

## Pt 및 SnO<sub>2</sub> 촉매하에서의 일산화탄소의 산화반응

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## Catalytic Oxidation of Carbon Monoxide on Pt and SnO<sub>2</sub>

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**요 약.** SnO<sub>2</sub>, Sb-doped SnO<sub>2</sub>, 그리고 백금촉매하에서 일산화탄소의 산화반응을 연구하였다.

SnO<sub>2</sub> 및 Sb-doped SnO<sub>2</sub> 촉매하에서 산화반응은 CO 및 O<sub>2</sub>에 대해서 각각 1차, 백금 촉매하에서는  $\frac{1}{2}$ 차 반응에 따랐다. SnO<sub>2</sub>에 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-doped SnO<sub>2</sub> 촉매(dopant composition: 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<sub>2</sub>, Sb-doped SnO<sub>2</sub>, and Pt catalyst were studied.

The oxidation reaction was found to be first order with respect to both CO and O<sub>2</sub> on SnO<sub>2</sub> and Sb-doped SnO<sub>2</sub> catalysts, and to be of half order on Pt catalyst. A small addition of Sb to SnO<sub>2</sub> (dopant 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<sub>2</sub> catalyst (dopant composition: 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<sup>1~4</sup> and transition metal oxide catalysts have been studied. Among the transition metal oxides, NiO<sup>5~8</sup>, MnO<sub>2</sub><sup>8~10</sup>, CuO<sup>11</sup> and Co<sub>3</sub>O<sub>4</sub>, etc. have been found to be active catalysts in the oxidation of carbon monoxide. The kinetics of oxidation reaction of carbon monoxide has also been

studied for platinum supported type catalyst.

As early as 1922, Langmuir<sup>1</sup> reported that the oxidation of carbon monoxide on platinum wire could involve the reaction of gaseous carbon monoxide with adsorbed atomic oxygen. Sklyarov<sup>2</sup> and the others<sup>3~4</sup>, however, found that the oxidation of carbon monoxide involved molecular oxygen and carbon monoxide. Shishu and Kowalczyk<sup>3</sup> 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  $\text{SnO}_2$  and impurity doped  $\text{SnO}_2$  and impurity doped  $\text{SnO}_2^{12-15}$  have been studied quite extensively. Carrol and Slack<sup>13</sup> reported that the addition of Sb(III) to  $\text{SnO}_2$  gave a large effect on the electrical conductivity of the semiconductor. A small addition of Sb(III) to  $\text{SnO}_2$  increased the electrical conductivity, on the contrary, a large addition 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  $\text{SnO}_2$  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.  $\text{SnO}_2$  (E.P) and HCl (E.P) were from Kanto Chemical Co.  $\text{NH}_4\text{OH}$  (E.P), anhydrous  $\text{SnCl}_4$ , and  $\text{NH}_4\text{NO}_3$  were from Wako Pure Chemical Ind., and  $\text{SbCl}_3$  from Merck.

**Preparation of Catalysts.** Sb-doped  $\text{SnO}_2$  polycrystalline semiconductors were prepared by the coprecipitation of antimony and tin hydroxides with ammonium hydroxide from appropriate mixtures of antimony and tin chloride solutions in HCl, followed by thorough wash-

ing and heat treatment.

Stock solutions of  $\text{SbCl}_3$  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  $\text{NH}_4\text{NO}_3$  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 :  $\text{SnO}_2$  (Kanto Chemical Co.) heated at 450 °C for 2 hours,

Sample 2 :  $\text{SnO}_2$  dried at 200 °C for 12 hours and followed by heat treatment at 450 °C for 2 hours,

Sample 3~7 are  $\text{SnO}_2$  and Sb(III) doped  $\text{SnO}_2$  dried at 80 °C for 12 hours and followed by heat treatment at 450 °C for 2 hours,

Sample 3 :  $\text{SnO}_2$ ,

Sample 4 : Sb-doped  $\text{SnO}_2$  (0.05 mole%),

Sample 5 : Sb-doped  $\text{SnO}_2$  (0.1 mole%),

Sample 6 : Sb-doped  $\text{SnO}_2$  (1 mole%),

Sample 7 : Sb-doped  $\text{SnO}_2$  (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<sup>8</sup> from this laboratory.

