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Pt 및 SnO_2 촉매하에서의 일산화탄소의 산화반응

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Catalytic Oxidation of Carbon Monoxide on Pt and SnO_2

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요 약. SnO_2, Sb-doped SnO_2, 그리고 백금촉매하에서 일산화탄소의 산화반응을 연구하였다.

SnO_2 및 Sb-doped SnO_2 촉매하에서 산화반응은 CO 및 O_2에 대해서 각각 1차, 백금 촉매하에서는 $\frac{1}{2}$차 반응에 따랐다. SnO_2에 소량의 Sb첨가(dopant composition: 0.05∼0.1 mole%)는 반응속도를 증가시키고 그 이상의 첨가는 오히려 반응속도를 감소시켰다. 백금 촉매하의 산화반응에서는 일산화탄소의 농도가 증가함에 따라 반응속도가 오히려 감소하는 억제효과를 보여주었다.

각 촉매하에서 산화반응의 활성화에너지는 Sb-dopoped SnO_2 촉매(dopant composito : 0.05 mole%)에서 5.7 kcal, 백금 촉매에서 6.4 kcal이었다.

실험적으로 얻은 반응차수와 doping 효과로부터 가능한 반응메카니즘을 제안하였다.

ABSTRACT. Oxidation reactions of carbon monoxide on SnO_2, Sb-doped SnO_2, and Pt catalyst were studied.

The oxidation reaction was found to be first order with respect to both CO and O_2 on SnO_2 and Sb-doped SnO_2 catalysts, and to be of half order on Pt catalyst. A small addition of Sb to SnO_2 (depant composition: 0.05∼0.1 mol%) increased the rate of oxidation. On the contrary, a large addition decreased the rate.

From the rate expression of oxidation on Pt catalyst, the inhibition effect of carbon monoxide on the rate of oxidation was deduced. The experimentally obtained activation energies were 5.7 kcal for the Sb doped SnO_2 catalyst (dopant composion: 0.05 mole%), and 6.4 kcal for the Pt catalyst.

A possible reaction mechanism was proposed from the experimentally obtained kinetic data.

INTRODUCTION

Oxidation reactions of carbon monoxide on Pt[1~4] and transition metal oxide catalysts have been studied. Among the transition metal oxides, NiO[5~8], MnO_2[8~10], CuO[11] and Co_3O_4, *etc.* have been found be active catalysts in the oxidation of carbon monoxide. The kinetics of oxidation reaction of carbon monxide has also been studied for platinum supported type catalyst.

As early as 1922, Langmuir[1] reported that the oxidation of carbon monoxide on platinum wire could involve the reaction of gaseous carbon monoxide with adsorbed atomic oxygen. Sklyarov[2] and the others[3~4], however, found that the oxidation of carbon monoxide involved molecular oxygen and carbon monoxide. Shishu and Kowalczyk[3] reported a power law type rate model which indicated the rate of oxidation to be directly proportional to the partial pressure of oxygen and inversely proportional to a half power on the partial pressure of carbon monoxide.

Some studies on the impurity doped semiconductors to examine the essential features of the catalytic effect and the reaction mechanism have recently been carried out. The electronic properties of SnO_2 and impurity doped SnO_2 and impurity doped SnO_2[12~15] have been studied quite extensively. Carrol and Slack[13] reported that the addition of Sb(III) to SnO_2 gave a large effect on the electrical conductivity of the semiconductor. A samll addition of Sb(III) to SnO_2 increased the electrical conductivity, on the contrary, a large addion of Sb(III) decreased the conductivity.

The purpose of this paper is to obtain rate equations, kinetic data and to study the effect of the addition of antimony to SnO_2 on the rate of carbon monoxide oxidation. Those results are to be compared with the electrical conductivity data to elucidate the relation between the electronic properties and the catalytic effect of semiconductors.

EXPERIMENTAL

Materials. Carbon monoxide and oxygen were purchased from Matheson Co. with 99.9 % purities. SnO_2(E.P) and HCl (E.P) were from Kanto Chemical Co. NH_4OH (E.P), anhydrous $SnCl_4$, and NH_4NO_3 were from Wako Pure Chemical Ind., and $SbCl_3$ from Merck.

Preparation of Catalysts. Sb-doped SnO_2 polycrystalline semiconductors were prepared by the coprecipitation of antiomony and tin hydroxides with ammonium hydroxide from appropriate mixtures of antimony and tin chloride solutons in HCl, followed by thorough washing and heat treatment.

