NiO 및 MnO₂ 촉매하에서의 일산화탄소의 산화반응

朱光烈 · 夫奉炫 · 張世憲

서울대학교 자연과학대학 화학과

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Oxidation Reactions of Carbon Monoxide on NiO and MnO₂ Catalysts

Kwang Yul Choo, Bong Hyun Boo and **Seihun Chang**

Department of Chemistry, College of Natural Sciences,

Seoul National University, Seoul 151, Korea

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요 약. Ni(NO₃)₂, Ni(OH)₂ 그리고 Mn(NO₃)₂를 진공 속에서 열분해시킨 산화니켈, 이산화망간의 비표면적(단위 : m²/g)을 측정하고 각 촉매의 단위 표면적에서 일산화탄소의 산화반응속도를 여러 온도에서 측정하였다.

낮은 압력에서 일산화탄소의 산화반응은 2차 반응에 따르며 각 촉매 표면에서의 산화반응의 활성화에너지는 Ni(NO₃)₂, Ni(OH)₂로부터 만든 산화니켈에서 각각 12, 17 kcal/mole 그리고 이산화망간에서 18 kcal/mole을 얻었다.

같은 제법으로 만들어진 산화니켈 촉매도 그것을 처리하는 방법에 따라 아레니우스 파라미터가 서로 다르게 얻어졌는데, 이것은 생성물인 이산화탄소에 의한 반응의 억제효과를 정량적으로 측정하므로써 설명이 가능하였다.

실험적으로 구한 반응차수로부터 가능한 반응메카니즘을 제안하였다.

ABSTRACT. The specific rate constants for the oxidation reactions of carbon monoxide on a unit catalytic surface area were measured. The catalysts used were NiO made from Ni(NO₃)₂, and Ni(OH)₂, and MnO₂ made from Mn(NO₃)₂. At low pressure the reaction rate was found to be of second order and the activation energies were 12 kcal/mole (on NiO made from Ni(NO₃)₂), 17 kcal/mole (on NiO made from Ni(OH)₂) and 18 kcal/mole (on MnO₂).

Plausible reaction mechanisms were proposed from the experimentally determined reaction orders.

INTRODUCTION

Carbon monoxide oxidation reactions on various catalytic surfaces have been studied for over 50 years. As early as 1922 Langmuir[1] reported that the adsorbed oxygen was responsible for the carbon monoxide oxidation reaction over Pt wire. Recently Shishu and Kwalszyk[2] and independently Nicholas and Shah[3] extensively studied the properties of various forms of Pt catalysts in the oxidation reaction of carbon monoxide.

It has long been known that various transition

metal oxides catalyze the oxidation reaction of carbon monoxide. Among the metal oxides $NiO^{4\sim6}$, $MnO_2^{7\sim8}$ and CuO^9 were found to be very effective in oxidizing carbon monoxide to carbon dioxide. Teichner and co-workers studied NiO catalyzed oxidation reactions of carbon monoxide and found that the oxidation reactions were primarily dependent on the nature and concentration of lattice defects in the surface layers and on the strength of the bond between oxygen and these defects. Wolkenstein proposed electron theory of catalysis to elucidate the relation between the catalytic and electronic properties of semiconductors.[10] A practical application of MnO_2 catalysts on the complete combustion of coal briquetts has recently been studied by Chung and Lee[9].

The stoichiometry for the oxidation reaction of carbon monoxide may be expressed as

$$2CO + O_2 \xrightarrow{\text{catalyst}} 2CO_2$$
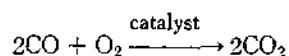
However, the reaction orders and the activation energies are strongly dependent on the preparation methods of the catalysts, the nature of the pretreatments and impurities, etc. Since the surface area and the catalytic activities depend very sensitively on the preparation methods of catalysts, it is desired that a single laboratory should carry out both macroscopic (kinetic) and microscopic (surface) characterization of catalysts made under identical conditions. The purpose of this research is, thus, to determine the kinetics and mechanisms of carbon monoxide oxidation reaction on NiO and MnO_2 catalysts prepared under controlled conditions, by using both kinetic and surface studies.
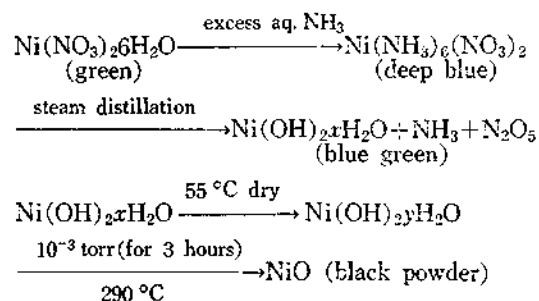
EXPERIMENTAL PROCEDURE

Meterials. Carbon monoxide, oxygen, carbon dioxide and nitrogen were purchased from Matheson Co. with purities higher than 99.9%.

