JOURNAL OF CATALYSIS 88, 283–288 (1984)

Kinetics and Mechanism of the Oxidation of Carbon Monoxide over Cadmium Oxide–Lanthanum Sesquioxide System

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Received October 14, 1983; revised February 22, 1984

The oxidation of carbon monoxide by gaseous oxygen in the presence of a powdered Cd-doped La_2O_3 catalyst has been investigated in the temperature range from 300 to 450°C under various CO and O_2 partial pressures. The conductivity of Cd-doped La_2O_3 has been measured at 450°C under various CO and O_2 pressures. The oxidation rates have been correlated with 1.5-order kinetics; the first-order with respect to CO and the 0.5-order with respect to O_2. For the above temperature range, the activation energy is around 11.3 kcal · mol^{-1}. CO appears essentially to be chemisorbed on the lattice oxygens of the Cd-doped La_2O_3, while O_2 adsorbs as ions on the oxygen vacancies induced by Cd-doping. The agreement between the kinetic data and conductivities supports the proposed oxidation mechanism and the dominant defect of Cd-doped La_2O_3.

INTRODUCTION

It has been known that metal oxides exhibit catalytic activity because of their nonstoichiometric composition. Most metal oxides contain an excess of oxygen or the metal in their crystal structures. It has been reported that the catalytic activity of NiO is due to excess oxygen (*1*) while the catalytic activity of ZnO, on the other hand, is due to oxygen vacancies induced by the excess zinc (*2–5*). Wagner and Hauffe report that the positive holes caused by the excess oxygen activate the reactant gas and the anion vacancies caused by the excess metal are responsible for the catalytic activity (*6*). On the other hand, Schwab reports that the catalytic activity of metal oxides on the oxidation of carbon monoxide varies with the amount of impurity incorporated in the oxide inducing the positive holes or anion vacancies (*7*). Cour found that the adsorption rate for oxygen in the oxidation of carbon monoxide is faster with Li^+-doped NiO than with Ga^{3+}-doped NiO (*8*).

Tascon *et al.* (*9*) confirmed by ir study that the CO_3^{2-} intermediate in the oxidation of carbon monoxide in the presence of a $LaCoO_3$ catalyst is formed on the surface of the catalyst in the temperature range of 100–150°C and that the activation energy is about 61 kJ · mol^{-1}.

La_2O_3 doped with Cd^{2+}, the catalyst used in this work, shows its extrinsic nature in the temperature range of 300–450°C. We have investigated the catalytic effect of Cd-doped La_2O_3 on the oxidation of carbon monoxide, its conductivity at 450°C under various CO and O_2 pressures, and its defect structure, and we suggest the oxidation mechanism by which this oxide acts as a catalyst.

EXPERIMENTAL

1. Material Preparation

(*a*) *The 4 mol% Cd-doped La_2O_3 powder.* Specpure La_2O_3 powder (99.99% purity) obtained from the Johnson-Mathey Company and CdO powder produced by the following chemical reaction were used for the preparation of CdO–La_2O_3 powder.

$Cd(NO_3)_2 \cdot 4H_2O$ (25.3 g) was dissolved in 200 ml of distilled water. NaOH (6.56 g) was dissolved in 200 ml of distilled water, giving a 0.082 *M* concentration.

These two solutions were combined and allowed to react for 30 min at 125°C. The

0021-9517/84 $3.00

precipitate was filtered, washed 6–7 times with distilled warm water, and then dried at 60°C. The chemical reaction involved is $Cd(NO_3)_2 \cdot 4H_2O + 2NaOH = Cd(OH)_2 + 2NaNO_3 + 4H_2O$. The $Cd(OH)_2$ powder was then heated at 250°C for 3 h and the result was a brownish CdO powder. Appropriate weights of the oxide powders for the 4 mol% $CdO–La_2O_3$ mixture were mixed in ethanol and stirred for 72 h to obtain a homogeneous dispersion.

The mixture was then filtered and dried. This powder was put on a small covered platinum crucible, placed in a preheated furnace, and fired in air pressure at 950°C for 5 h and then slowly cooled to room temperature. The amount of uncombined CdO in the fired sample was identified by chemical analysis (*10*). A 2-g sample (100–160 mesh) was treated with ammonium sulfate solution, in which only uncombined CdO was soluble, and the uncombined CdO was not found by EDTA titration in pH 10 using Eriochrome black T as an indicator. For identification of phase, X-ray powder diffractometry for the crystalline phase of sample was performed. The 4 mol% Cd-doped La_2O_3 catalyst powder was found to have a Blain test surface area of 11,230 cm^2/g and the amount of Cd dopant present was measured with an atomic absorption spectrometer.

