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CATALYTIC PROPERTIES OF SURFACE SITES ON METAL OXIDES AND THEIR CHARACTERIZATION BY X-RAY PHOTOELECTRON SPECTROSCOPY

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Catalytic Properties of Surface Sites on Metal Oxides and Their Characterization by X-Ray Photoelectron Spectroscopy

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Catalytic Properties of Surface Sites on Metals and Metal Oxides and Their Characterization by X-Ray Photoelectron Spectroscopy

SUMMARY

A. Technical Problem

The long range objective of this research program is to modify the distribution of oxidation states which are stable at the surface of a metal oxide catalyst by controlling the dispersion of the catalyst on its inert support. The catalytic activity and selectivity of the catalyst will then be correlated against the oxidation state of the surface sites--which will be measured using x-ray photoelectron spectroscopy.

This technique has general applicability to a large number of catalyst systems. We plan to expand the scope of our research to include the study of selective hydrocarbon synthesis over supported bimetallic cluster catalysts.

B. General Methodology

The catalytic activity and selectivity of many oxide catalysts can be varied by controlling the oxidation state of the surface oxide. The development of techniques to control and to measure the surface oxidation state (or states) would make possible novel catalysts with enhanced activity and/or dual site catalysts with unique selectivity properties.

Two methods of controlling the surface states will be investigated. (A) The dispersion of the active catalysts on an inactive support will be varied in hopes that the stable oxidation state at given ambient conditions will be influenced by the degree of dispersion of the catalysts. (B) Reactions at electrode surfaces will be studied in hopes that controlled potentials applied to the electrode will influence the oxidation state of the surface sites.

In the course of development of concepts and methodology for characterizing catalysts and understanding the chemical origin of catalytic activity, we plan to expand the scope of our research to include investigation of the catalysis by metals. A new research area for the next year will be the study of selective hydrocarbon synthesis from CO and H_2 over supported bimetallic cluster catalysts. The synthesis reaction is central to production of clean fuel and substitute petrochemical feedstocks from coal.

The success of these techniques will be determined by measuring the catalytic activity and selectivity of various reactions on the oxide catalysts and measuring the resulting surface oxides formed by x-ray photoelectron spectroscopy (ESCA). ESCA is a tool uniquely suited to this research since it can measure the oxidation state and chemical composition of surface specie.

C. Technical Results

The primary objective of this investigation was to understand the catalyst surface behavior during the reduction of nitric oxide by carbon monoxide over chromia-silica catalysts. A technique for the simultaneous measurement of the reaction kinetics and the infrared spectra of the chemisorbed species on solid catalyst surface was developed. The information obtained from this approach was used for determination of the reaction mechanism, identification of the kinetically important surface species, and elucidation of active site character and poison effects.

The reduction of nitric oxide by carbon monoxide over a chromia-silica catalyst at 250°C was studied. The catalyst was prepared by the impregnation method and calcined at 500°C. During the reaction, the catalyst surface was predominantly covered by chemisorbed nitric oxide species. Stable carbonates were also observed. However, chemisorbed carbon monoxide, nitrous oxide, and nitrogen were not detected.

The catalyst activity can be correlated with an active surface specie of nitric oxide at 1735 cm^{-1}. The observed rate expression of CO_2 formation was $r_{CO_2} = a\, P_{CO} \log (I_o/I)_{min,1735\ cm^{-1}}$. Nitric oxide was reduced to nitrous oxide and nitrogen. The formation of nitroux oxide was substantial in this study. The selectivity to nitrous oxide is dependent on the partial pressure of CO as well as NO, and surface concentration of chemisorbed nitric oxide at 1735 cm^{-1}. In general the selectivity decreases as either partial pressure of CO or the surface concentration of chemisorbed NO increases. However, a higher partial pressure of NO leads to a higher selectivity to nitrous oxide if other variables are fixed.

Chemisorption of NO on reduced surface gives rise to the IR bands at 1735 cm^{-1}, 1795 cm^{-1}, 1846 cm^{-1}, and two shoulders at 1750 cm^{-1} and 1860 cm^{-1}. The 1735 cm^{-1} and 1846 cm^{-1} bands were tentatively assigned to dinitrosyl complex onthe surface. Two shoulders at 1750 cm^{-1} and 1860 cm^{-1} were also assigned to dinitrosyl complex on the surface. The 1795 cm^{-1} band was ascribed to mononitrosyl complex on the surface.