Nickel nitrate and manganese nitrate were from Waco Pure Chemical Co. and recrystallized.

Preparation of Catalysts. Nickel oxides were prepared in the following two ways: Nickel oxide (I) was prepared by decomposing pure nickel nitrate at 300 °C for three hours under reduced atmosphere, then slowly cooled to room temperature. The NiO black powder was put in the reactor and heated at 268° C for two hours under vacuum (ca. 10^{-3} torr). The BET surface area of nickel oxide(I) measured by adsorption of nitrogen (16.2 Å²) at –195° C is 5.62 m²/g. The catalyst is definitely crystalline as its X-ray diffraction pattern shown in *Fig.* 1 gives lines of NiO sharpened owing to the large particle size (the particle size calculated from the spectrum: 230 Å).

Nickel oxide (II) was prepared by dehydrating pure nickel hydroxide under vacuum (ca. 10^{-3} torr) at 290 °C for three hours. The nickel hydroxide itself was prepared by the steam distillation of a solution of nickel nitrate containing excess aqueous ammonia. The hydroxide prepared by this method had a small particle size with a blue green color.

$$Ni(NO_3)_2 6H_2O \xrightarrow{\text{excess aq. NH}_3} Ni(NH_3)_6(NO_3)_2$$
$$\text{(green)} \qquad\qquad\qquad \text{(deep blue)}$$

$$\xrightarrow{\text{steam distillation}} Ni(OH)_2 x H_2O + NH_3 + N_2O_5$$
$$\text{(blue green)}$$

$$Ni(OH)_2 x H_2O \xrightarrow{55\,°C \text{ dry}} Ni(OH)_2 y H_2O$$

$$\xrightarrow[290\,°C]{10^{-3}\,\text{torr(for 3 hours)}} NiO \text{ (black powder)}$$

The X-ray diffraction pattern (*Fig.* 2) of the nickel oxide(II) prepared from nickel hydroxide shows lines of NiO broadened owing to the small (particle size: 90 Å). The BET surface area was found to be 90 m²/g.

The recrystallized hydrated manganese nitrate was decomposed at 150 °C for three hours. The
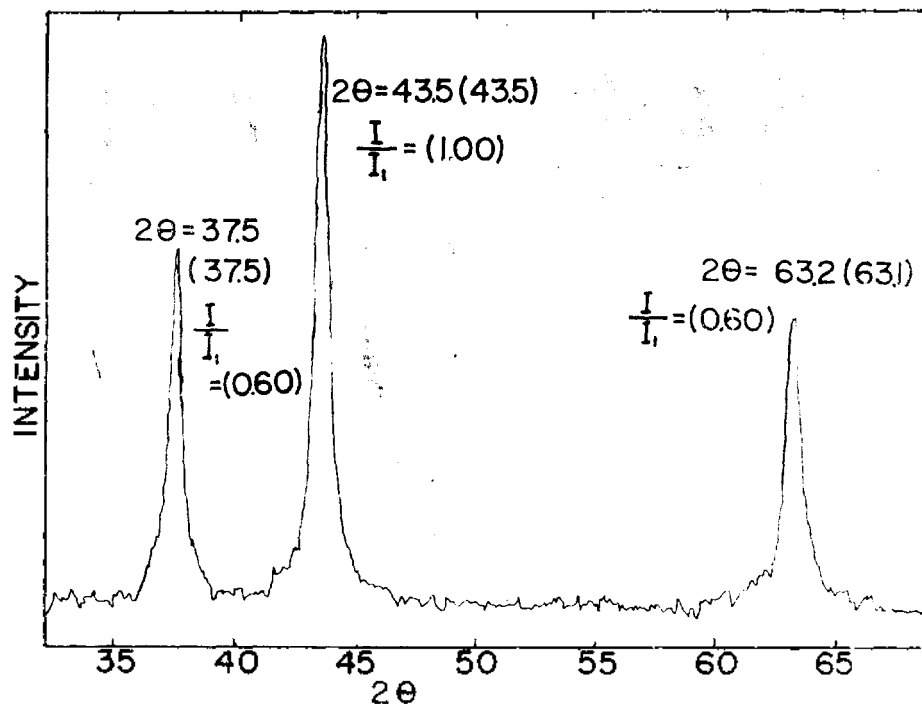
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$2\theta = 43.5 \, (43.5)$

$\dfrac{I}{I_1} = (1.00)$

$2\theta = 37.5 \, (37.5)$

$\dfrac{I}{I_1} = (0.60)$

$2\theta = 63.2 \, (63.1)$

$\dfrac{I}{I_1} = (0.60)$

Fig. 1. X-ray diffraction curve of NiO(I) by powder method. The values in the braces are obtained in the literature.