(*b*) *The 4 mol% Cd-doped La_2O_3 pellet.* In order to measure the conductivity, some of the powder prepared by the above procedure was compressed under a pressure of 1.2 $tons/cm^2$ into a pellet and sintered at 600°C for 4 h. After sintering, the sample was given a light abrasive polish on one surface, then turned over and polished until the voids on this face of the specimen were fully eliminated. The sample was then cut into a rectangular shape with dimensions of $0.8 \times 0.5 \times 0.1$ cm and polished again.

(*c*) *CO and O_2.* CO—Carbon monoxide was prepared by the method given in the Weinhouse report (*11*). The mixture of $CaCO_3$ and Zn powders was heated to 800°C and held at that temperature until the reaction was complete ($CaCO_3 + Zn \rightarrow CaO + ZnO + CO$). O_2—Oxygen gas obtained from heating potassium chlorate at about 600°C was purified by passing it over glass wool, phosphorus pentoxide, and calcium chloride. This method of purification was found to give an oxygen gas sufficiently free of catalytic poisons for use in catalytic reactions. The purity of the CO and O_2 gases was confirmed by gas chromatography.

2. *Measurement of the Reaction Rate and Conductivity*

The details of the experimental apparatus, instruments, kinetic tests, and conductivity measurements have been given in previous papers (*1, 12, 13*). The rates of oxidation of carbon monoxide were measured in the completely closed all-glass reaction chamber with a total volume of 162 ml. The catalyst was etched with $(NH_4)_2S_2O_8$ and dilute HNO_3, washed in deionized distilled warm water, and then dried in a vacuum desiccator. The catalyst powder was placed in the reaction chamber and sintered at 450°C under 1×10^{-3} Torr for 1 h, then cooled to room temperature before gas introduction. The reaction chamber was then placed in the electric furnace maintained at a constant temperature within ±0.5°C. The grain size of the catalyst was 100–160 mesh and the amount of catalyst used was 0.5 g, and then the catalyst was distributed uniformly in the reaction chamber. The total initial pressure of the stoichiometric reactant mixture ($CO + \frac{1}{2}O_2$) was 210 Torr. The change in pressure due to the progress of the reaction was monitored by a capillary manometer connected to the reaction chamber at regular time intervals and read by scaled microscope. To investigate the effect of P_{CO} and P_{O_2}, the P_{CO} and P_{O_2} were varied at 350 and 450°C. The product gas was confirmed to be carbon dioxide by gas chromatography after reaction. The experimental error in the determination of the rate constant was

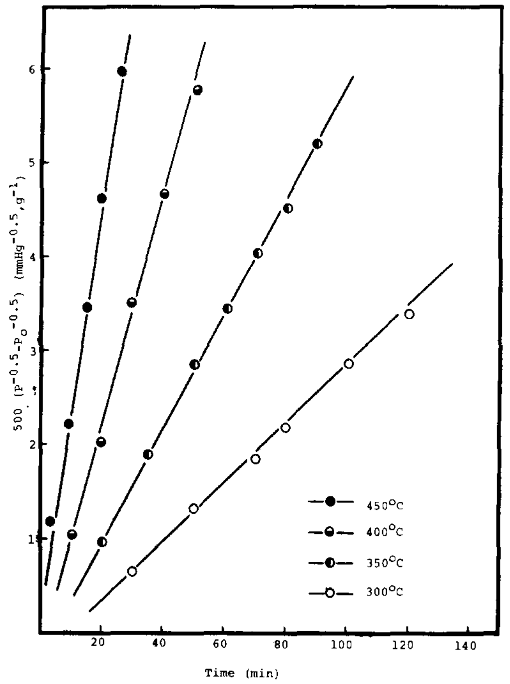

FIG. 1. The rate of oxidation of CO on Cd-doped La_2O_3 at temperatures from 300 to 450°C. P_{CO} = 140 Torr; P_{O_2} = 70 Torr; catalyst = 0.5 g; P = total pressure; P_O = total initial pressure.

≤8%, and of the activation energy, E, ±1 kcal/mol.

