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A Study on the Kinetics and Mechanism of the Oxidation of Carbon Monoxide over Zinc Oxide

Jae Shi Choi and Bo Won Kim
Department of Chemistry, Yonsei University, Seoul, Korea

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A kinetic study on the oxidation reaction of carbon monoxide has been carried out between 260 and 350°C by means of the static method using *n*-type ZnO semiconductor as a catalyst under various oxygen and carbon monoxide pressure. The order of reaction between 260 and 320°C was found to be 1.5, with $\mathrm{d}P_{CO_2}/\mathrm{d}t=kP_{CO}\cdot P_{O_2}{}^{1/2}$. The Roginsky-Zeldovitsch equation,[1] $\mathrm{d}P_{CO_2}/\mathrm{d}t=ke^{-ap}$, fits well at 350°C. The mechanism of the reaction can be explained by the *n*-type character of ZnO.[2-4]

Hauffe,[5] Wagner,[6] and Schwab[7] studied the oxidation reaction of CO using metal oxide semiconductors. Several papers have affected on the activity and electronic configuration. Wagner and Schwab, who measured the conductivity on various metallic oxides, continued their researches on ZnO containing impurities such as Al_2O_3 and Li_2O. However, their theories did not agree with each other, or with those of many other investigators after them. Ambigues and Teichner[8] showed that a kinetic study combined with measurements of catalyst conductivity in the presence of reagents or products gives valuable information on the mechanism of the reaction. Chizhikova[9] studied the oxidation of CO over pure ZnO, ZnO (0.5 at % In), ZnO (0.5 at % Li) and ZnO (1.0 at % Li) *in vacuo* (10^{-2}–1 mmHg) from room temperature to 450°C. Their results and also those of the others did not agree with each other.

Ambigues and Teichner[8] showed that correlations between the electronic conductivity and catalytic activity could be investigated in two ways. First, a correlation exists between the conductivity and the rate constant of the reaction or the apparent activation energy of the reaction. The conductivity is usually modified by doping the catalyst with altervalent cations. Second, the electrical properties of the catalyst without doping can be studied during the course of reaction. From the change of the conductivity the state of the solid can be clarified.

Krause[10] conducted research on the oxidation of CO to CO_2 on oxide catalysts such as ZnO, NiO, and V_2O_5, and offered explanation in term of chemisorption of oxygen or carbon monoxide on the catalyst and desorption of the oxidized product. Otsuka[11] *et al.* studied the oxidation of CO over ZnO by measuring the adsorption of CO, O_2, and CO_2 on the catalyst in the temperature range 200—250°C under 50—300 mmHg. They concluded that the reaction rate was independent of the adsorption of CO and O_2. Matsuura *et al.*[12] also studied the oxidation of CO in the presence of ZnO as a catalyst at 200—500°C under 0.1—760 mmHg by both the flow and static methods. They concluded that the chemisorption of oxygen is the rate determining step.

We carried out research on the CO oxidation on pure ZnO prepared under various conditions by the static method. The kinetics and mechanism are discussed in this paper.

Experimental

Materials. Four samples A, B, C, and D of ZnO were prepared under different initial conditions (temperature and pressure).

ZnO: *Sample A*: Prepared by the thermal decomposition of c.p. $ZnCO_3$ in an electric furnace at 350°C in air for 1 hr.

After being cooled to room temperature, it was etched with $(NH_4)_2S_2O_8$ and dilute HNO_3, washed in distilled water and then dried in a vacuum desiccator.

Sample B: Prepared by the same method as for Sample A except for the decomposition temperature being 500°C, kept in a vacuum desiccator until used in experiment.

Sample C: Prepared by the same method as for Sample A except for the decomposition temperature being 650°C.

Sample D: Prepared by the same method as for Sample C except for the pressure of 10^{-3} mmHg.

Sample of ZnO prepared by the above methods were verified by X-ray diffraction. The yellow color was found to deepen in the order $A<B<C<D$.

The degree of nonstoichiometry (Zn excess) in Samples A, B, C, and D increased in the order $A<B<C<D$.[13]

Carbon Monoxide: The apparatus used for preparation of the CO gas is shown in Fig. 1.