$2\theta = 43.5 \, (43.5)$

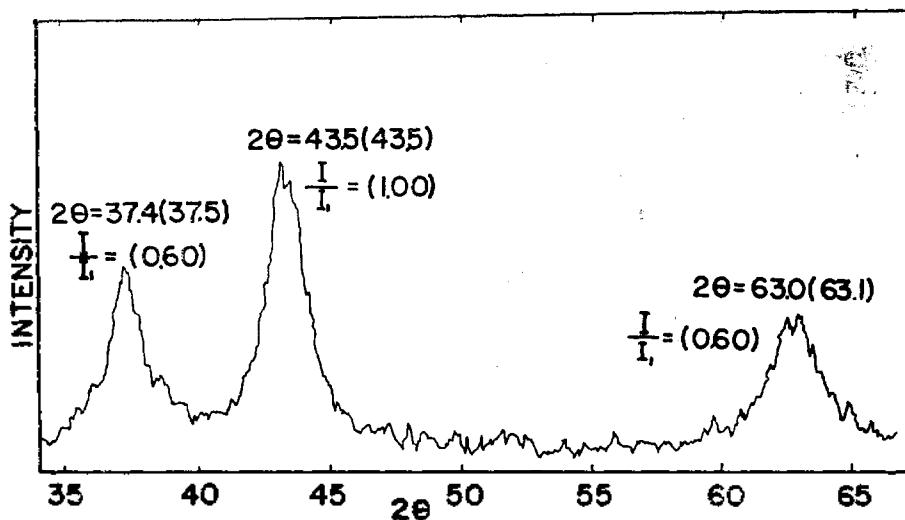$\dfrac{I}{I_1} = (1.00)$

$2\theta = 37.4 \, (37.5)$

$\dfrac{I}{I_1} = (0.60)$

$2\theta = 63.0 \, (63.1)$

$\dfrac{I}{I_1} = (0.60)$

Fig. 2. X-ray diffraction curve of NiO(II).

powderly MnO_2 was heated at 150 °C for four hours under vacuum (*ca.* 10^{-3} torr) before use. **Apparatus & procedure**. All the kinetic studies and surface characterization were carried out under high vacuum. The detailed instrumentation for the surface study has been published elsewhere.[11] Briefly the amount of nitrogen adsorption on NiO and MnO_2 was measured with Nernst-Donau

type quartz microbalance at liquid nitrogen temperature. From the amount of adsorbed nitrogen, the amount of catalyst, and accepted nitrogen surface area, [12~13] the surface area of the catalysts was measured.

The schematic diagram of the apparatus for the experiments is shown in *Fig.* 3. The static catalytic reactor was made of quartz glass tube (20 mm, ID and 270 mm length) that was connec ted to the vacuum line *via* capillary tube and balljoints. To reduce the dead space of the reactor all the connections to the pressure manometer were made of 1 mm ID thick wall pyrex capillary tubes. The premixed $(CO+O_2)$ mixture was stored in 500 ml round bottom flask and used directly from the reservoir.

The Gas Chromatographic column was made of $\frac{1}{4}$ ID copper tubing filled with molecular sieve 13X and the detection was made with TCD at room temperature. The peak areas of each gas were corrected with known concentration of each gas respectively.

RESULTS

Determination of Reaction Order. The general rate expression for the oxidation of

carbon monoxide on the unit catalytic surface area is

$$Rate = k(CO)^m(O_2)^n$$

where k is the specific rate constant for a unite surface area of catalyst and m, n are reaction orders with respect to carbon monoxide and oxygen respectively. When one of the reactants is in excess, *i. e.*, $(CO)\rangle\rangle(O_2)$, the decrease of oxygen concentration with reaction time is shown in *Fig.* 4.

Rate equation is

$$-\frac{d(O_2)}{dt} = k_{obs}(O_2)^n$$

The $\ln(O_2)$ *vs.* t plot gives good straight line as shown in *Fig.* 5. Therefore it was concluded that carbon monoxide oxidation reaction is first order with respect to oxygen. Exactly same procedure was applied for the determination of reaction order with respect to carbon monoxide concentration. It was found to be 1.0, $m=1$.