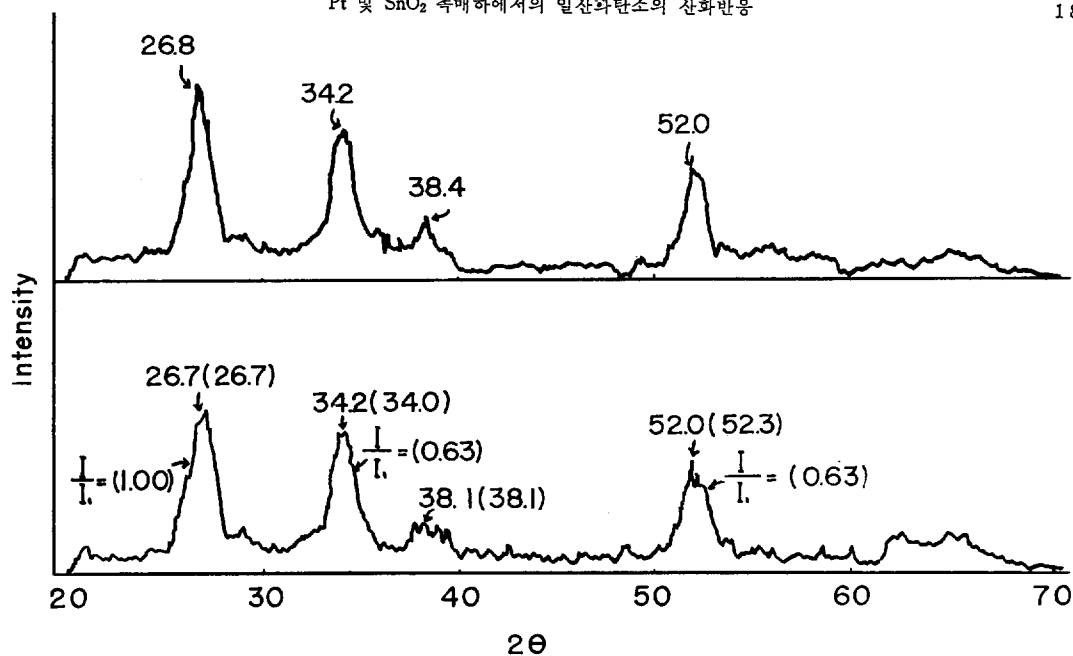


Fig. 1. X-Ray diffraction pattern of sample 3 (SnO<sub>2</sub> polycrystalline) and sample 7 (Sb-doped SnO<sub>2</sub>, dopant; 2.0 mole%).

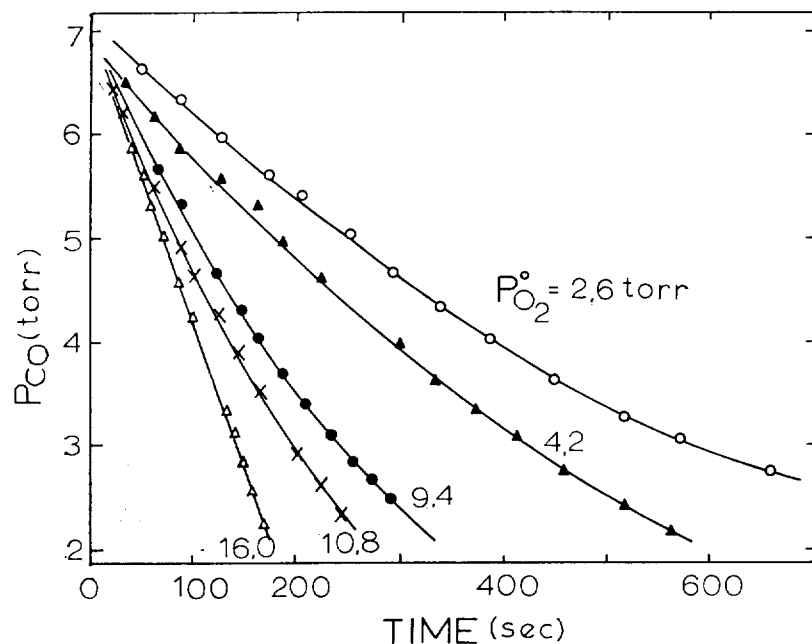


Fig. 2.  $P_{CO}$  vs. reaction time ( $t$ ) plot at various initial O<sub>2</sub> partial pressure on Pt catalyst (0.27 g) at 180 °C.