Carbon monoxide was prepared by the reaction of formic acid with concentrated sulfuric acid. The reaction was carried out by passing formic acid through concentrated sulfuric acid in an evacuated Pyrex flask connected to a vacuum system. CO was purified with glass wool, KOH, $CaCl_2$, and P_2O_5, and stored in a container, which had been

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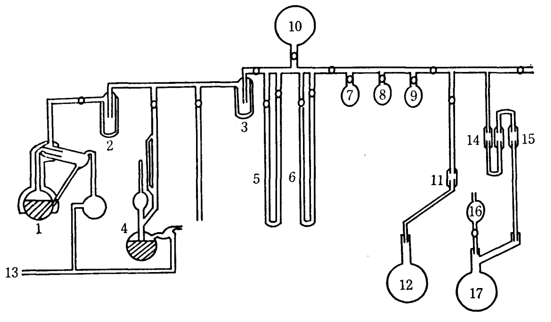

Fig. 1. Vacuum system.
1: Diffusion pump, 2,3: Dry ice trap, 4: McLeod gauge, 5,6: Manometer, 7,8,9: O_2 Storage tank, 10: CO Strorage tank, 11: $CaCl_2$ tube, 12: $KClO_3$ flask, 13: to Vacuum pump 14: $CaCl_2$ tube, 15: NaOH tube 16: HCOOH flask 17: H_2SO_4 flask.

evacuated to 10^{-5} mmHg.

Oxygen: The apparatus used for preparation of O_2 gas is shown in Fig. 1.

Oxygen obtained by heating potassium chlorate at about 600°C[14] was purified by passing over glass wool, P_2O_5 and $CaCl_2$. This was found to give a oxygen sufficiently free of catalytic poisons when used in catalytic reactions. The purity of the CO and O_2 gases was confirmed by gas chromatography.

Experimental Procedure. A half gram of ZnO (200 mesh) was distributed uniformly in the reaction chamber. After the pressure was reduced to 10^{-3}mmHg at room temperature, oxygen and carbon monoxide were added in a ratio of 70:140 (mmHg). The chamber was then placed in the electric furnace maintained at a constant temperature.

The change in pressure due to the progress of the reaction was monitored by a manometer connected to the reaction chamber at regular time intervals. To check separately the influence on this reaction of P_{O_2} and P_{CO} which are almost interdependent, the ratio of P_{O_2} and P_{CO} was varied, 70:70, 70:210, and 140:140 (mmHg), and the reaction rate measured in the same manner.

The resulting gas was confirmed to be carbon dioxide by gas chromatography after the reaction.

Results

The results from the reactions with Samples A, B, C, and D as catalysts at 260°C, 290°C, 320°C, and 350°C, respectively are given in Figs. 2—7.

The order of reaction is 1.5 for Samples A, B, C, and D at 260—320°C giving $dP_{CO_2}/dt=kP_{CO}P_{O_2}{}^{1/2}$. At 350°C, the Roginsky-Zeldovitsch equation,[1] $dP_{CO_2}/dt=ke^{-ap}$ (a; parameter, p; the amount of conversion, k; rate constant) holds; $\log(t+t_0)=ap-\log ka$ (Fig. 6). The rate constants from Figs. 2—6 are given in Tables 1 and 2. The activation energies calculated from Figs. 2—5 and Tables 1 and 2 are 16.04, 15.97, 14.86, and 13.69 kcal/mol, respectively. To check the influence of P_{O_2} and P_{CO} on these reactions separately, the ratio of P_{O_2} and P_{CO} was varied; 70:210, 70:140, 70:70, 140:70, and 140: 140 (mmHg) at 260°C on Sample C. The results can be seen in Fig. 6 and the rate constants in Table 2.

Discussion

The rate equations on Samples A, B, C, and D can be classified into two types; one between 260 and 320°C and the other at 350°C. The 260 to 320°C readings do not agree with those of Ambigues and Teichner,[8] who showed that the rate is proportional to the square root of the oxygen pressure and independent of CO pressure, nor with those of Chizhikova,[9] who proposed that the kinetics of the oxidation of CO over pure ZnO is given by the equation $-dP_{CO}/dt=kP_{CO}^{0.5}$ and that over Li- and In-doped ZnO by the equation $-dP_{CO}/dt=kP_{CO}^{0.7}$. However, there is an agreement with the results