Determination of Rate Constants. Although, the determination of reaction order automatically gives the rate constant from the slope of the plot, the gas chromatographic procedure to analyze and monitor the concenrations at different reaction
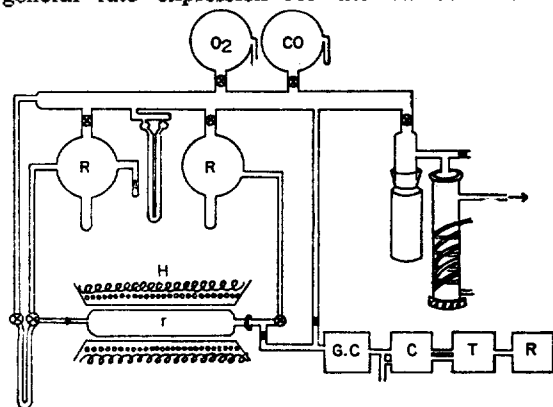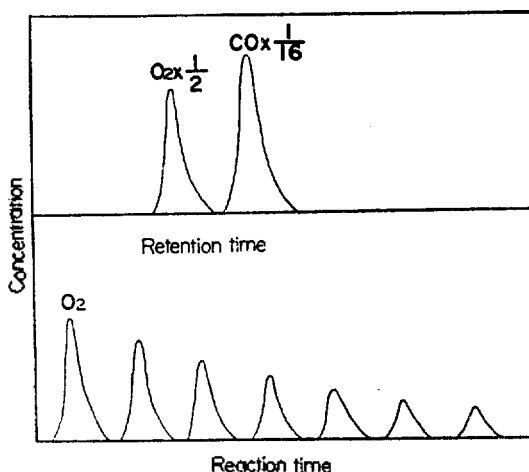
Fig. 3. The Schematic diagram of kinetic system.
R : reactant reservoir,   r : quartz reactor,
H : heating block,   G. C. : Sampling valve,
C : molecular sieve 13X culumn,   T : TCD detector,
R : recorder.

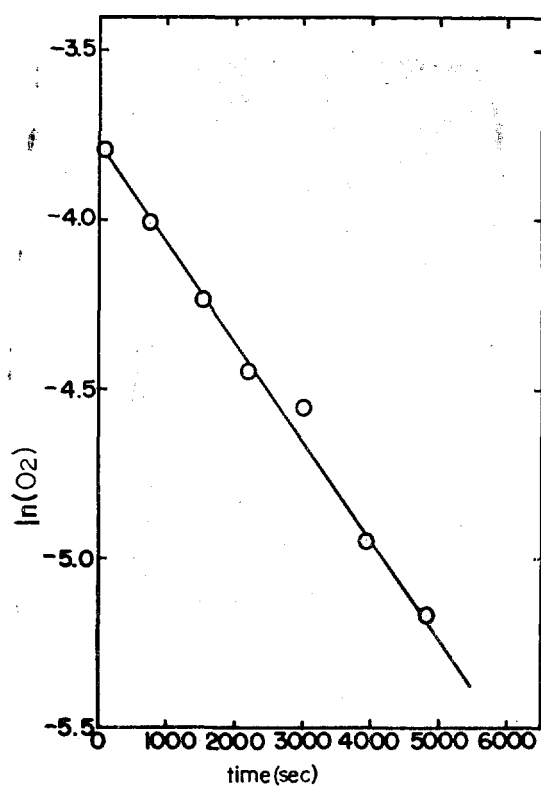*Fig.* 4. Gas Chromatogram (mixture containing oxygen and excess carbon monoxide)

Fig. 5. ln(O₂) *vs.* time(*t*) plot on the total NiO(I) surface area at 44 °C. The value in the ordinate is expressed in arbitrary unit.

Table 1a. Specific rate constants on NiO(I) catalyst.

Temp. (°C)	Rate constant	
	$k\,(l/\text{mole}\cdot\text{sec}\cdot\text{m}^2)$	$k\,(l/\text{mole}\cdot\text{sec}\cdot\text{gm})$
44	3.5×10^{-3}	2.0×1.0^{-2}
58	9.1×10^{-3}	5.2×10^{-2}
68	1.4×10^{-2}	7.9×10^{-2}

Table 1b. Specific rate constants on activated NiO(I) catalyst.

Temp. (°C)	Rate constant	
	$k\,(l/\text{mole}\cdot\text{sec}\cdot\text{m}^2)$	$k\,(l/\text{mole}\cdot\text{sec}\cdot\text{gm})$
30	1.9×10^{-2}	1.1×10^{-1}
52	5.4×10^{-2}	3.1×10^{-1}
61	8.4×10^{-2}	4.8×10^{-1}

Table 1c. Specific rate constants on NiO (II) catalyst.

Temp. (°C)	Rate constant	
	$k\,(l/\text{mole}\cdot\text{sec}\cdot\text{m}^2)$	$k\,(l/\text{mole}\cdot\text{sec}\cdot\text{gm})$
18	1.8×10^{-4}	1.6×10^{-2}
26	6.2×10^{-4}	5.6×10^{-2}
32	9.6×10^{-4}	8.7×10^{-2}
44	2.6×10^{-3}	2.4×10^{-1}
53	4.6×10^{-3}	4.2×10^{-1}

Table 1d. Specific rate constants on MnO₂ catalyst.