RESULTS

The kinetics was assumed to be first-order in carbon monoxide and 0.5-order in oxygen. The differential rate expression confirming this kinetics was integrated, and the experimental data were tested with the integrated rate expression. Figure 1 shows a plot using an integrated rate expression for various temperatures from 300 to 450°C and the plot shows a good linearity. From the rate expression of oxidation on this catalyst, the inhibition effect of carbon dioxide was not observed. The conversion over the catalyst of 0.5 g was 70–80% and the conversion increased with increasing of temperature. The data in Table 1 are the rate constants from the slopes of the lines in Fig. 1. Figure 2 is an Arrhenius plot of the rate constants in Table 1. Using the slope of the curve obtained from the plot, the activation energy has been found to be about 11.3 kcal/mol. The data in Table 2 are the initial reaction rates under various partial pressures of CO and O_2 in the presence of 0.5 g catalyst. From the data in Table 2, the partial orders for CO and O_2 have been found to be 1 and 0.5, respectively. Figure 3 shows the conductivity of the 4 mol% Cd-doped La_2O_3 under various CO pressures (P_{CO}) as a function of time at 450°C. The conductivity under CO pressures increased with increasing CO pressure. Figure 4

TABLE 1

Specific Rates for the Oxidation of Carbon Monoxide on Cd-Doped La_2O_3

Reaction temperature (°C)	k (liter$^{0.5}$ mol$^{-0.5}$ sec^{-1} g^{-1})
300	1.02×10^{-3}
350	2.13×10^{-3}
400	4.17×10^{-3}
450	8.92×10^{-3}

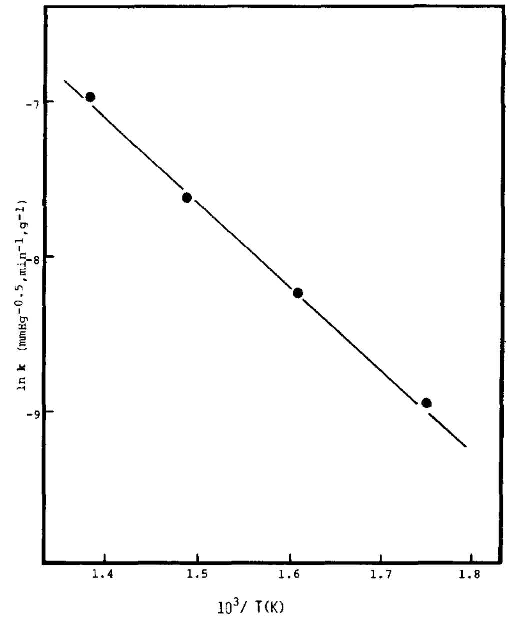

FIG. 2. Arrhenius plot for the rate of oxidation of CO on Cd-doped La_2O_3.

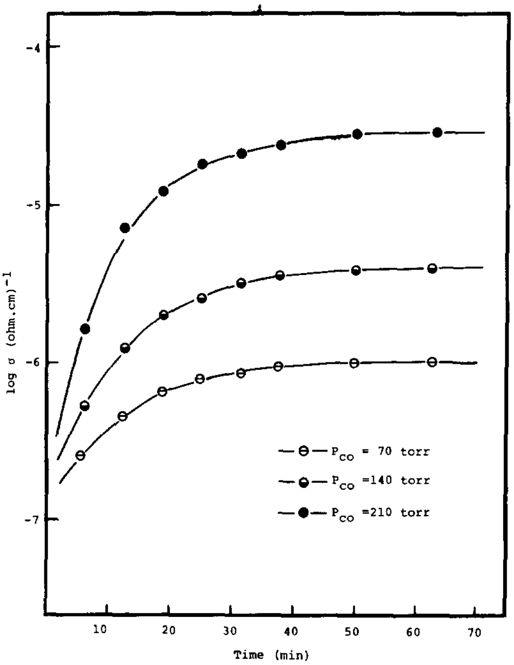

FIG. 3. The conductivity of Cd-doped La_2O_3 under various pressures of CO as a function of time at 450°C.

shows the conductivity under various O_2 pressures (P_{O_2}) and the conductivity decreased with increasing O_2 pressure. Figure 5 shows the variation of the conductivity under consecutive atmospheres of O_2 and CO ($P_{CO}:P_{O_2} = 2:1$).