## RESULTS AND DISCUSSION

**Reaction Order.** The rate of oxidation of

carbon monoxide on a catalyst is generally expressed as follows:

$$\text{Rate} = k(\text{O}_2)^m(\text{CO})^n \quad (1)$$

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 various  $O_2$  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,  $m$  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.

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

(ii) On  $SnO_2$  Catalyst

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

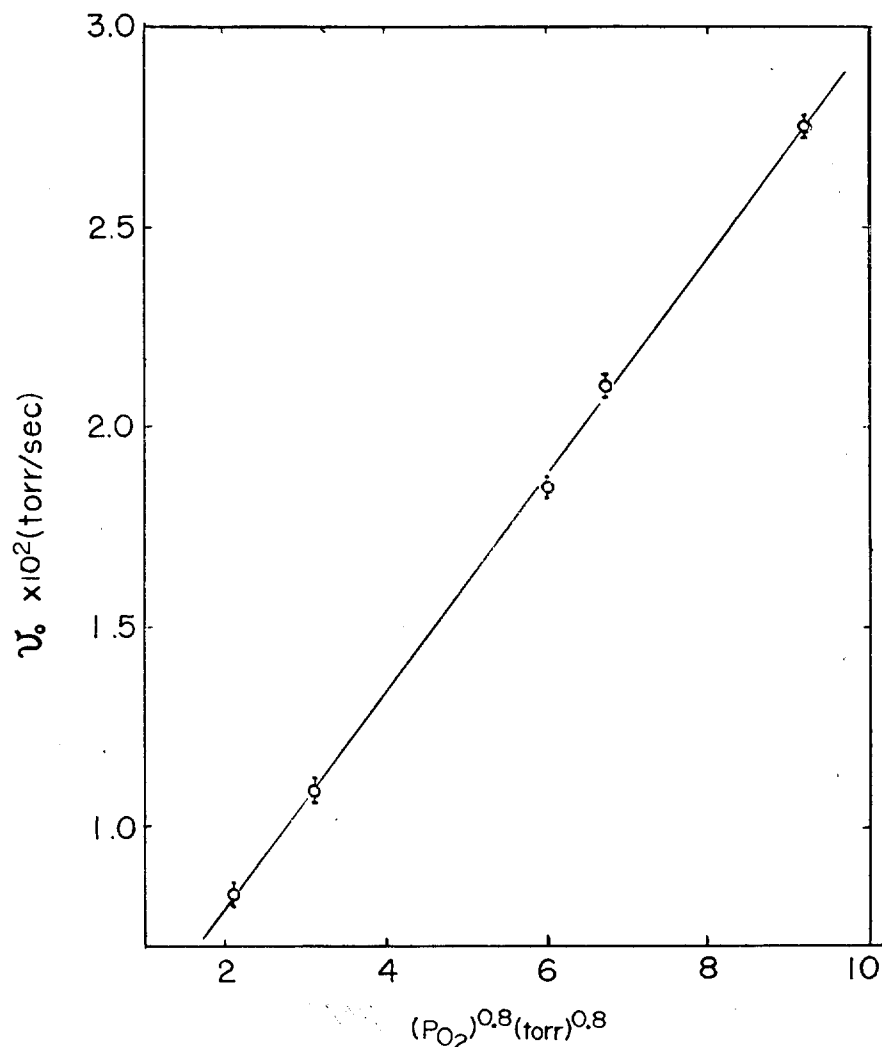


Fig. 3. Initial rate of oxidation ( $v$ ) vs.  $(P_{O_2})^{0.8}$  plot on Pt catalyst at 180 °C.