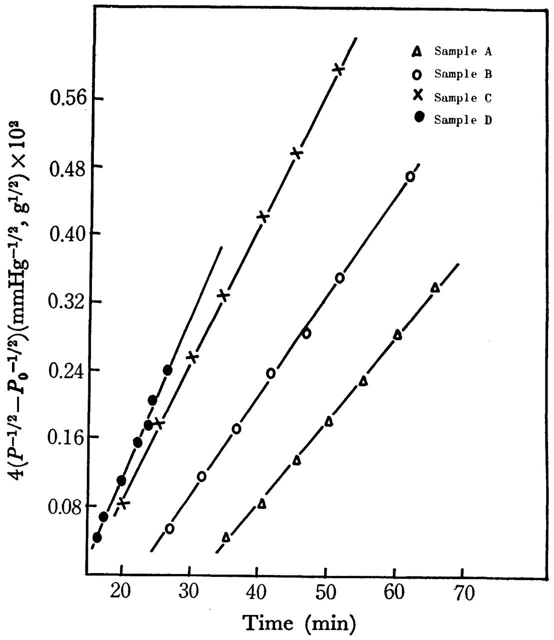

Fig. 2. The rates of oxidation reaction of carbon monoxide on ZnO at 260°C; P_{O_2}:P_{CO}=70:140; ZnO, 0.5 g (200mesh).

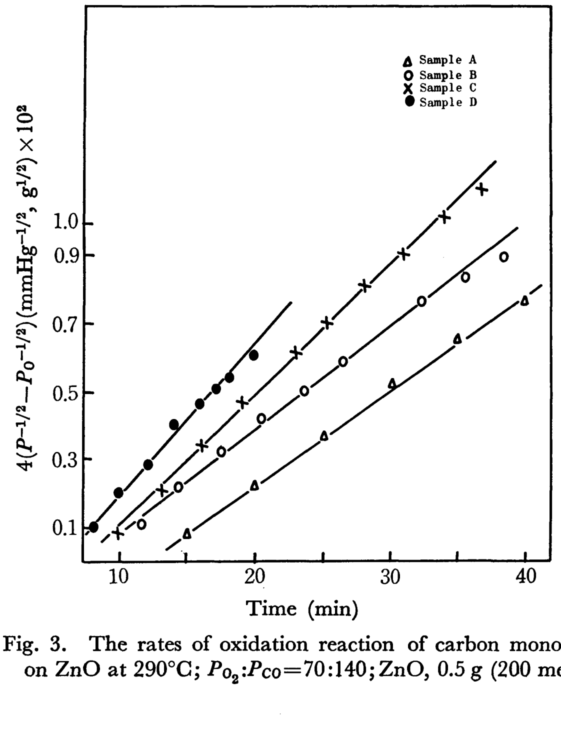

Fig. 3. The rates of oxidation reaction of carbon monoxide on ZnO at 290°C; P_{O_2}:P_{CO}=70:140; ZnO, 0.5 g (200 mesh).

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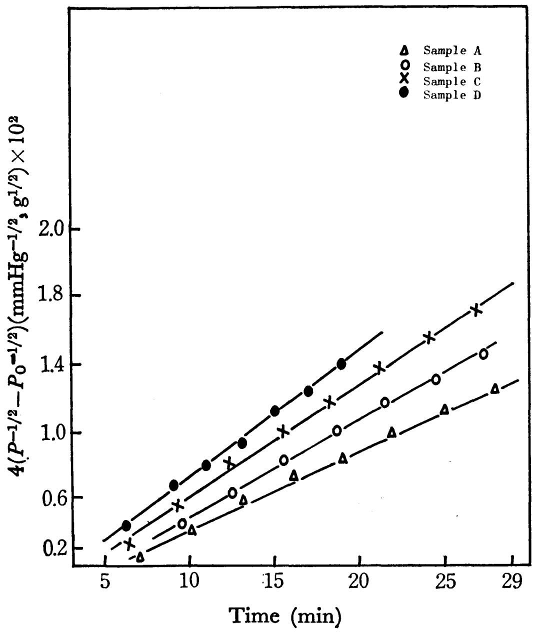

Fig. 4. The rates of oxidation reaction of carbon monoxide on ZnO at 320°C; P_{O_2}:P_{CO}=70:140; ZnO, 0.5 g (200 mesh).