Stock solutions of $SbCl_3$ were prepared in HCl. The composition range of dopant were *ca.* 0.05~2.0 mole%. The solution was maintained at 100 °C and 10 % ammonia solution was added dropwise until pH of 3.2 achieved. The resulting mixed hydroxide precipitate was washed alternatively with NH_4NO_3 solution and with water until the washings showed no trace of chloride ion. Finally the precipitate was washed with water and filtered. The yellow gel like precipitates were dried for 12 hours at 80 °C. Samples of this material were broken up and subjected to heat treatment at 450 °C for 2 hours.

Sample 1 : SnO_2 (Kanto Chemical Co.) heated at 450°C for 2 hours.,
Sample 2 : SnO_2 dried at 200 °C for 12 hours and followed by heat treatment at 450 °C for 2 hours.,
Sample 3~7 are SnO_2 and Sb(III) doped SnO_2 dried at 80 °C for 12 hours and followed by heat treatment at 450 °C for 2 hours,
Sample 3 : SnO_2,
Sample4 : Sb-dopdd SnO_2 (0.05 mole%),
Sample 5 : Sb-doped SnO_2 (0.1 mole%),
Sample 6 : Sb-doped SnO_2 (1 mole%),
Sample 7 : Sb-doped SnO_2 (2 mole%),
Pt : metal powder.

The X-ray diffraction patterns of the Sample 3 and 7 are shown in *Fig.* 1.

Pretreatment of Catalysts. All the catalyst used were evacuated under vacuum ($<10^{-3}$ torr) at 200 °C for 2 hours and slowly cooled to reaction temperatures.

Apparatus and Procedure. The instrumentation and the procedure for the kinetic measurements are essentially the same as described in the previous paper[8] from this laboratory.

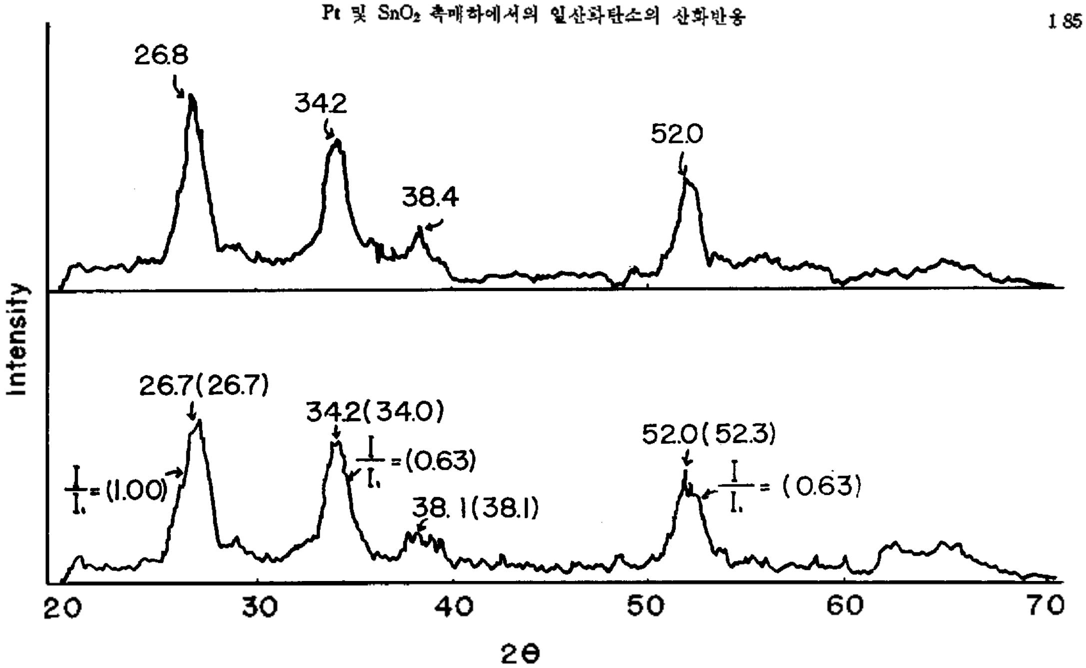

Fig. 1. X-Ray diffraction pattern of sample 3 (SnO_2 polycrystalline) and sample 7 (Sb-doped SnO_2, dopant; 2.0 mole%).