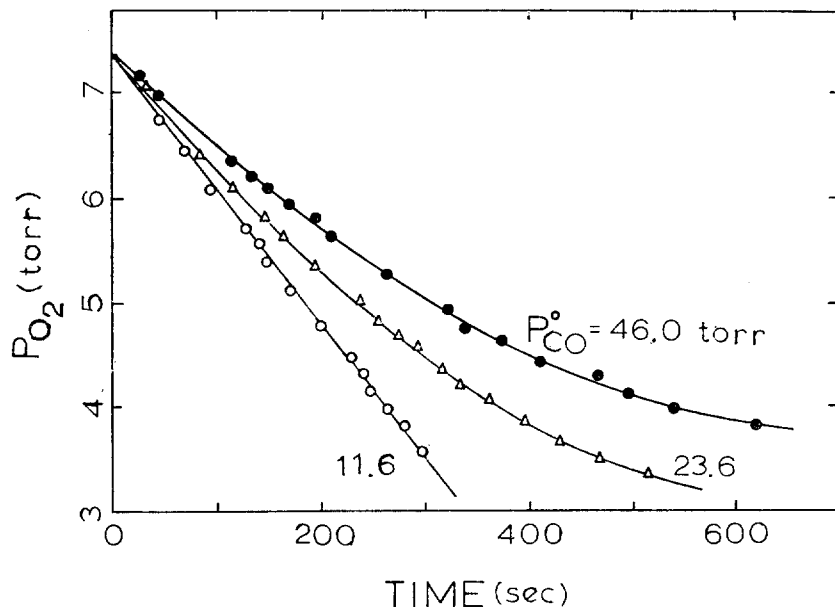


Fig. 4.  $P_{O_2}$  vs. reaction time ( $t$ ) plot at various initial CO partial pressures on Pt catalyst at 170 °C.

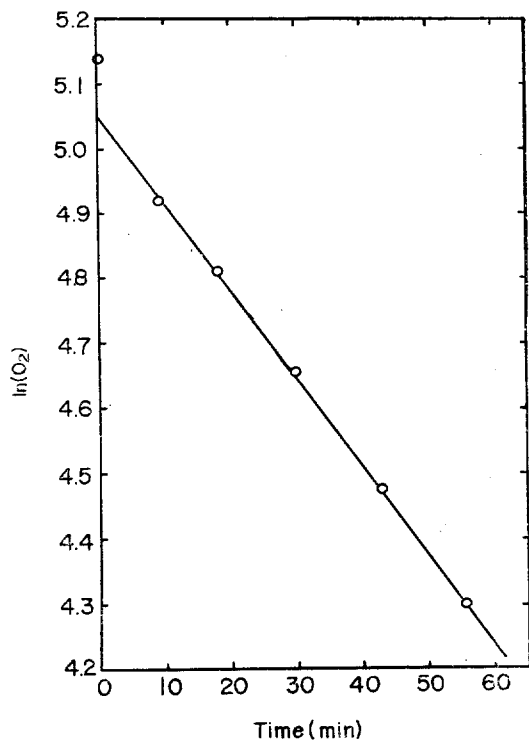


Fig. 5.  $\ln(O_2)$  vs. Reaction time ( $t$ ) plot on Sample 4 catalyst (0.5 g) at 120 °C, values in ordinate are in arbitrary unit.

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<sub>2</sub> catalyst can be given as follows:

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

From the kinetic data, Fuller and Warwick<sup>16</sup> proposed the reaction mechanism which involves successive reduction and reoxidation of the SnO<sub>2</sub> catalyst. However, the orders obtained in our experiment, *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<sub>2</sub> catalyzed oxidation of carbon monoxide. There have been many attempts to detect the surface intermediate species. By using the infrared spectroscopy, Gundrizer and Davydov<sup>17</sup> have observed a number of absorption bands of adsorbed oxygen on SnO<sub>2</sub> in the range of 1200~900  $\text{cm}^{-1}$ , and

attributed them to the adsorbed  $\text{O}_2^-$  radical forms. Harrison<sup>18</sup> observed three absorption bands at 1580, 1290, and  $1020\text{ cm}^{-1}$  shifting to 1460, 1265 and  $1020\text{ cm}^{-1}$  on  $\text{O}^{18}$  substitution during the adsorption of  $\text{CO} + \text{O}_2$  mixtures on  $\text{SnO}_2$  catalyst. These absorption bands were assigned to a bidentate carbonate complex.