As shown in Fig. 5, the conductivity with 70 Torr of oxygen showed a gradual decrease. When the conductivity with oxygen showed a constant value, 140 Torr of carbon monoxide was introduced, and then the conductivity was gradually increased. When the conductivity showed a constant value, the oxygen was reintroduced after evacuating the reactor, and then the conductivity was decreased again.

TABLE 2

Effect of P_{CO} and P_{O_2} on the Initial Rate for the Oxidation of Carbon Monoxide on Cd-Doped La_2O_3

Reaction temperature (°C)	P_{O_2}	P_{CO}	r (Torr · min^{-1} g^{-1})
350	70	140	1.12
350	34	70	0.38
350	35	140	0.78
450	70	140	3.60
450	36	70	1.25
450	35	138	2.56

DISCUSSION

1. *Possible Defects and Adsorption Sites*

From the conductivity data shown in Figs. 3–5 and the magnitude of the activation energy (11.3 kcal/mol), it is clear that the reactants can be chemisorbed on the surface of catalyst. Table 2 shows that the overall rates are dependent on the CO and O_2 partial pressures and in view of the half-order with respect to O_2 it seems likely that O_2 adsorbs as two species, i.e., $2O^-$(ads). Based on the principle of controlled valency, an oxygen vacancy induced by Cd doping is the defect structure in the Cd-doped La_2O_3 ($O_o \rightleftharpoons \frac{1}{2}O_2(g) + V\ddot{o} + 2e'$). This oxygen vacancy is served as a possible adsorption site for CO or O_2. Figure 1 shows that the adsorption rate of the reactants and the desorption rate of the product

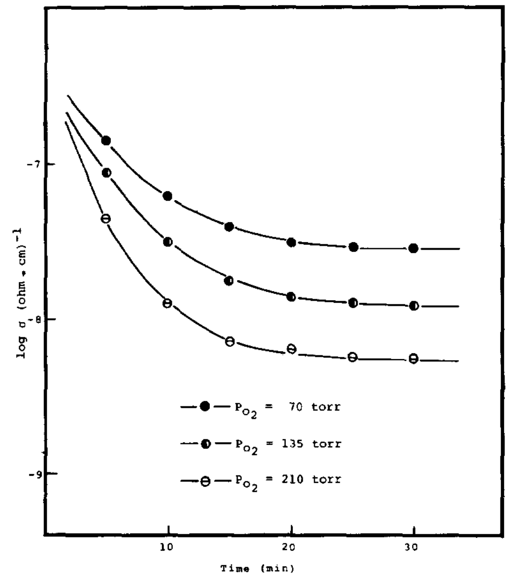

FIG. 4. The conductivity of Cd-doped La_2O_3 under various pressures of O_2 as a function of time at 450°C.

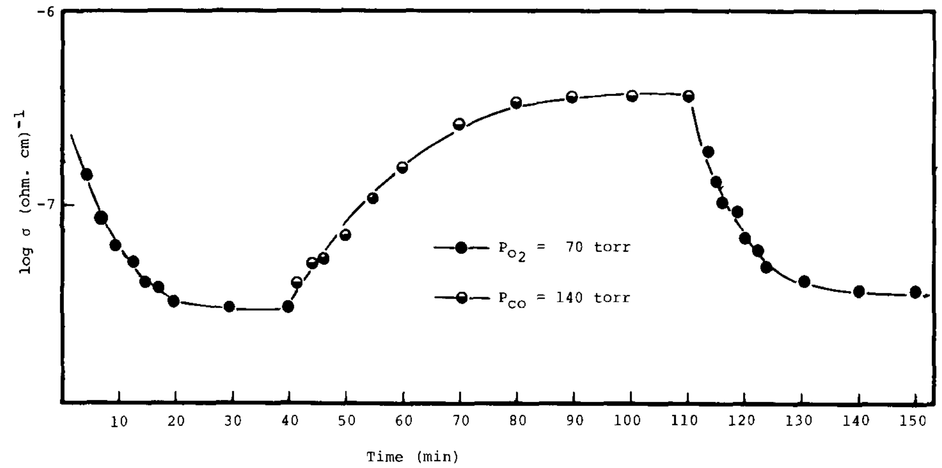

FIG. 5. Variation of the conductivity of Cd-doped La$_2$O$_3$ with O$_2$, then with the introduction of CO, and again with the introduction of O$_2$ as a function of time at 450°C.