Temp. (°C)	Rate constant	
	$k\,(l/\text{mole}\cdot\text{sec}\cdot\text{m}^2)$	$k\,(l/\text{mole}\cdot\text{sec}\cdot\text{gm})$
80	—	8.0×10^{-4}
100	—	6.3×10^{-3}
120	—	1.3×10^{-2}
140	—	4.3×10^{-2}

times was found to be time consuming. Since the reaction is simple and the orders have been determined, the rate constants can be determined by measuring the total pressure at different intervals. For the stoichiometric mixture of carbon monoxide and oxygen, total pressure P is related to the rate constant by the equation shown below,

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

where P is the total pressure (torr) at time t, P° is the initial total pressure, T is absolute temperature and k is the rate constant (/total surface area) expressed in $l/\text{mole}\cdot\text{sec}$ unit. *Table* 1and *Fig.* 6 show the typical data for the kinetic equation given above.

Dependence of Reaction Order on the Total Pressure. All the pressure dependent experiments were carried out with NiO(II) as a catalyst. *Fig.* 7 shows the dependence of the rate constants upon the total pressure of the reaction mixture. As noticed in *Fig.* 7 the apparent rate constants do not change with the total pressure in the region of lower total pressure, while at higher
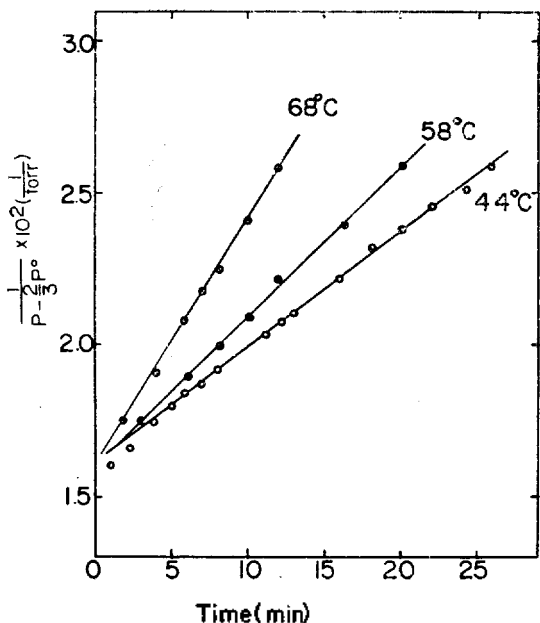
Fig. 6a. $1/(P-2/3P^*)$ vs. time(t) plot on the NiO (I) catalyst at various reaction temperatures. P=total pressure at time t, P^* =initial total pressure (P_{to}=120 torr, $P^*_{O_2}$=60 torr), surface area of NiO(I)=16.4m^2
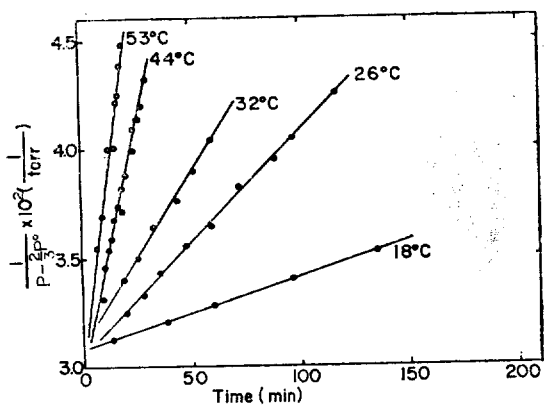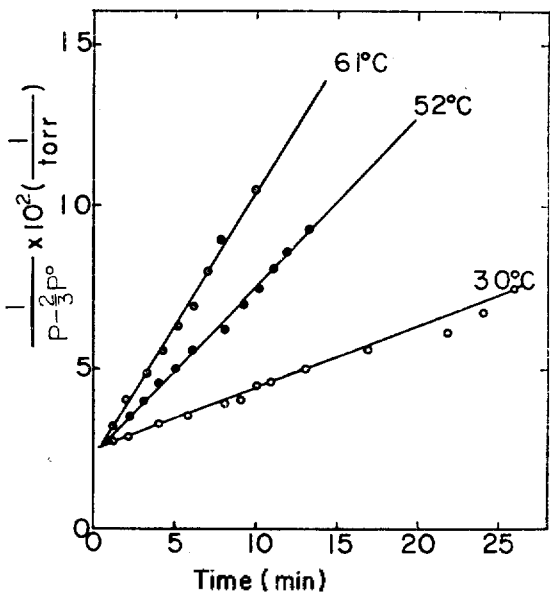

Fig. 6b. $1/(P-2/3P^*)$ vs. time (t) plot on the activated NiO(I) catalyst which was degassed at 92 °C for 24 hours. P^*_{co}=80 torr $P^*_{o_2}$=40 torr.
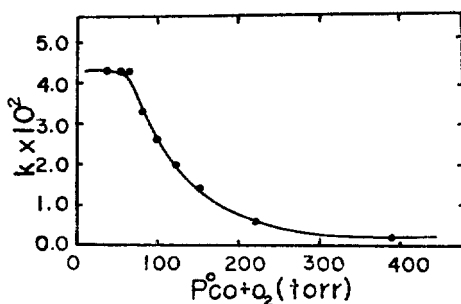