It can be concluded from our kinetic and reported spectroscopic data that the interaction of chemisorbed molecular oxygen with carbon monoxide (gaseous or chemisorbed) on  $\text{SnO}_2$  catalysts produces the intermediate  $\text{CO}_3$  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 ( $P_{\text{CO}}/P_{\text{O}_2}=2$ ), we obtained the relations between the total pressure and reaction time( $t$ ) as follows:

(i) On Pt catalyst

$$\left(P - \frac{2}{3}P^0\right)^{\frac{1}{2}} = \frac{1}{\sqrt{3}}P^0\frac{1}{2} - 3.21T^{\frac{1}{2}}kt \quad (4)$$

(ii) On  $\text{SnO}_2$  catalyst

$$\frac{1}{P - \frac{2}{3}P^0} = \frac{3}{P^0} + \frac{2k}{62.3T}t \quad (5)$$

where  $P$  is the pressure in torr at reaction time ( $t$ );  $P^0$ , initial pressure in torr;  $T$ , absolute reaction temperature;  $t$ , reaction time in sec and  $k$ , the rate constant in  $\text{mole}^{\frac{1}{2}}/\text{l}^{\frac{1}{2}}\cdot\text{sec}$  on Pt catalyst, in  $\text{l}/\text{mole}\cdot\text{sec}$  on  $\text{SnO}_2$  catalyst.

Fig. 6 shows  $\left(P - \frac{2}{3}P^0\right)^{\frac{1}{2}}$  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

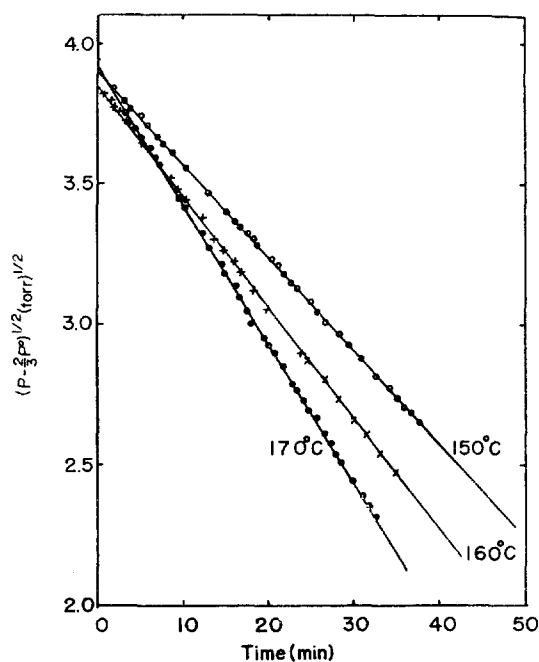


Fig. 6.  $\left(P - \frac{2}{3}P^0\right)^{\frac{1}{2}}$  vs. time plot on Pt catalyst at various reaction temperatures.