The specie giving rise band at 1735 cm^{-1} is active for the reaction and the specie showing shoulder at 1750 cm^{-1} is inactive. The former is chemisorption of NO on the high oxidation state chromium sites. The latter is chemisorption of NO on the low oxidation state sites.

Carbon monoxide were both reversibly and irreversibly chemisorbed on the calcined surface at high temperatures. The reversibly chemisorbed CO gives rise to a band around 2200 cm^{-1}, which is attributed to carbonyl specie.

The irreversibly adsorbed CO produces IR bands at 1550 cm^{-1}, 1365 cm^{-1}, and 1430 cm^{-1}. These bands are assigned to carbonates. The carbonates are formed on the high oxidation state chromium sites.

The catalyst activity decreased during the course of experiments. The deactivation was accompanied with the decrease in intensity of the 1735 cm^{-1} band. The deactivation mechanisms may include changes in the surface oxidation state, formation of stable carbonate on active sites, adsorption of poisoning water vapor. The active sites have a high oxidation state, which are generated during the calcination at high temperatures.

In addition to characterizing the surface composition and oxidation state of the chromia-silica system, ESCA has been used to characterize surface states in the following systems:

(i) Nickel-Oxygen: Our results present the first direct spectroscopic evidence for Ni_2O_3 and indicates that CO adsorbs more readily on an Ni_2O_3-rich surface than on an NiO-rich surface, which may be a catalytically significant result.

(ii) Ion-bombardment of metal-oxygen surfaces has been studied to develop methods in profiling oxidation states and in preparing well-characterized surfaces.

(iii) Chemical shifts due to binding effects: Our studies indicate that these effects may be useful in estimating particle size of small metal clusters, which are extremely important in industrial catalysts.

(iv) Electrode surfaces: The surface chemistry of electrodes and the relationship between coulometric data and surface compositions has been studied. Electrode reaction studies on the platinum cathode of a low temperature hydrogen oxygen fuel cell have demonstrated that significant differences of the concentration of surface oxides are occurring as the fuel cell is used.

D. Implications for Further Research

Studies on Cr/Si-O_2 catalyst system will continue. Kinetic studies will be made to see if the treatment changes detected by ESCA affect catalytic properties.

A study of the methanation reaction, $CO + 3H_2 \rightarrow CH_4 + H_2O$, important in upgrading synthetic natural gas produced from coal, is now underway on ruthenium catalysts. Ruthenium is intriguing because in excess H_2 it has a high specific activity for CH_4 formulation, while in excess CO it catalyzes the production of high molecular weight waxes. Control of catalyst selectivity will be attempted by mixing Ru with other metals to form well dispersed, multimetallic clusters on high surface area catalyst support. The kinetics of the reaction will be measured and the adsorbed species-catalyst interaction followed by infrared spectroscopy during reaction. These results will be used to identify the catalytically important surface species and the relationship between these species and the ESCA data will be a major point of investigation.

We anticipate that ESCA will enable us to investigate, in greater detail than previously achieved, the metal-support interactions, supported alloy formulation, and metal particle size. A technique for measuring the chemical stoichiometry of the active surface will be further developed and the catalytic properties of unique surface chemistry will be investigated.

In addition, present electrode reaction studies, showing that surface oxide concentration as seen by ESCA on platinum electrodes varies with fuel cell operating conditions, will continue. The electrode studies will take full advantage of the ESCA surface techniques discussed above.

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I. Introduction

The catalytic activity and selectivity of many oxide catalysts can be varied by controlling the oxidation state of the surface oxide. The development of techniques to control and to measure the surface oxidation state (or states) would make possible novel catalysts with enhanced activity and/or dual site catalysts with unique selectivity properties.

Two methods of controlling the surface states will be investigated. (a) The dispersion of the active catalysts on an inactive support will be varied in hopes that the stable oxidation state at given ambient conditions will be influenced by the degree of dispersion of the catalysts. (b) Reactions at electrode surfaces will be studied in hopes that controlled potentials applied to the electrode will influence the oxidation state of the surface sites.

The success of these techniques will be determined by measuring the catalytic activity and selectivity of various reactions on the oxide catalysts and measuring the resulting surface oxides formed by x-ray photoelectron spectroscopy (XPS or ESCA).