Fig. 6c. $1/(P-2/3P^*)$ vs. time (t) plot on the NiO(II) catalyst. Total surface area=25.9m^2. P^*_{co}=60 torr $P^*_{O_2}$=30 torr.
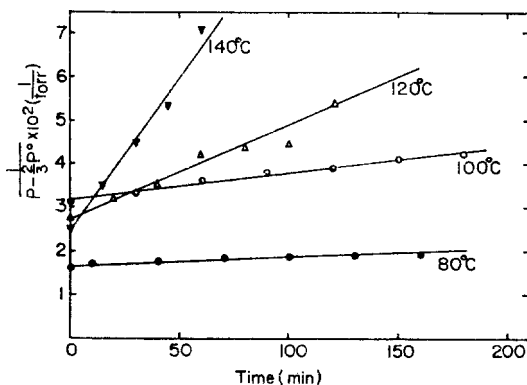
Fig. 6d. $1/(P-2/3P^*)$ vs. time(t)plot on the MnO₂ catalyst (3.02 g). $P^*_{co}/P^*_{O_2}$=2, P=110~180 torr.

Fig. 7. Apparent rate constant k vs. total pressure ($P^*_{co}/P^*_{o_2}$=2) on the NiO(II) catalyst at 32°C.

total pressure the apparent rate constants decreased with total pressure. The following expression gave the best fit for the pressure dependence in *Fig.* 7

$$k_{app} = k' (P^o{}_{(O_2+CO)})^{-1.8}$$

Inhibition Effects. *Fig.* 8 shows the effects of carbon dioxide pressure on the oxidation reaction rate of carbon monoxide. The rate constants decrease with increasing initial CO_2 pressure as shown in *Fig.* 9. From the data of *Fig.* 9, the rate constant at the given CO_2 pressure can be written in terms of initial CO_2 partial pressure as follows:

$$k = k' (1 - K(p^o{}_{co_2})^{0.7})$$

In the above expression k' is the rate constant when $p^o{}_{co_2} = 0$, K is constant, $0.014(1/(torr)^{0.7})$ and $p^o{}_{co_2}$ is initial CO_2 partial pressure (torr). Therefore, rate expression should be corrected in the range of high CO_2 pressure as follows:

$$Rate = k' p_{O_2} p_{CO} (1 - K(p_{CO_2})^{0.7})$$

However, in our experimental conditions (very low CO_2 pressure) inhibition effect was found to be negligible.

Determination of Arrhenius Parameter. *Table* 1 lists the rate constants determined from the total pressure *vs.* time data at various temperatures. The activation energy was determined by plotting ln k *vs.* $\frac{1}{T}$ as shown in *Figs.* 10~12.

Dependence of Arrhenius Parameters on the Pretreatment of Catalyst. In a given consecutive experiments (*ca.* 5) the rate constants are reproducible at various temperatures. However, prolonged use of the catalyst seems to reduce the catalytic efficiency. The data (a) of the *Fig.* 10 was taken after *ca.* 60 to 70 experiments, while the data (b) was taken after activating the catalyst at 92 °C for 1 day under vacuum. As shown in *Fig.* 10 the efficiency of the catalyst improved considerably after the
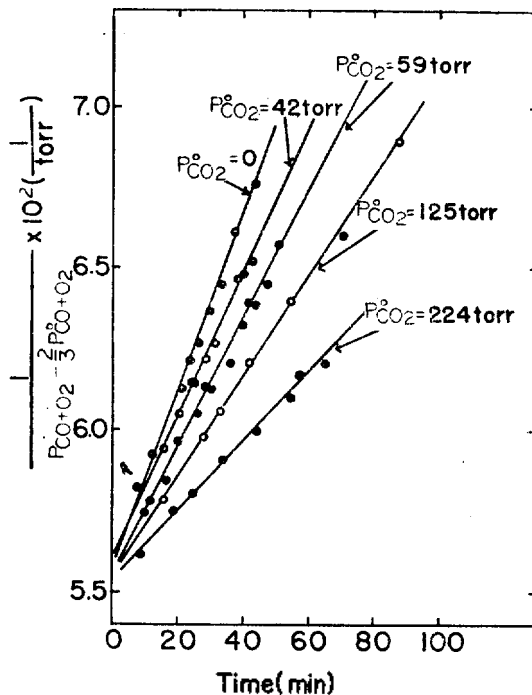