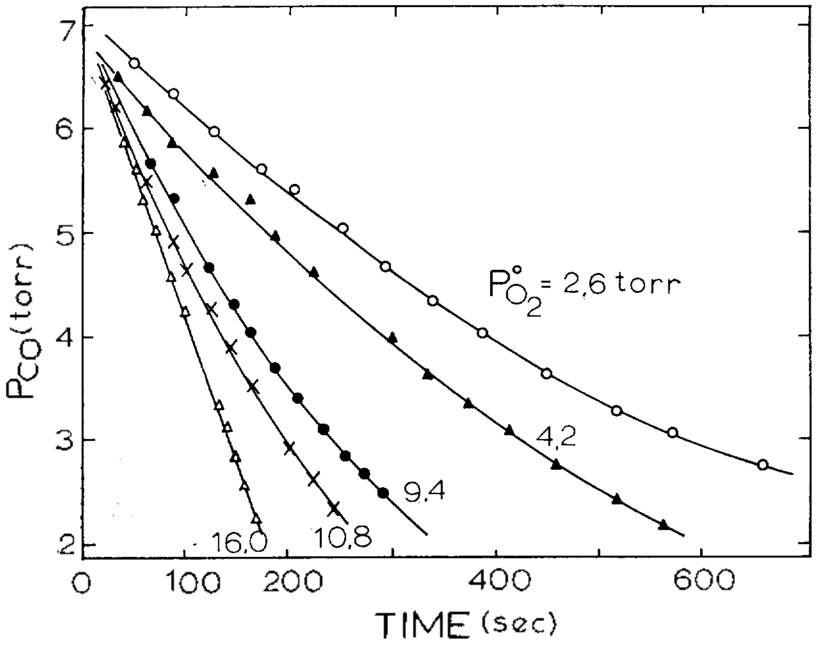

Fig. 2. P_{CO} *vs.* reaction time (t) polt at various initial O_2 partial pressure on Pt catalyst (0.27 g) at 180 °C.

RESULTS AND DISCUSSION

Reaction Order. The rate of oxidation of carbon monoxide on a catalyst is generally expressed as follows:

$$\text{Rate}=k(O_2)^m(CO)^n \quad (1)$$

where m and n are the reaction orders with respect to oxygen and carbon monoxide, and k is the rate constant.

(i) On Pt catalyst

Fig. 2 shows the decrease of CO partial pressure against reaction time (t) at various O_2 partial pressures. For a given CO partial pressure, the initial rates were obtained at vaious O_2 partial pressures. The initial rate, v, which was obtained from the data in *Fig.* 2, against $(P_{O_2})^{0.8}$ plot gave a good straight line as shown in *Fig.* 3. This indicates that the O_2 partial order order, m must be 0.8. In a similar way, the CO partial order, n was found to be −0.3. Thus the following rate expression gave the best fit for the reaction on Pt catalyst.

$$\text{Rate}=k(O_2)^{0.8}(CO)^{-0.3} \qquad (2)$$

(ii) On SnO_2 Catalyst

The mixture of oxygen and excess carbon monoxide was seprated with gas chromatography, and their peaks were recorded with