The technique of characterizing catalysts by controlling surface composition on oxidation state has general applicability. We plan to expand the scope of our research to include the study of selective hydrocarbon synthesis from CO and H_2 over supported bimetallic cluster catalysts.

The following report will therefore be divided into three sections: (II) Catalytic Studies, (III) Characterization of Surface States by ESCA, and (IV) Electrode Reaction Studies.

II. Catalytic Studies

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1. Objective

The long range objective of this research program for the past year has been to modify the distribution of oxidation states which are stable at the surface of a metal oxide catalyst by controlling the dispersion of the catalyst on its inert support. The catalytic activity and selectivity of the catalyst were then correlated against the oxidation state of the surface sites--which were measured using x-ray photoelectron spectroscopy.

This technique obviously has general applicability to a large number of catalytic systems--an even larger number than might first come to mind since many "metal" catalysts are, in their active state, covered by an oxide layer which is the active specie. Numerous example systems are discussed in section IV.

(1) CO and NO reactions on chromina supported on silica: The goal of this specific study is to determine the effects of the relative dispersion of chromia supported on silica on the activity and selectivity of the catalyst for the reactions:

$$2CO + O_2 \rightarrow 2CO_2$$

$$2CO + 2NO \rightarrow N_2 + 2CO_2$$

The proposed research program can be separated into the attainment of a number of specific objectives:

(a) To determine whether the two different methods of catalyst preparation stabilize different oxidation states of chromium oxide supported on silica.

(b) To determine whether the BET surface area is altered by the two differing methods.

(c) To determine whether the two methods produce catalysts that chemisorb different amounts of O_2 or CO, i.e. have differing relative dispersions of chromia on silica.

(d) To determine the effect of the dispersion on the activity and selectivity of the catalyst for (i) CO oxidation by O_2, (ii) CO oxidation by NO, and (iii) competitive oxidation of CO by O_2 and NO.

(e) To determine the relationship between activity and % Cr.

(f) To determine whether the stable oxidation state can be controlled by the catalyst preparation method.

(g) To determine whether it is possible to produce a dual site catalyst for simultaneous oxidation of CO and reduction of NO in the presence of excess O_2. This might be possible if the preparation procedure can be used to control certain catalyst characteristics, i.e. dispersion, oxidation state, activity, etc.

(2) Hydrocarbon synthesis over bimetallic metal clusters: In the course of development of concepts and methodology for characterizing catalysts and understanding the chemical origin of catalytic activity, we plan to expand the scope of our research to include investigation of the catalysis by metals. A new research area for the next year will be the study of selective hydrocarbon synthesis from CO and H_2 over supported bimetallic cluster catalysts. The synthesis reaction is central to production of clean fuel and substitute petrochemical feedstocks from coal. Specific objectives include development of catalysts with high activity for synthesis of specific low molecular weight hydrocarbons, study of chemisorbed species present on selected bimetallic cluster catalyst surfaces during the synthesis reaction, and improvement of ESCA as a quantitative tool for analyzing this new and important class of catalysts.

2. Background and Technical Need

(1) CO and NO reactions on chromia supported on silica: Supported metal and metal oxide catalysts have found wide acceptance in the chemical and petroleum industries. It is not surprising, then, that a great deal of fundamental

research is directed at the active surfaces of these catalysts. Oxide catalysts are of special interest since there seems to be a definite relationship between the stable surface oxidation state and reaction conditions[1,2].

The chromia catalyst chosen for study is especially attractive as it can exist in a variety of oxidation states from +2 to +6. The supported chromium oxide catalyst, industrially important in dehydrogenation and polymerization reactions, has been the subject of numerous fundamental research investigations.

The catalytic activity and selectivity of a chromia catalyst can be a function of the oxidation state of the surface oxide[2]. This stable surface oxide is definitely dependent on the reaction conditions[1,2] and may also be dependent on the relative degree of dispersion of the chromium oxide on an inert support[3,4]. There is evidence[5,6] that the dispersion of the metal oxide may well be a controllable factor. If this is the case, then it follows that a catalyst with controllable activity/selectivity characteristics would result.

Shelef[2] recently reported that supported chromium oxide was an effective catalyst for the oxidation of CO by NO. The oxidation state of the chromium oxide was found by these authors to be an important factor since the CO + NO reaction was nearly completely inhibited by the presence of oxygen. Different oxidation states were found to be required for optimal conversion by the two reactions:

$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2$$

$$2CO + 2NO \rightarrow N_2 + 2CO_2$$

When CO was oxidized in the simultaneous presence of O_2 and NO, very little reduction of NO was found until nearly all of the O_2 was taken up by the first reaction.