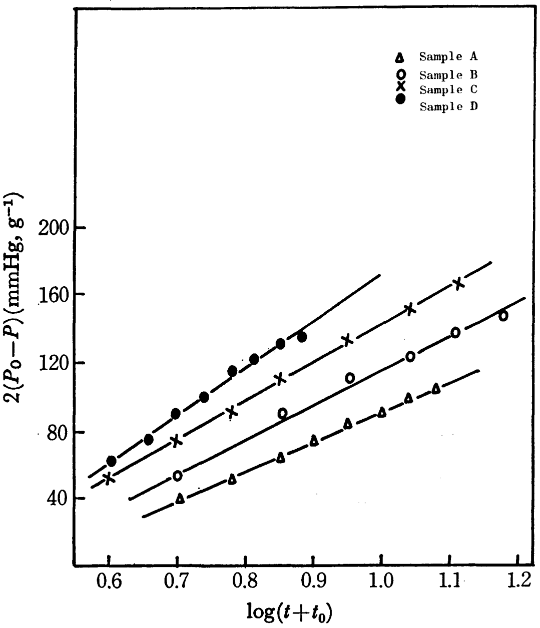

Fig. 5. The rates of oxidation reaction of carbon monoxide on ZnO at 350°C; P_{O_2}:P_{CO}=70:140; ZnO, 0.5 g (200 mesh).

TABLE 1. k VALUES AS A FUNCTION OF TEMPERATURE

k Sample	$k(\text{mmHg}^{-1/2}\ \text{g}^{1/2}\ \text{min}^{-1})$ 260°C	290°C	320°C	$k(\text{g}^{-1}\ \text{min}^{-1})$ 350°C
A	1.00×10^{-4}	2.82×10^{-4}	4.63×10^{-4}	1.69×10^{-1}
B	1.20×10^{-4}	3.00×10^{-4}	5.52×10^{-4}	1.78×10^{-1}
C	1.62×10^{-4}	3.65×10^{-4}	6.70×10^{-4}	2.38×10^{-1}
D	1.95×10^{-4}	4.40×10^{-4}	7.21×10^{-4}	2.81×10^{-1}

of Otsuka *et al.*,[11] who showed that the over all reaction is $dP_{CO_2}/dt=kP_{CO}P_{O_2}{}^{1/2}$, and those of Matsuura *et al.*,[12] who explained that the initial rate of reaction as determined by the static method is $dP_{CO_2}/dt=kP_{CO}P_{O_2}{}^{1/2}$.

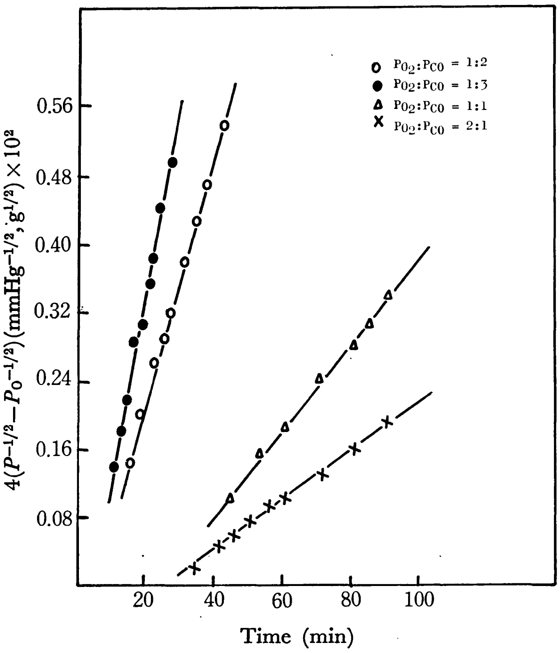

Fig. 6. The rates of oxidation reaction of carbon monoxide on ZnO (Sample C) under the various P_{CO} and P_{O_2} at 260°C; ZnO, 0.5 g (200 mesh).

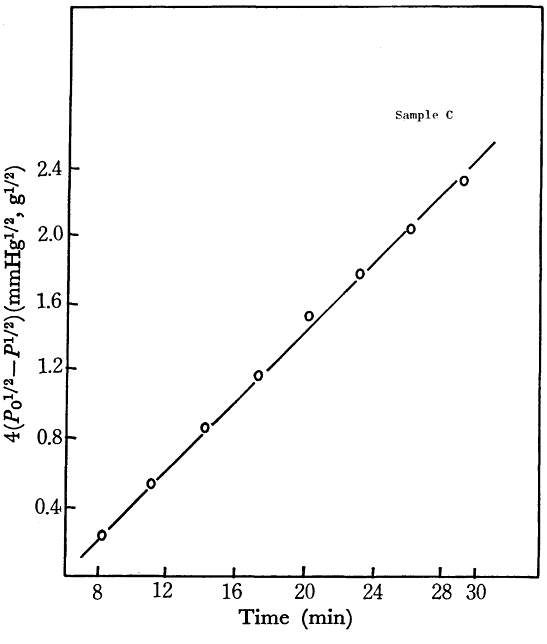

Fig. 7. The determination of the order of oxygen pressure in this kinetic equation at 260°C; P_{O_2}:P_{CO}=20:255; $dP_{CO_2}/dt=KP_{O_2}{}^{1/2}$