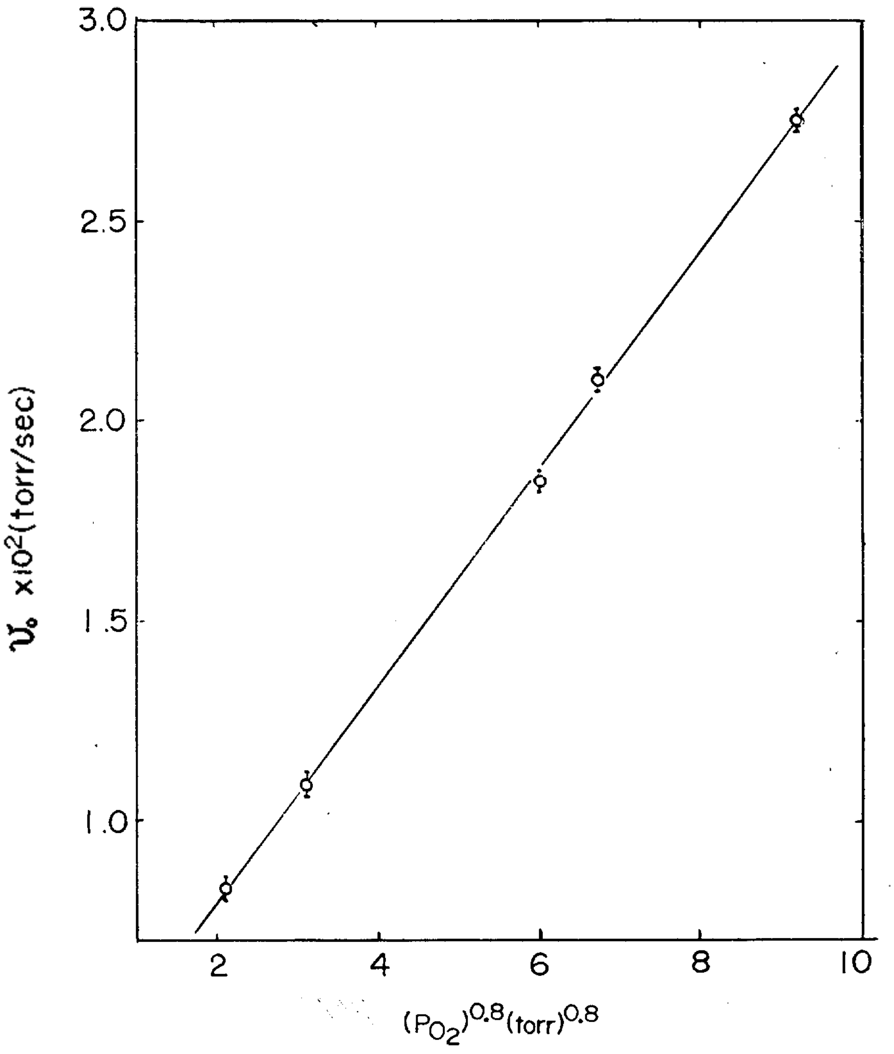

Fig. 3. Initial rate of oxidation (v) *vs.* $(P_{O_2})^{0.8}$ plot on Pt catalyst at 180 °C.

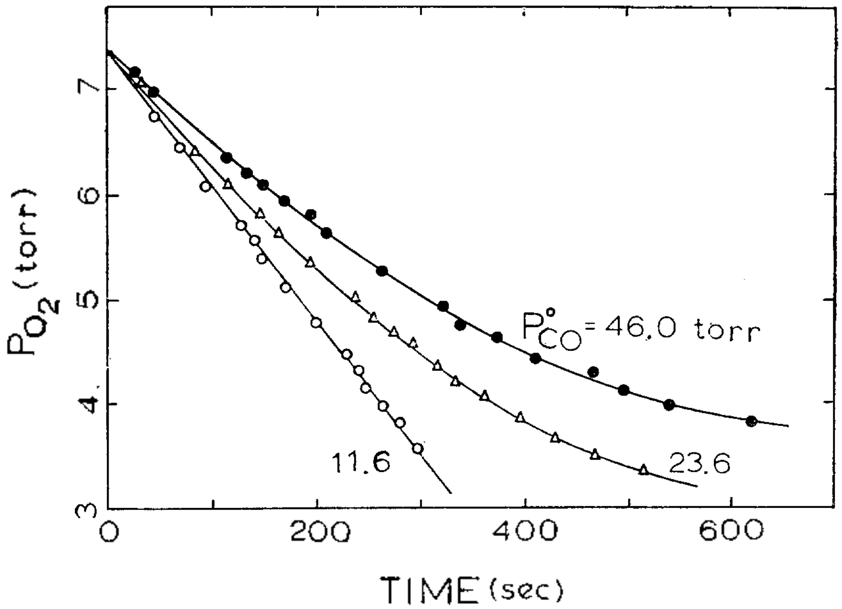

Fig. 4. P_{O_2} *vs.* reaction time (t) plot at various initial CO partial pressures on Pt catalyst at 170 °C.

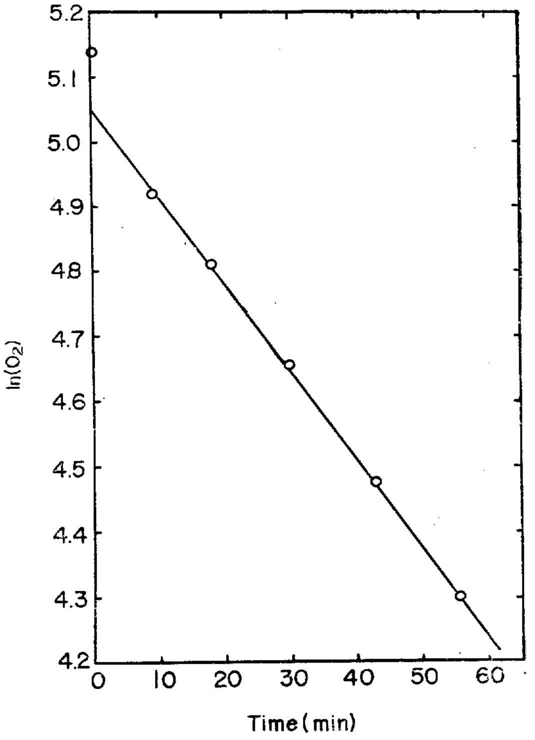

Fig. 5. ln(O_2) *vs.* Reaction time (t) plot on Sample 4 catalyst (0.5 g) at 120 °C, values in ordinate are in arbitrary unit.