The approach to the problem presented here is to study the activity and selectivity of chromium oxide supported on silica by controlling its oxidation state. If different oxidation states of chromium oxide can be stabilized at reaction conditions, it might be possible to produce a catalyst capable of oxidizing carbon monoxide and reducing oxides of nitrogen in the presence of excess oxygen. This "dual site" catalyst would have a possible application to the control of exhaust emissions.

A fourteen page background and literature review convering the physicio-chemical properties of supported and unsupported chromium oxide and kinetics of CO oxidation over supported chromium oxide including 78 references, was included in the June 1974 Annual Report and will not be repeated here.

3. Accomplishments

The primary objective of this investigation was to understand the catalyst surface behavior during the reduction of nitric oxide by carbon monoxide over chromia-silica catalysts. A technique for the simultaneous measurement of the reaction kinetics and the infrared spectra of the chemisorbed species on solid catalyst surface was developed. The information obtained from this approach was used for determination of the reaction mechanism, identification of the kinetically important surface species, and elucidation of active site character and poison effects.

I. Simultaneous Studies of IR Spectroscopy and Kinetics

A. Deactivation of Catalysts

The fresh catalyst, calcined at 500°C, shows a high activity and gives rise to two strong IR bands at 1735 cm^{-1} and 1846 cm^{-1} under the reaction conditions. The activity decreased during the course of the experiments. At the biginning the deactivation was more rapid, becoming slower after several hours. The steady-state had never been reached. During this deactivation, changes in IR spectra were noted. Figure 1 and Figure 2 show the spectra taken during the reaction.

