in Table 1 and the conductivity data of Fig 5 lead us to believe that O^{2-}(latt) and oxygen vacancy are the adsorption sites involved in the oxidation of carbon monoxide The increasing and decreasing conductivities with P_{CO} and P_{O_2} in Fig 5 indicate that equilibria (*1*) and (2) proceed to the right On the other hand, the kinetic data in Table 1 indicate that the following elementary reaction may be included in the overall reaction

$$CO_2^-(ads) + O^-(ads) \xrightarrow{K} CO_2 + O^{2-}(latt) \quad (3)$$

The adsorption rate of CO on lattice oxygen, indicating the equilibrium (1), is slower than that of O_2 on an oxygen vacancy, showing the equilibrium (2) Therefore, one can conclude that the rate-controlling is equilibrium (1)

If the elementary reactions (1)–(3) are true in the oxidation reaction of CO, the rate law which is derived from the above mechanism must agree with the experimental rate law, $d(CO_2)/dt = k P_{CO} \; P_{O_2}{}^{1/2}$ From here the obvious subscripts are omitted $(CO_2^-) = K_1(CO)(O^{2-})/(e^-)$ in equilibrium

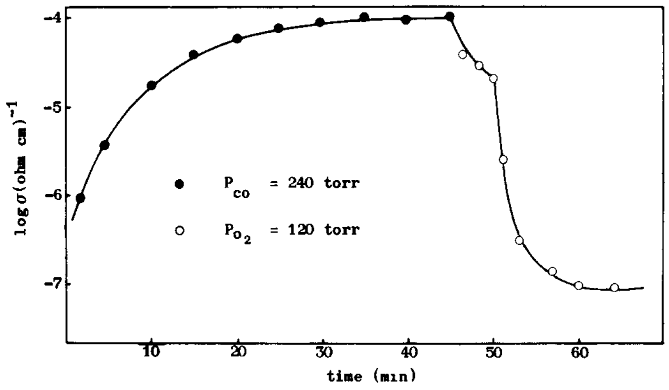

FIG 5 Conductivity of 8 mol% Cd-doped α-Fe_2O_3 with CO and after the introduction of O_2 as a function of time at 400°C

(1) and $(O^-) = (K_2)^{1/2}(O_2)^{1/2}(e^-)$ in equilibrium (2) The reaction rate which produces CO_2 in elementary step (3) is $d(CO_2)/dt = K\,(CO_2^-)\,(O^-)$ Substituting $(CO_2^-) = K_1\,(CO)\,(O^{2-})/(e^-)$ and $(O^-) = (K_2)^{1/2}(O_2)^{1/2}(e^-)$ into the above reaction rate equation,

$$
\begin{aligned}
\frac{d(CO_2)}{dt} &= K\,K_1(CO)(O^{2-})(e^-)^{-1} \\
&\quad (K_2)^{1/2}(O_2)^{1/2}(e^-) \\
&= K\,K_1(K_2)^{1/2}(CO)(O_2)^{1/2}(O^{2-}) \\
&\simeq K'\,(CO)(O_2)^{1/2}
\end{aligned}
$$

This is consistent with the experimental rate law and thus, since the suggested mechanism leads to the observed rate law, the equilibria (1), (2), and elementary reaction (3) are the reasonable mechanism

SUMMARY

The catalytic oxidation of CO has been investigated on Cd-doped α-Fe_2O_3 at temperatures from 300 to 460°C under various partial pressures of CO and O_2 The oxidation rates have been correlated with 1 5-order kinetics, first-order with respect to CO and 0 5-order with respect to O_2 CO appears to be adsorbed on the lattice oxygen as a molecular species, while O_2 adsorbs on an oxygen vacancy as an ionic species The adsorption process of CO is the rate-determining and the dominant defect of Cd-doped α-Fe_2O_3 is suggested from the agreement between kinetic and conductivity data

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