reaction time(t). As show in *Fig.* 5, ln(O_2) *vs.* time (t) plot shows good linearity. Therefore, the O_2 partial order, m should be 1.0. In a similar way, CO partial order, n was determined to be 1.0. The rate expression on SnO_2 catalyst can be given as follows:

$$\text{Rate} = k(O_2)(CO) \tag{3}$$

From the kinetic data, Fuller and Warwick[16] proposed the reaction mechanism which involves successive reduction and reoxidation of the SnO_2 calyst. However, the orders obtained in our experimet, *i. e.*, first with respect to both O_2 and CO indicate that adsorbed O_2 species may interact with adsorbed or gaseous CO, and that adsorbed CO_3 species is presumably the intermediate complex for the SnO_2 catalyzed oxidation of carbon monoxide. There have been many attempts to detect the surface intermediate species. By using the infrared spectroscopy, Gundrizer and Davydov[17] have observed a number of absorption bands of adsorbed oxygen on SnO_2 in the range of 1200～900 cm^{-1}, and attributed them to the adsorbed O_2^- radical forms. Harrison[18] observed three absorption bands at 1580, 1290, and 1020 cm^{-1} shifting to 1460, 1265 and 1020 cm^{-1} on O^{18} substitution during the adsorption of $CO+O_2$ mixtures on SnO_2 catalyst. These absorption bands were assigned to a bidentate carbonate complex.

It can be conculded from our kinetic and reported spectroscopic data that the interaction of chemisorbed molecular oxygen with carbon monoxide (gaseous or chemisorbed) on SnO_2 catalysts produces the intermediate CO_3 species.

Determination of Rate Constants. With the experimentally determined reaction orders, the rate constants could be determined by measuring the total pressure change for various catalysts. Solving the rate equation(1) for the stoichiometric mixture ($P_{CO}/P_{O_2}=2$), we obtained the relations between the total pressure and reaction time(t) as follows:

(i) On Pt catalyst

$$\left(P-\frac{2}{3}P^\circ\right)^{\frac{1}{2}}=\frac{1}{\sqrt{3}}P^{\circ\frac{1}{2}}-3.21T^{\frac{1}{2}}kt \qquad (4)$$

(ii) On SnO_2 catalyst

$$\frac{1}{P-\frac{2}{3}P^\circ}=\frac{3}{P^\circ}+\frac{2k}{62.3T}t \qquad (5)$$

where P is the pressure in torr at reaction time (t); P°, initial pressure in torr; T, absolute reaction temperature; t, reaction time in sec and k, the rate constant in mole$^{\frac{1}{2}}/l^{\frac{1}{2}}\cdot$sec on Pt catalyst, in l/mole·sec on SnO_2 catalyst.

Fig. 6 shows $\left(P-\frac{2}{3}P^\circ\right)^{\frac{1}{2}}$ *vs.* reaction time (t) plot on Pt catalyst. The rate constants were obtained from the slopes and the equation (4). A good linearity of the plot again indicates the correctness of the reaction orders determined

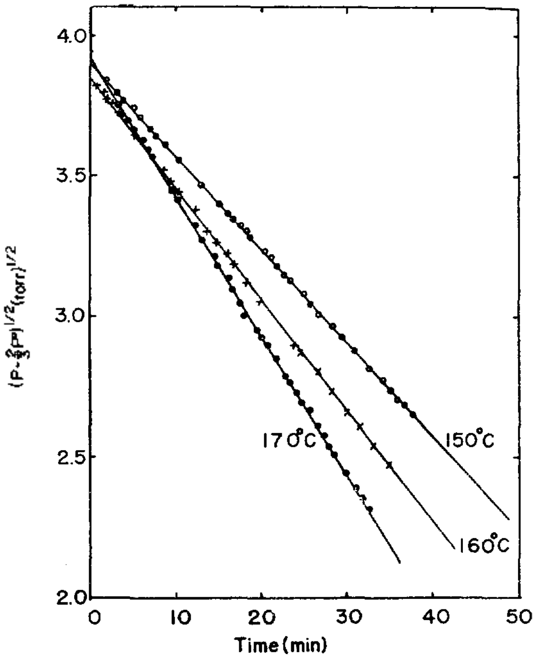

Fig. 6. $\left(P-\frac{2}{3}P^\circ\right)^{\frac{1}{2}}$ *vs.* time plot on Pt catalyst at various reaction temperatres.