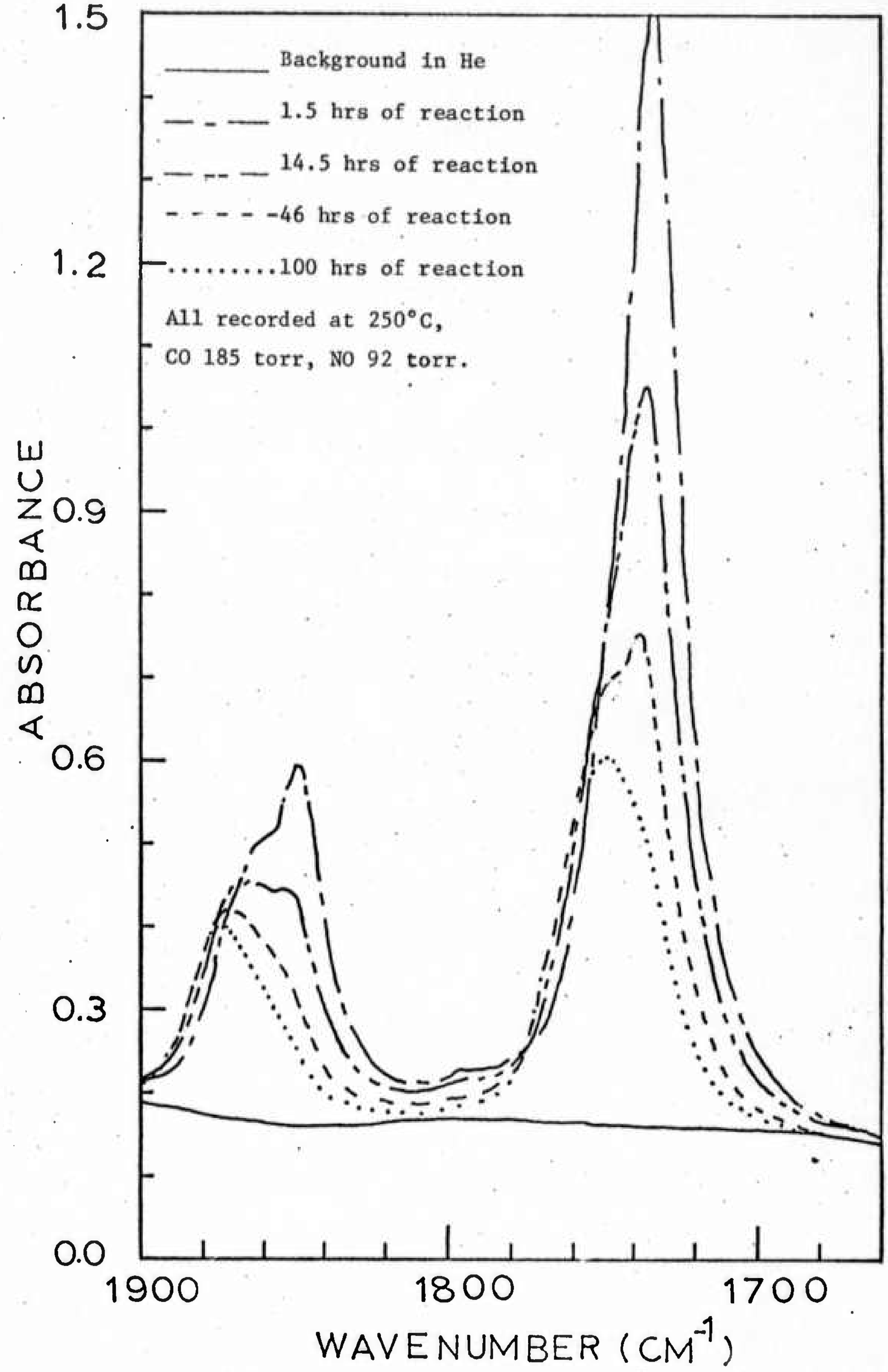

Figure 1. IR Spectra during the NO/CO Reaction over Chromia-Silica.