TABLE 2. k VALUES AS A FUNCTION OF P_{CO} AND P_{O_2} AT 260°C ON SAMPLE C

P_{O_2}	P_{CO}	$k(\text{mmHg}^{-1/2}\ \text{g}^{1/2}\text{min}^{-1})$
70	210	2.24×10^{-4}
70	140	1.62×10^{-4}
70	70	0.52×10^{-4}
140	70	0.30×10^{-4}
140	140	0.96×10^{-4}

The 350°C reading does not correspond to any of the above research. We see from Fig. 3 that the catalytic activity of the ZnO Samples is in the order A<B<C<D. Thus the effect can be explained by the increase of *n*-type characteristic. Oxygen deficiency in ZnO can be due to the excess Zn dissolved in the interstitial sites of ZnO$^{15-19)}$ when $ZnCO_3$ is decomposed thermally. The catalytic activity of ZnO dependent on the amount of excess Zn (or the amount of oxygen deficiency). The mechanism of the CO oxidation reaction is explained as follows; at first oxygen accepts electrons from the activated ZnO surface to be adsorbed on the active sites, O^-(ads) being thus formed.

$$\frac{1}{2}O_2(g) + e = O^-(ads)$$

Carbon monoxide reacts then with the O^-(ads) forming CO_2(ads). Carbon dioxide is then desorbed from the ZnO surface. This corresponds to Ambigues and Teichner's conclusions$^{8)}$ that oxygen gas is adsorbed weakly while carbon monoxide gas is strongly adsorbed on the ZnO surface and carbon monoxide gas reacts on the O^-(ads) to form CO_2(g), *viz.*

$$\frac{1}{2}O_2(g) + e^- = O^-(ads)$$

$$O^-(ads) + CO(g) = CO_2(ads) + e^-$$

$$CO_2(ads) = CO_2(g)$$

where (g) is an abbreviation for the gas state and (ads) the adsorbed state. The mechanism is explained by means of the Rideal mechanism. For the same catalyst the reaction rate at high temperature is greater than that at a low temperature. At the same temperature the reaction rate for the catalyst prepared at high temperature is greater than that for the catalyst prepared at a lower temperature. The reaction rate for the case in which the catalyst prepared in a vacuum (the same temperature condition) is used is greater than that for the catalyst prepared in air (Table 1). At 260°C for Sample C the reaction rate is small when P_{O_2} is greater than P_{CO} and great when P_{O_2} is smaller than P_{CO} (Table 2). The results correspond to the deductions from the conductivity data obtained by Ambigues and Teichner$^{8)}$ and also the degree of nonstoichiometry of ZnO (Zn excess). They correspond also to the result by Teichner. The conductivity at $P_{O_2}=3$ mmHg was greater than that at $P_{O_2}=160$ mmHg. After evacuation to 10^{-5} mmHg again, the conductivity at the initial oxygen pressure of $P_{O_2}=3$ mmHg became greater than that at $P_{O_2}=160$ mmHg.

	P_{O_2}	
log σ	3(mmHg)	160(mmHg)
log σ	$\bar{6}.80$	$\bar{7}.1$
log σ_0	$\bar{3}.50$	$\bar{4}.50$

Cited from *Discuss. Faraday Soc.*, **41**, 362 (1966).

These results show that if the oxygen pressure is increased, the amount of irreversibly adsorbed oxygen is increased, and if the oxygen pressure is decreased, the amount of irreversibly adsorbed oxygen is decreased. The mechanism for the CO oxidation reaction proposed here with is in line with the findings of Otsuka *et al.*$^{11)}$ in that the adsorbed carbon monoxide did not influence this reaction either. The catalytic effect of ZnO depends on the sintering temperature and pressure, and the amount of excess Zn (or the amount of deficient oxygen) has an important effect on these reaction rates.

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