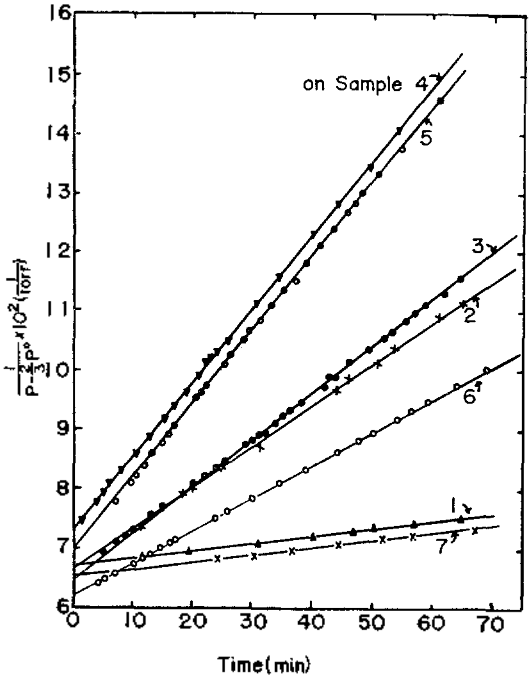

Fig. 7. $\frac{1}{P-\frac{2}{3}P^\circ}$ *vs.* time plot on Sb-doped SnO_2 at 150°C (Sb composition varies from 0 to 2.0 mole%).

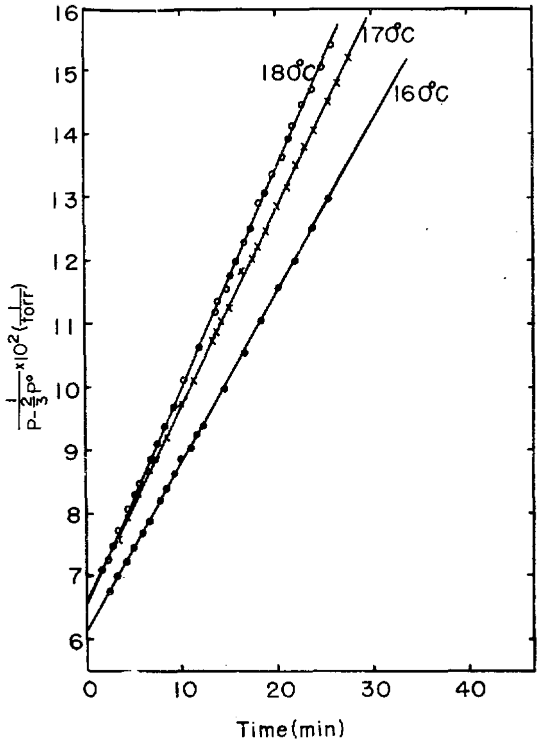

Fig. 8. $\frac{1}{P-\frac{2}{3}P^\circ}$ *vs.* time plot on sample 4 catalyst at different reacton temperature.

Table 1. Specific rate constants on Pt catalyst.

Reaction temperature	150°C	160°C	170°C
k* ($mol_e^{\frac{1}{2}}/l^{\frac{1}{2}}\cdot sec\cdot g$)	3.1×10^{-5}	3.7×10^{-5}	4.4×10^{-5}

*Rate constant.

separately. *Figs.* 7~9 show $\frac{1}{P-\frac{2}{3}P^\circ}$ *vs.* reaction time (t) polots.

The specific rate constants for the various catalysts were listed in *Table* 1~4. As shown in *Table* 5. NiO (made from $Ni(OH)_2$) was found to be the most active catalyst for the oxidation of carbon monoxide in the low temperatures.

Pretreatment of the Catalyst. The rate of oxidation was measured at 160 °C for the sample 4 catalyst evacuated at various temperatures, 200, 250, and 270 °C for 2 hours. *Fig.* 9 and *Table* 4 show the maked dependence of the evacuation temperature upon the initial rate of oxidation. The rate of oxidation increased with increasing evacuation temperature.

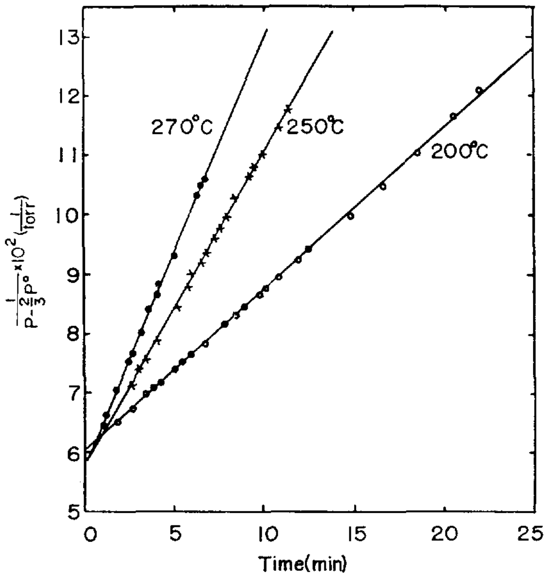

Fig. 9. $\frac{1}{P-\frac{2}{3}P^\circ}$ *vs.* time plot on sample 4 catalyst evacuated at various emperature for 2 hours. Reaction temperature is 160 °C.

Table 2. Specific rate constants on sample 1~7 catalyst at 150 °C.