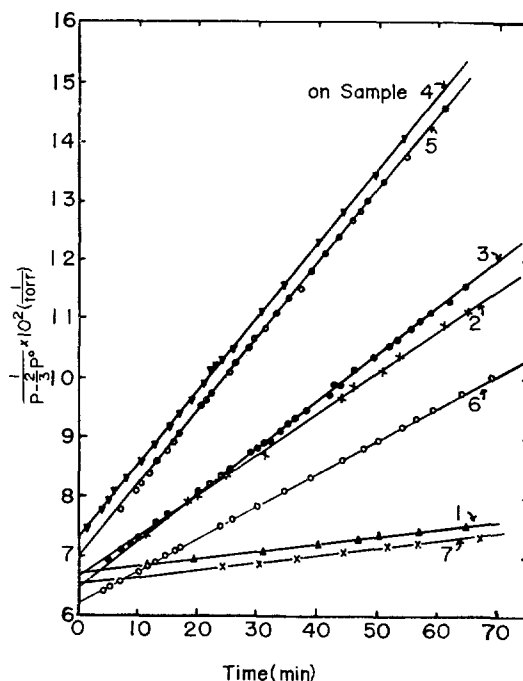


Fig. 7.  $\frac{1}{P - \frac{2}{3}P^0}$  vs. time plot on Sb-doped  $\text{SnO}_2$  at  $150^\circ\text{C}$  (Sb composition varies from 0 to 2.0 mole%).

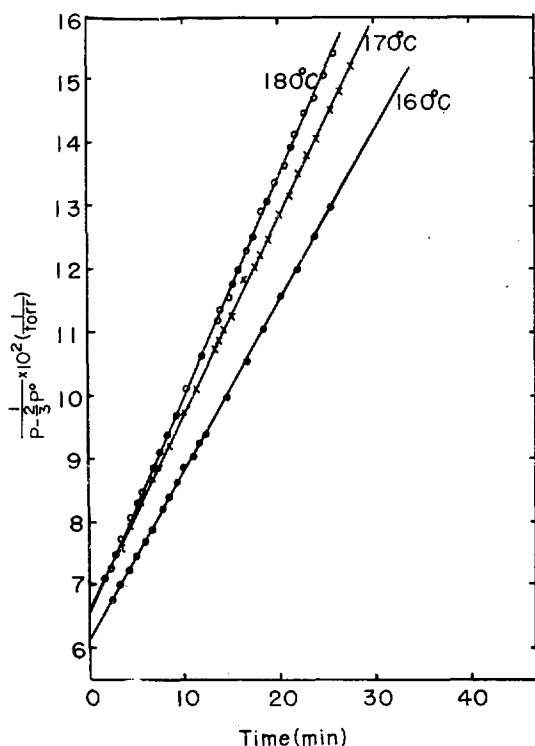


Fig. 8.  $\frac{1}{P - \frac{2}{3}P^0}$  vs. time plot on sample 4 catalyst at different reaction temperature.

Table 1. Specific rate constants on Pt catalyst.

Reaction temperature	150°C	160°C	170°C
$k^*$ (mol <sub>e</sub> <sup>1/2</sup> /l <sup>1/2</sup> ·sec·g)	$3.1 \times 10^{-5}$	$3.7 \times 10^{-5}$	$4.4 \times 10^{-5}$

\*Rate constant.

separately. Figs. 7~9 show  $\frac{1}{P - \frac{2}{3}P^0}$  vs. reaction time (*t*) plots.

The specific rate constants for the various catalysts were listed in Table 1~4. As shown in Table 5, NiO (made from Ni(OH)<sub>2</sub>) 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

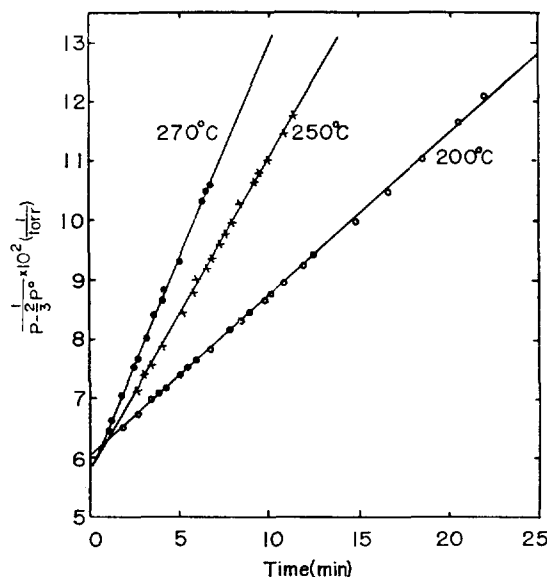


Fig. 9.  $\frac{1}{P - \frac{2}{3}P^0}$  vs. time plot on sample 4 catalyst evacuated at various temperature for 2 hours. Reaction temperature is 160 °C.