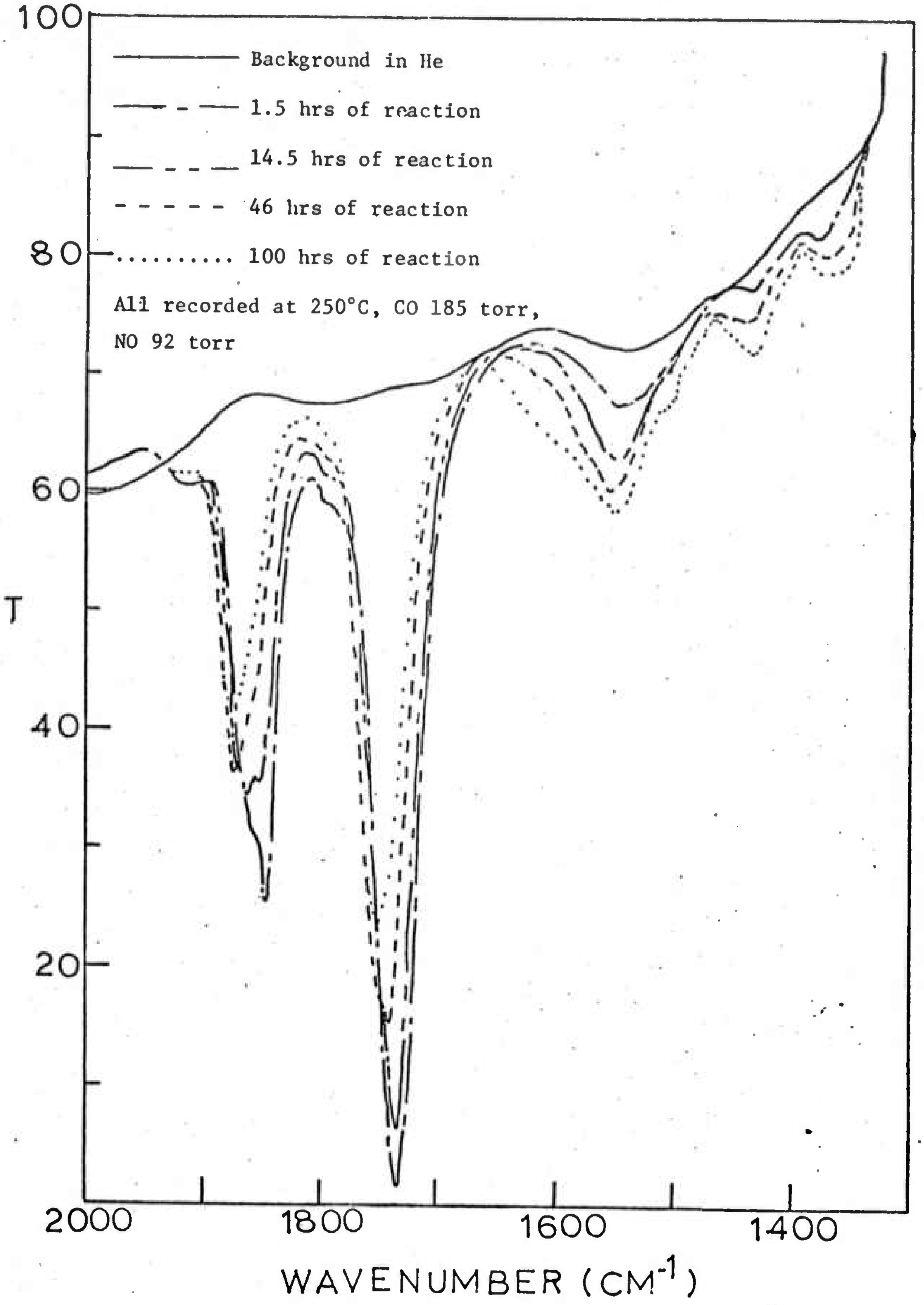

Figure 2. IR Spectra during the NO/CO Reaction over Chromia-Silica

In addition to the 1735 cm^{-1} band and the 1846 cm^{-1} band, there are several bands in the 2000 cm^{-1} - 1200 cm^{-1} region: a weak band at 1790 cm^{-1}, a strong band at 1550 cm^{-1} and two weak bands at 1430 cm^{-1} and 1365 cm^{-1}. The intensity of the 1550 cm^{-1} band slowly increased and seemed to increase in width. A slow increase in intensity of both the 1430 cm^{-1} and 1365 cm^{-1} bands was found. However, the change in the 1375 cm^{-1} band intensity was not clearly observed; this was due to a poor background transmission in this region.

A more remarkable change of the spectra associated with the deactivation of the catalyst is the decreasing intensities of the 1735 cm^{-1} and the 1846 cm^{-1} bands. A linear correlation between the band area of the 1735 cm^{-1} band (i.e. surface concentration) and the rate of CO_2 formation has been found. In order to show this correlation, a run with fixed partial pressures of CO and NO was performed. In Figure 3, the rate of CO_2 formation is plotted versus the surface concentration of the 1735 cm^{-1} band (expressed as $_{\nu_1}^{\nu_2} \log I_o/I \, d\nu$). This linear relation holds for a wide range of the concentration of the surface specie which gives rise to the 1735 cm^{-1} band. However, in the range of low surface concentrations the correlation seems not to hold.

As shown in Figure 3 a positive intercept for surface concentration is obtained as the rate of CO_2 formation approaches zero. This implies that some species in this band are inactive for the reaction. When the 1735 cm^{-1} band in Figure 1 is closely examined, it is found that this band includes a shoulder at 1750 cm^{-1}. The center of this band gradually shifted to 1750 cm^{-1} as its intensity decreased. Similarly and more clearly, the fresh sample has a shoulder at 1860 cm^{-1} associated with the 1846 cm^{-1} band. In the later of the course of the experiments, the 1845 cm^{-1} band becomes the shoulder of the 1860 cm^{-1} band as shown in Figure 1 and Figure 2.