Sample	Rate constant (l/mole·sec·g)
1	5.6×10^{-2}
2	3.0×10^{-1}
3	3.6×10^{-1}
4	5.6×10^{-1}
5	5.6×10^{-1}
6	2.5×10^{-1}
7	5.6×10^{-2}

Determination of Arrhenius Parameters. Arrhenius A factors activation energies could be determined by plotting ln$k$ *vs.* $\frac{1}{T}$, which

Table 3. Specific rate constants on sample 4 catalyst.

Reaction temperature	160°C	170°C	180°C
k* (l/mole·sec·g)	1.2	1.4	1.6

*Rate constant.

Table 4. Specific rate constant on sample 4 catalyst at 160 °C at various evacuation temperatures.

Rate constant	Evacuation temperature		
	200°C	250°C	270°C
k* (l/mole·sec·g)	1.2	2.4	3.2

Table 5. Rate constants and Arrhenius parameters for various catalysts. (NiO(I) was made from $Ni(NO_3)_2$, NiO(II) from $Ni(OH)_2$, and MnO_2 from $Mn(NO_3)_2$)[8]

Catalst	k Rate constant	A Arrhenius Parameter	E_a (kcal) activation energy
Pt	3.1×10^{-5}(150°C) (mole$^{\frac{1}{2}}$/$l^{\frac{1}{2}}$·sec·g)	6.3×10^{-2}(mole$^{\frac{1}{2}}$/$l^{\frac{1}{2}}$·sec·g)	6.4
Sb(Ⅲ) doped SnO_2 (.05%)	5.6×10^{-1}(160°C) (l/mole·sec·g)	9.4×10^{2} (l/mole·sec·g)	5.7
NiO(I)	2.0×10^{-2}(44°C) (l/mole·sec·g)	5×10^{6} (l/mole·sec·g)	12
NiO(II)	1.6×10^{-2}(18°C) (l/mole·sec·g)	1×10^{10} (l/mole·sec·g)	17
MnO_2	8.0×10^{-4}(80°C) (l/mole·sec·g)	5×10^{8} (l/mole·sec·g)	18

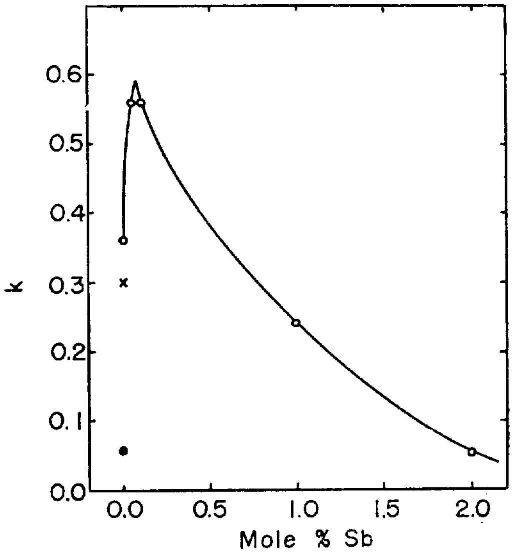

Fig. 10. Rate constant of oxidation *vs*. Sb mole%.

are shown in *Figs*. 10 and 11. Arrhenius parameters and specific rate constants for the various catalyst are listed in *Table* 5 to compare the actvities of various metal oxides studied in our laboratory.

Inhibition Effect. As shown in the *Fig*. 4, the initial rate (v) of the disappearance of O_2 was decreased as partial pressure of CO was increased. This implies that carbon monoxide inhibited the rate of oxidation. The initial rate is inversely proportional to CO concentration to the 0.3 power. Shishu and Kowalczyk[3] also obtained similar order (−0.5). Neglecting the adsorption of product CO_2 molecules or the surface coverage by CO_2 molecule to be insignificant, we have

$$K_{O_2}P_{O_2}(N^*-N_{CO}-N_{O_2})=N_{O_2} \qquad (6)$$

$$K_{CO}P_{CO}(N^*-N_{O_2})=N_{CO} \qquad (7)$$

where N^* is the total number of catalytic surface sites, N_{O_2} and N_{CO} are the surface concentration of adsorption centers for mclecular oxygen and carbon monoxide, respectively, K_{O_2} and K_{CO} are the adsorption equilibrium constants for the oxygen and carbon monoxide, respectively. From the equations (6) and (7), we can have the following rate expression known as Langmuir-Hinshellwood dual site model

$$\text{Rate}\propto\frac{K_{O_2}K_{CO}(O_2)(CO)}{(1+K_{O_2}(O_2)+K_{CO}(CO))^2} \qquad (8)$$