Fig. 8. $1/(P_{O_2+co}-2/3P_{b_2+co})$ *vs.* time (*t*) plot on the NiO(II) at 32 °C at various CO_2 partial pressures. $P^o{}_{co}$ = 36 torr $P^o{}_{o_2}$ = 18 torr.
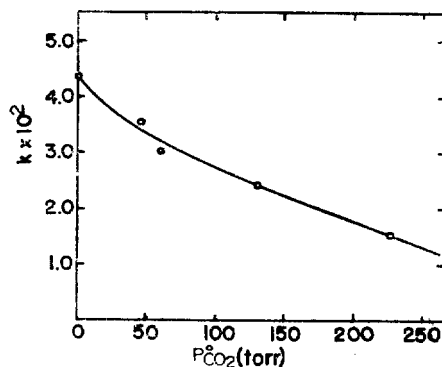

Fig. 9. Rate constant k *vs.* CO_2 partial pressure.

activation. This high efficiency again reduced to the original one after more than 50 to 60 experiments. The reason, probably, is that the active site may be slowly poisoned by the products of the reaction (CO_3 or CO_2 etc). No conclusive evidence can be given at present time.
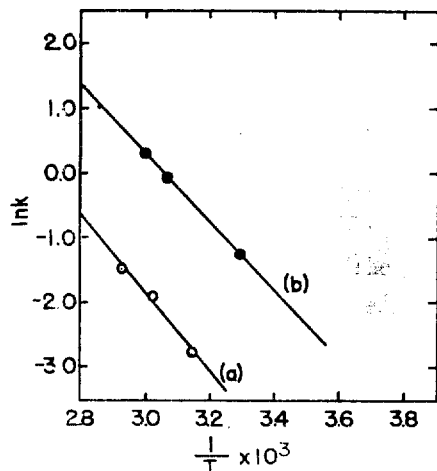
Fig. 10. (a) ln *k* *vs.* 1/*T* plot on the NiO(I) catalyst. (b) ln *k* *vs.* 1/*T* on the activated NiO(I) catalyst which was degassed at 92 °C for 24 hours.
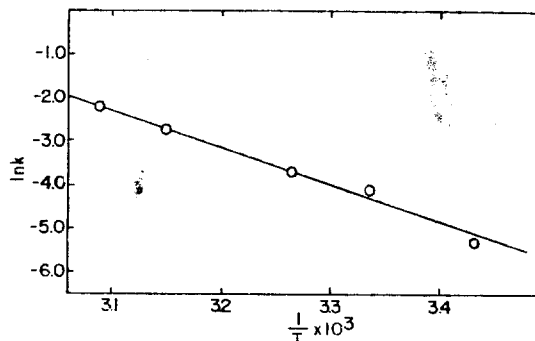

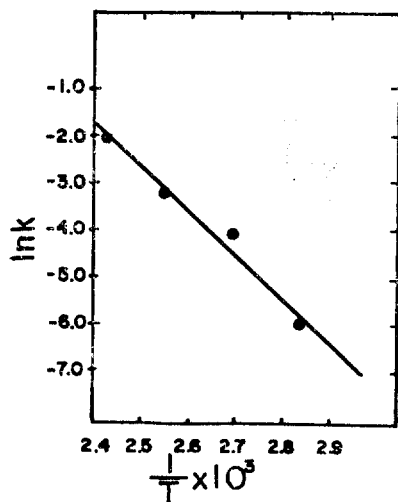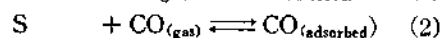*Fig.* 11. ln *k* *vs.* 1/*T* plot on the NiO(II) catalyst.

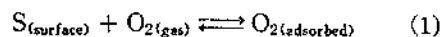*Fig.* 12. ln *k* *vs.* 1/*T* plot on the MnO₂ catalyst.

Table 2. Arrhenius parameters on catalytic surfaces.

Catalyst	Arrhenius parameters		
	A (l/mole·sec)		E_a (kcal /mole)
	/m²	/gm	
NiO(I)	5×10^{14}	3×10^{15}	12
Activated NiO(I)	1×10^{14}	6×10^{14}	10
NiO (II)	2×10^{21}	2×10^{23}	17
MnO₂	—	1×10^{20}	18

DISCUSSION

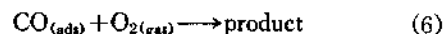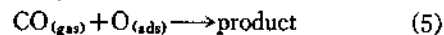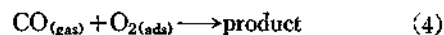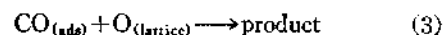**Reaction Mechanisms.** Following possible steps can be written down for the catalytic oxidation of carbon monoxide, if the diffusion and desorption steps are assumed not to be the rate limiting

$$S_{(surface)} + O_{2(gas)} \rightleftharpoons O_{2(adsorbed)} \quad (1)$$
$$S \quad + CO_{(gas)} \rightleftharpoons CO_{(adsorbed)} \quad (2)$$