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

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

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 marked dependence of the evacuation temperature upon the initial rate of oxidation. The rate of oxidation increased with increasing evacuation temperature.

#### 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  $\text{Ni}(\text{NO}_3)_2$ , NiO(II) from  $\text{Ni}(\text{OH})_2$ , and  $\text{MnO}_2$  from  $\text{Mn}(\text{NO}_3)_2$ )<sup>8</sup>

Catalyst	Rate constant $k$	Arrhenius Parameter $A$	$E_a$ (kcal) activation energy
Pt	$3.1 \times 10^{-5}$ (150°C) ( $\text{mole}^{1/2}/l^{1/2} \cdot \text{sec} \cdot \text{g}$ )	$6.3 \times 10^{-2}$ ( $\text{mole}^{1/2}/l^{1/2} \cdot \text{sec} \cdot \text{g}$ )	6.4
Sb(III) doped $\text{SnO}_2$ (.05%)	$5.6 \times 10^{-1}$ (160°C) (l/mole·sec·g)	$9.4 \times 10^2$ (l/mole·sec·g)	5.7
NiO(I)	$2.0 \times 10^{-2}$ (44°C) (l/mole·sec·g)	$5 \times 10^6$ (l/mole·sec·g)	12
NiO(II)	$1.6 \times 10^{-2}$ (18°C) (l/mole·sec·g)	$1 \times 10^{10}$ (l/mole·sec·g)	17
$\text{MnO}_2$	$8.0 \times 10^{-4}$ (80°C) (l/mole·sec·g)	$5 \times 10^8$ (l/mole·sec·g)	18

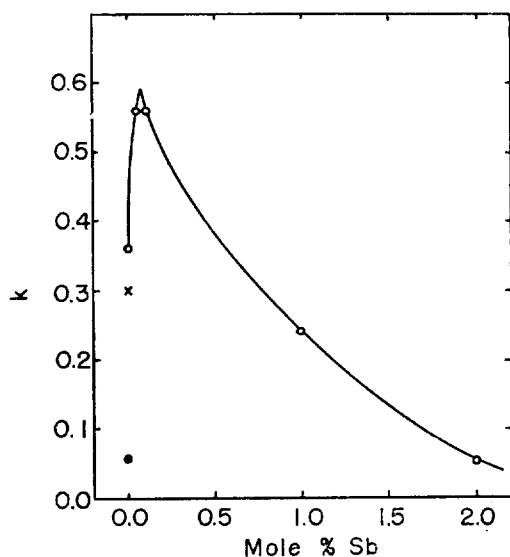


Fig. 10. Rate constant of oxidation vs. Sb mole%.

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 activities of various metal oxides studied in our laboratory.

**Inhibition Effect.** As shown in the Fig. 4, the initial rate ( $v$ ) of the disappearance of  $\text{O}_2$

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<sup>3</sup> also obtained similar order ( $-0.5$ ). Neglecting the adsorption of product  $\text{CO}_2$  molecules or the surface coverage by  $\text{CO}_2$  molecule to be insignificant, we have