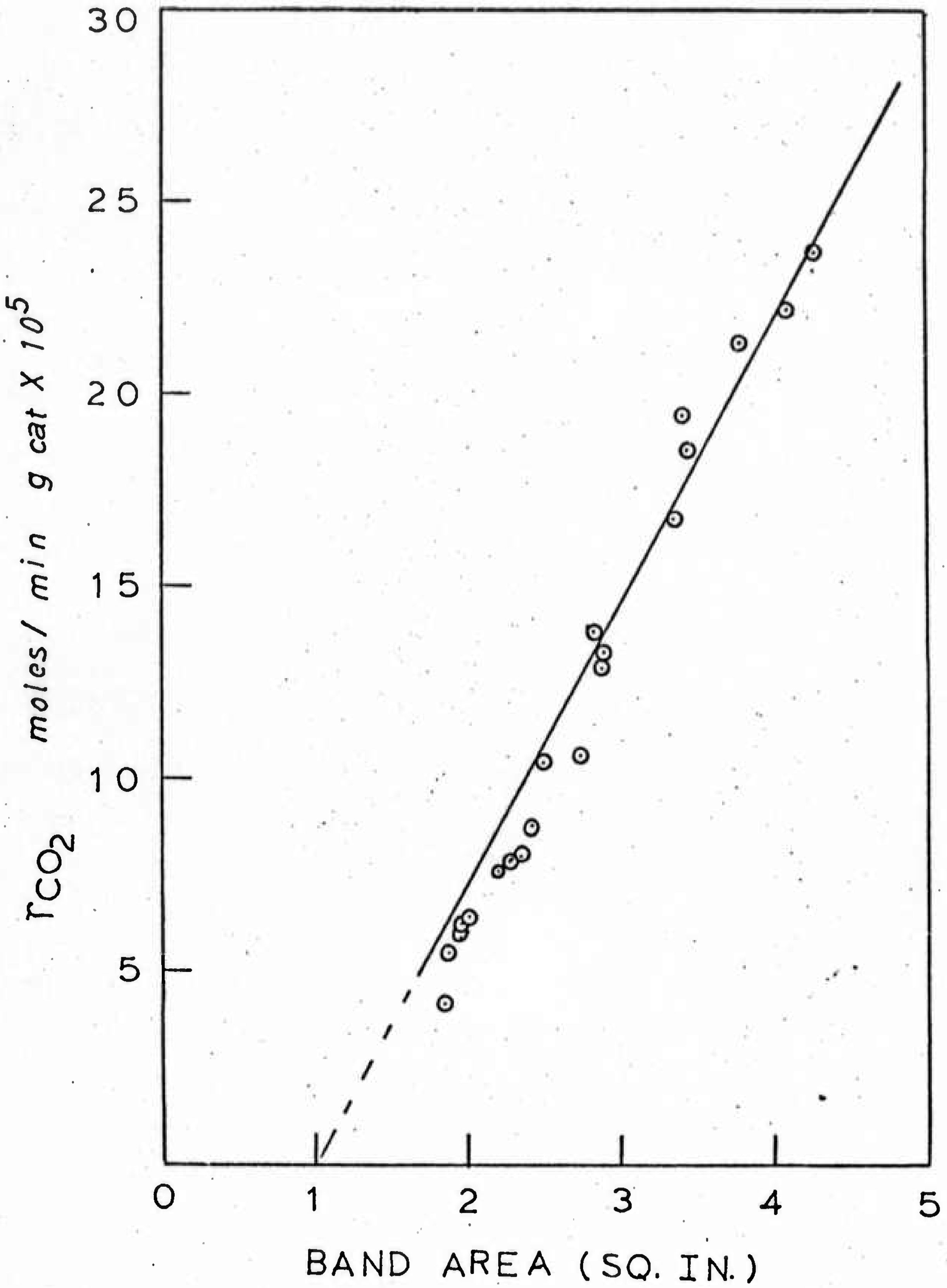

Figure 3. Rate of CO_2 Formation versus Band Area at 1735 CM^{-1}.

Reaction temperature 250°C, P_{CO} 185 torr, P_{NO} 92 torr.

B. Reaction Rate Dependence on Reactant Partial Pressure

The quantity, log $(I_o/I)_{min}$ of the 1735 cm^{-1} band, is proportional to the band area; here, Figure 3 is re-plotted as shown in Figure 5. The straight line in Figure 5 indicates the rate of CO formation is a well-behaved function of log $(I_o/I)_{min}$. This relation does not hold in the region of low values of log $(I_o/I)_{min}$. In this region, the contribution of the shoulder at 1750 cm^{-1} is significant. To minimize this interference all data were taken before log $(I_o/I)_{min}$ had fallen below 0.5.

In Figure 6 and Figure 7 (some typical) the rates of CO_2, N_2O, and N_2 formation are plotted versus log $(I_o/I)_{min}$ 1735 cm^{-1} at various reaction conditions. The predicted values of the rates of CO_2, N_2O, and N_2 formation from the proposed reaction mechanism are also indicated (see next section). In Figure 8 the rates of CO_2 formation which have been correlated with log $(I_o/I)_{min}$, 1735 cm^{-1} are plotted versus the partial pressures of carbon monoxide. The linearity in Figure 8 clearly indicates that the rate of CO_2 formation is first order with respect to CO partial pressure. The rate of CO_2 formation is zero order in NO partial pressure as shown in Figure 8.