Adsorption of oxygen as atomic oxygen (charged or uncharged) is regarded as involving further step

$$O_{2(ads)} \rightleftharpoons 2O_{(ads)}$$
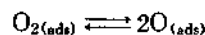
The possible reactions responsible for the product formations are:

$$CO_{(ads)} + O_{(lattice)} \longrightarrow product \quad (3)$$
$$CO_{(gas)} + O_{2(ads)} \longrightarrow product \quad (4)$$
$$CO_{(gas)} + O_{(ads)} \longrightarrow product \quad (5)$$
$$CO_{(ads)} + O_{2(gas)} \longrightarrow product \quad (6)$$
$$CO_{(ads)} + O_{2(ads)} \longrightarrow product \quad (7)$$
$$CO_{(ads)} + O_{(ads)} \longrightarrow product \quad (8)$$
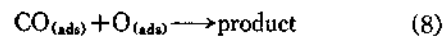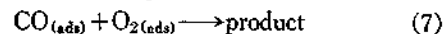
The controversial subject for the catalytic oxidation has been whether adsorbed oxygen molecule (charged or uncharged) or adsorbed atom (charged or uncharged) (which includes the lattice oxygen) is responsible species for the oxidation. Our experimentally determined reaction orders, *i. e.*, first order with respect to both carbon monoxide and oxygen concentrations,

indicate that the mechanism which involves the molecular oxygen is more plausible than the others *i. e.*, the reactions (4), (6) and (7) rather than reactions (3), (5) and (8). Using Langmuir-Hinshelwood treatment under low coverage conditions, the rates of reactions can be given

$$\text{Rate} = kK_{O_2} p_{O_2} p_{CO} = k_{obs} p_{O_2} p_{CO} \text{ (steps 1 and 4)}$$
or $\text{Rate} = kp_{O_2} K_{CO} p_{CO} = k_{obs} p_{O_2} p_{CO}$ (steps 2 and 6)
or $\text{Rate} = kK_{O_2} p_{O_2} K_{CO} p_{CO} = k_{obs} p_{O_2} p_{CO}$
$$\text{(steps 1, 2 and 7)}$$

while steps 2 and 3 yield

$$\text{Rate} = k_{obs} p_{CO}$$

and steps 1 and 5 or 1, 2 and 8 yield

$$\text{Rate} = k_{obs} p_{CO} p_{O_2}^{1/2}$$

Therefore, steps 1 and 4, steps 2 and 6, and steps 1, 2 and 7 are in agreement with our experimentally obtained reaction orders. There have been many attempts to detect the intermediate species for the carbon monoxide catalytic oxidations. By using surface IR techniques the surface carbonate ion ($S-CO_3^{2-}$) complex was detected by Eischens *et al.*[14] and by Blyholder[15]. The detection of this intermediate supports our mechanism since the reaction of carbon monoxide and oxygen molecule must give the CO_3-S species, while the atomic oxygen with CO does not give the complex. Winter[16] showed that the lattice oxygen plays no part in CO oxidation from the O_2^{18} oxygen study. This also partially supports our reaction mechanism which suggests the involvement of molecular oxygen on the surface. At present the detailed mechanism for the product of the reaction, CO_2 formation, could not be deduced. The plausible mechanism may be the reaction of surface carbonate with gaseous carbon monoxide to give carbon dioxide

$$CO_{3(ads)} + CO_{(gas)} \longrightarrow 2CO_{2(ads)} \longrightarrow 2CO_{2(gas)}$$
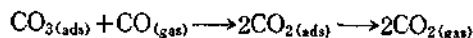
Inhibition Effects. As shown in *Fig.* 8 and *Fig.* 9 carbon dioxide seems to interact with unoccupied catalytic surface site

$$\text{Surface} + CO_{2(gas)} \overset{K}{\rightleftharpoons} CO_{2(adsorbed)}$$
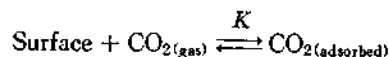
It is assumed that the rate constant is proportional to the number of the unoccupied catalytic surface sites or to the fraction of unoccupied sites

$$\theta_{free} = 1 - \theta_{CO_2},$$
$$k = k' \theta_{free}$$

It has been known that an empirical isotherm due to Freundlich[17] is more successful at high surface coverage

$$\theta = K(p)^{1/m}$$

where θ : coverage, K : adsorption equilibrium constant, $m \geq 1$. This isotherm may be applied to CO_2 adsorption

$$\theta_{CO_2} = K(p_{CO_2})^{1/m}$$

Thus we have

$$k = k' \theta_{free} = k'(1 - \theta_{CO_2}) = k'(1 - K(p_{CO_2})^{1/m})$$

This coincides with our experimentally obtained equation when $\frac{1}{m} = 0.7$

$$k = k'(1 - K(p_{CO_2})^{0.7})$$

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