increase with increasing temperature. If O$_2$ is adsorbed on an oxygen vacancy defect (Vö − 2e'), the electrical conductivity should decrease according to the equilibrium

$$O_2(g) + 2e^- \overset{K_1}{\rightleftharpoons} 2O^-(ads) \qquad (1)$$

where e^- is a conduction electron trapped at an oxygen vacancy. Figure 4 shows that the conductivities decrease with increasing O$_2$ pressure. This result indicates that equilibrium (1) can exist in the catalyst and that O$_2$ adsorbs on the oxygen vacancies. On the other hand, Fig. 3 shows that the conductivities increase with increasing CO pressure and also the conductivities in Fig. 5 increase with the introduction of CO after O$_2$ adsorption. These results indicate that during CO adsorption electrons are added to the Fermi surface. Therefore, one must consider that a different site is involved in the adsorption of CO. If CO is chemisorbed on a lattice oxygen, the electrical conductivity should increase according to the equilibrium

$$CO(g) + O^{2-}(latt) \overset{K_2}{\rightleftharpoons} CO_2^-(ads) + e^- \qquad (2)$$

where O^{2-}(latt) is a lattice oxygen and CO_2^-(ads) is the CO adsorbed on the lattice oxygen. In equilibrium (2) the concentration of electrons increases with increasing CO partial pressure, and thus the conductivity will increase. The experimental data in Figs. 3 and 5 satisfy the equilibrium (2). Therefore, in view of the conductivity data shown in Figs. 3–5, one can conclude that the adsorption site for CO is lattice oxygen and the adsorption site for O$_2$ is oxygen vacancy.

2. *Oxidation Mechanism*

Table 2 shows that the foreward reaction rate increases with increasing partial pressures of CO and O$_2$. This result supports that the reaction

$$CO_2^-(ads) + O^-(ads) \xrightarrow{k} CO_2(g) + O^{2-}(latt) \qquad (3)$$

is involved in the oxidation process of CO.

The rate equation obtained from the kinetic data in Table 2 is $r = k''P_{CO} \cdot P_{O_2}^{1/2}$. On the other hand, one can derive the above rate equation from equilibria (1), (2), and reaction (3). From equilibrium (1), the equilibrium constant is

$$K_1 = \frac{(O^-_{(ads)})^2}{(e^-)^2(O_2)} \qquad (4)$$

From Eq. (4),

$$(O^-_{(ads)}) = K_1^{1/2}(e^-)(O_2)^{1/2}.$$

The equilibrium constant in equilibrium (2) is

$$K_2 = \frac{(CO^-_{2(ads)})(e^-)}{(CO)(O^{2-}_{(latt)})} \qquad (5)$$

From Eq. (5),

$$(CO^-_{2(ads)}) = \frac{K_2(CO)(O^{2-}_{(latt)})}{(e^-)}.$$

From reaction (3), the rate of production of CO_2 can be represented as

$$\frac{d(CO_2)}{dt} = k(CO^-_{2(ads)})(O^-_{(ads)}). \qquad (6)$$

The above rate equation can be rewritten with the substitutions of

$$(CO^-_{2(ads)}) = K_2(CO)(O^{2-}_{(latt)})(e^-)^{-1}$$

and

$$(O^-_{(ads)}) = K_1^{1/2}(e^-)(O_2)^{1/2}$$

$$\begin{aligned}\frac{d(CO_2)}{dt} &= k \cdot K_2 \frac{(CO)(O^{2-}_{(latt)})}{(e^-)} K_1^{1/2}(e^-)(O_2)^{1/2} \\ &= k \cdot K_2 \cdot K_1^{1/2}(CO)(O_2)^{1/2} (O^{2-}_{(latt)}). \qquad (7)\end{aligned}$$

The concentration of $O^{2-}_{(latt)}$ can be taken to be constant.

Therefore, Eq. (7) is as follows and is consistent with experimental rate law.

$$\frac{d(CO_2)}{dt} \simeq k'(CO)(O_2)^{1/2}. \qquad (8)$$

This derived rate law (8), which is based on the suggested oxidation mechanism, gives the same orders as the observed rate law; one-half order for O_2 and first-order for CO. From this result, one can suggest that equilibria (1), (2), and reaction (3) constitute the oxidation mechanism of CO in the presence of a Cd-doped La_2O_3 catalyst.

ACKNOWLEDGMENTS

We are grateful to the Ministry of Education of Korea for financial support and to Dr. Young Hwan Kang and Professor Ki Hyun Yoon for helpful discussions.

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