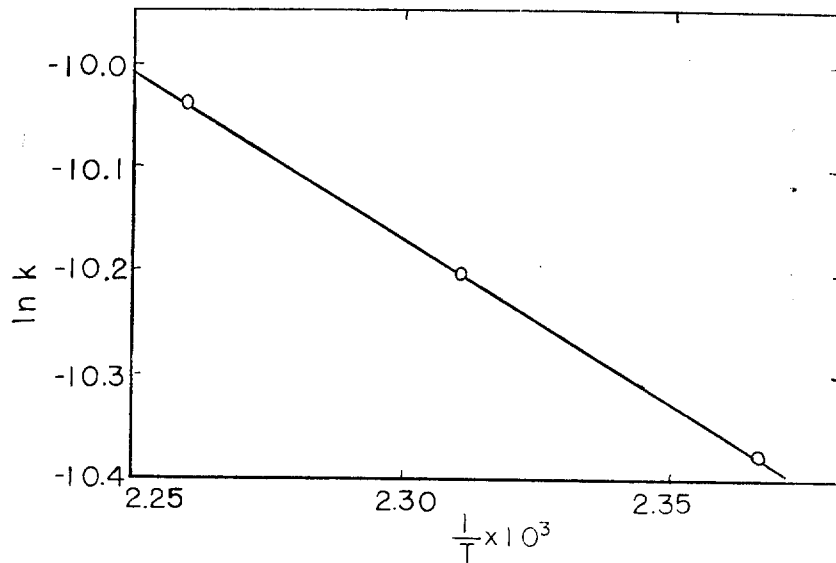
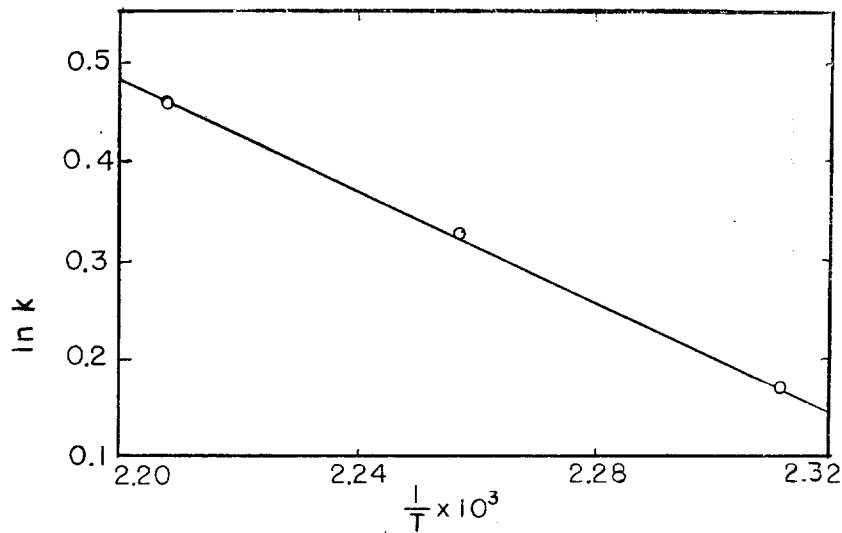
$$K_{\text{O}_2} P_{\text{O}_2} (N^* - N_{\text{CO}} - N_{\text{O}_2}) = N_{\text{O}_2} \quad (6)$$

$$K_{\text{CO}} P_{\text{CO}} (N^* - N_{\text{O}_2}) = N_{\text{CO}} \quad (7)$$

where  $N^*$  is the total number of catalytic surface sites,  $N_{\text{O}_2}$  and  $N_{\text{CO}}$  are the surface concentration of adsorption centers for molecular oxygen and carbon monoxide, respectively,  $K_{\text{O}_2}$  and  $K_{\text{CO}}$  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

$$\text{Rate} \propto \frac{K_{\text{O}_2} K_{\text{CO}} (\text{O}_2) (\text{CO})}{(1 + K_{\text{O}_2} (\text{O}_2) + K_{\text{CO}} (\text{CO}))^2} \quad (8)$$



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-Hinshelwood 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<sub>2</sub> and SnO<sub>2</sub> etc.) catalyzed oxidation indicate that O<sub>2</sub> and CO surface coverage may be low (*i. e.*  $K_{O_2}(O_2), K_{CO}(CO) \ll 1$ ). However, in the Pt catalyzed oxidation, CO surface coverage is so high that CO may in-

hibit the rate of oxidation (*i.e.*  $K_{\text{CO}}(\text{CO}) \gg 1$ ).

**Doping Effect.** Figs. 7 and 10 show that that the addition of Sb to  $\text{SnO}_2$  (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<sup>13</sup> have carried out the electrical conductivity measurement of  $\text{SnO}_2$  with various concentration of Sb. Their results showed that larger than 1 mole% addition of Sb decreased the electrical conductivity of  $\text{SnO}_2$ . 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  $\text{O}_2^-$  species may be the precursor for formation of carbonate ion.

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