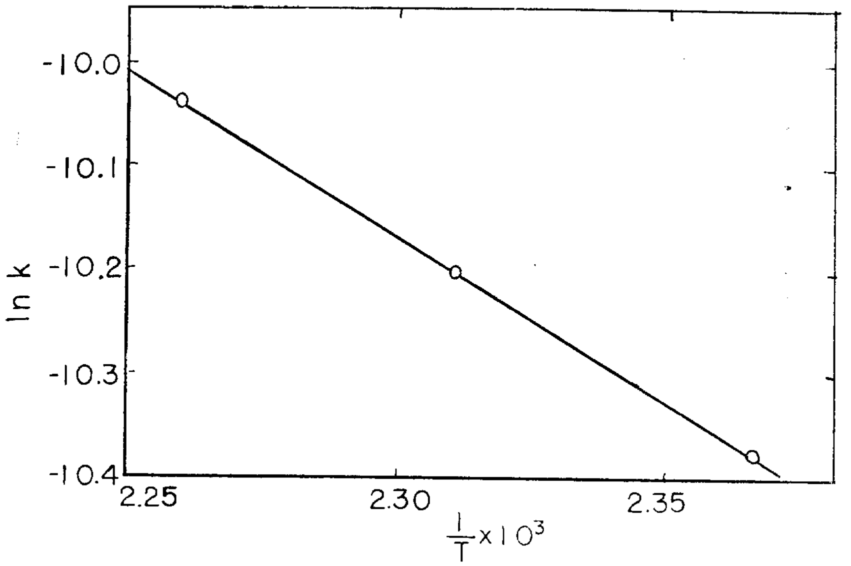

Fig. 11. ln k *vs.* $\frac{1}{T}$ plot on Pt catalyst.

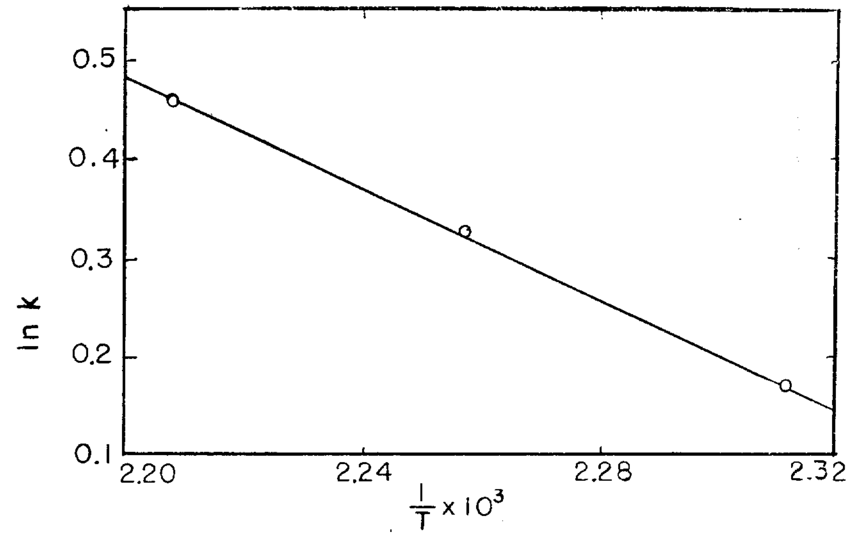

Fig. 12. ln k *vs.* $\frac{1}{T}$ plot on sample 4 catalyst.

The adsorption constant for oxygen, K_{O_2} is considerably smaller than that of carbon monoxide ($K_{CO} \gg K_{O_2}$). This Langmuir-Hinshellwood dual site model gave a qualitative explanation of the negative power dependence of the reaction rate on CO concentration.

The reaction orders in the transition metal oxides (NiO, MnO_2 and SnO_2 *etc.*) catalyzed oxidation indicate that O_2 and CO surface coverage may be low (*i. e.* $KO_2(O_2)$, $K_{CO}(CO) \ll 1$). However, in the Pt catalyzed oxidation, CO surface coverage is so high that CO may inhibit the rate of oxidation (*i. e.* $K_{CO}(CO) \gg 1$).

Doping Effect. *Figs.* 7 and 10 show that that the addition of Sb to SnO_2 (dopant composition: 0.05~0.1mole%) increased the rate of oxidation. However, an excess addition of Sb (>1 mole%) decreased the rate of oxidation. Carroll and Slack[13] have carried out the electrical conductivity measuremnt of SnO_2 with various concentration of Sb. Their results showed that larger than 1 mole% addition of Sb decreased the electrical conductivity of SnO_2. Our kinetic results are in good correlation with the electrical conductivity data. The maximum rate in our work is found to be at about 0.1% Sb. The correlation seems to indicate that O_2^- species may be the precurser for formation of carbonate ion.

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