Other products in the NO/CO reaction are nitrous oxide (N_2O) and nitrogen. In this research, nitric oxide is predominantly converted into nitrous oxide. In Figure 9 the selectivity of nitrous oxide (defined as $r_{N_2O}/-r_{NO}$) is plotted versus the partial pressure of nitric oxide at fixed values of CO partial pressure and log $(I_o/I)_{min}$. In Figure 10 the selectivity is plotted versus CO partial pressure. The selectivity of

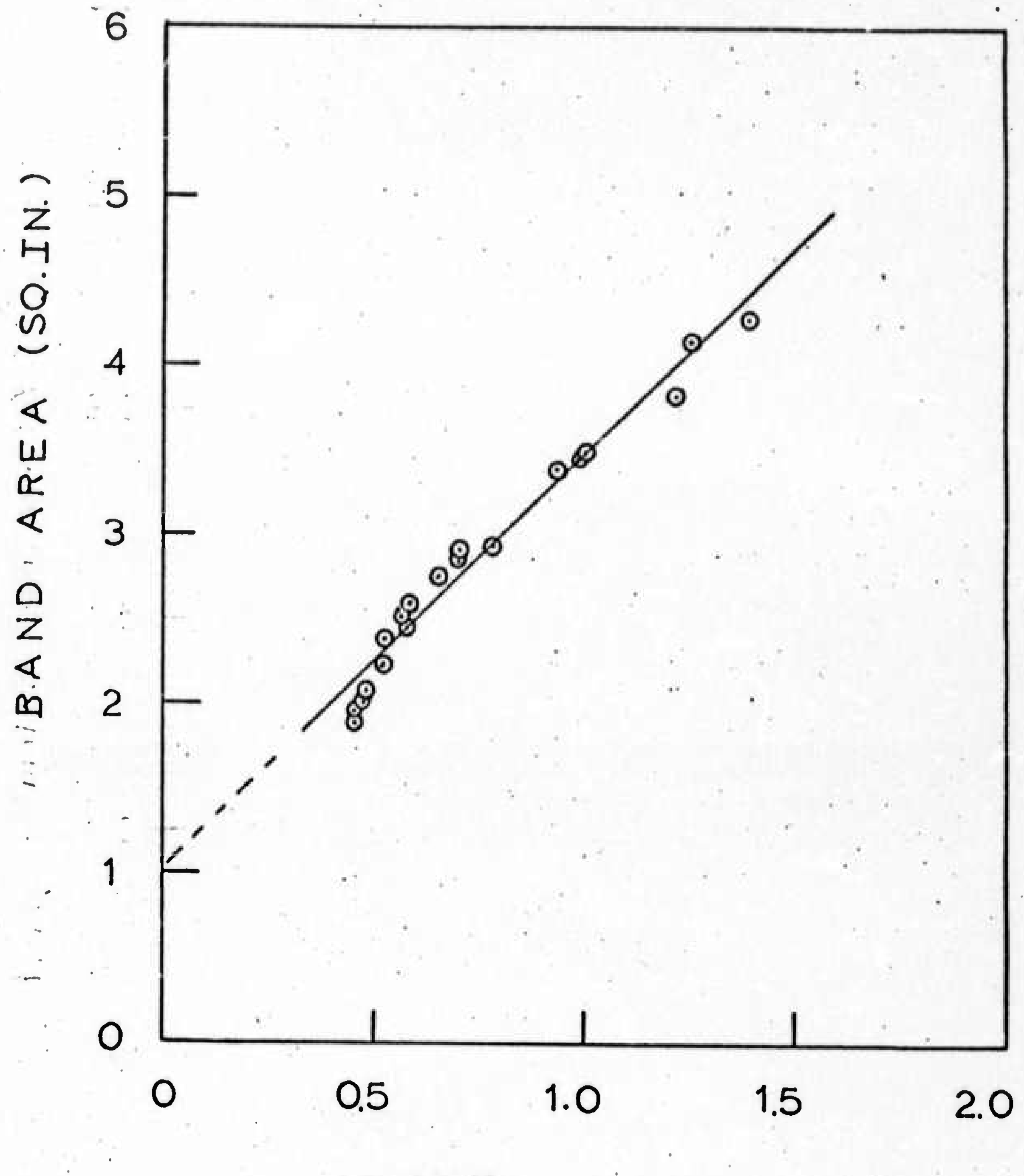

Figure 4. Band Area versus $\log(I_o/I)_{min}$ of the 1735 CM^{-1} Band.

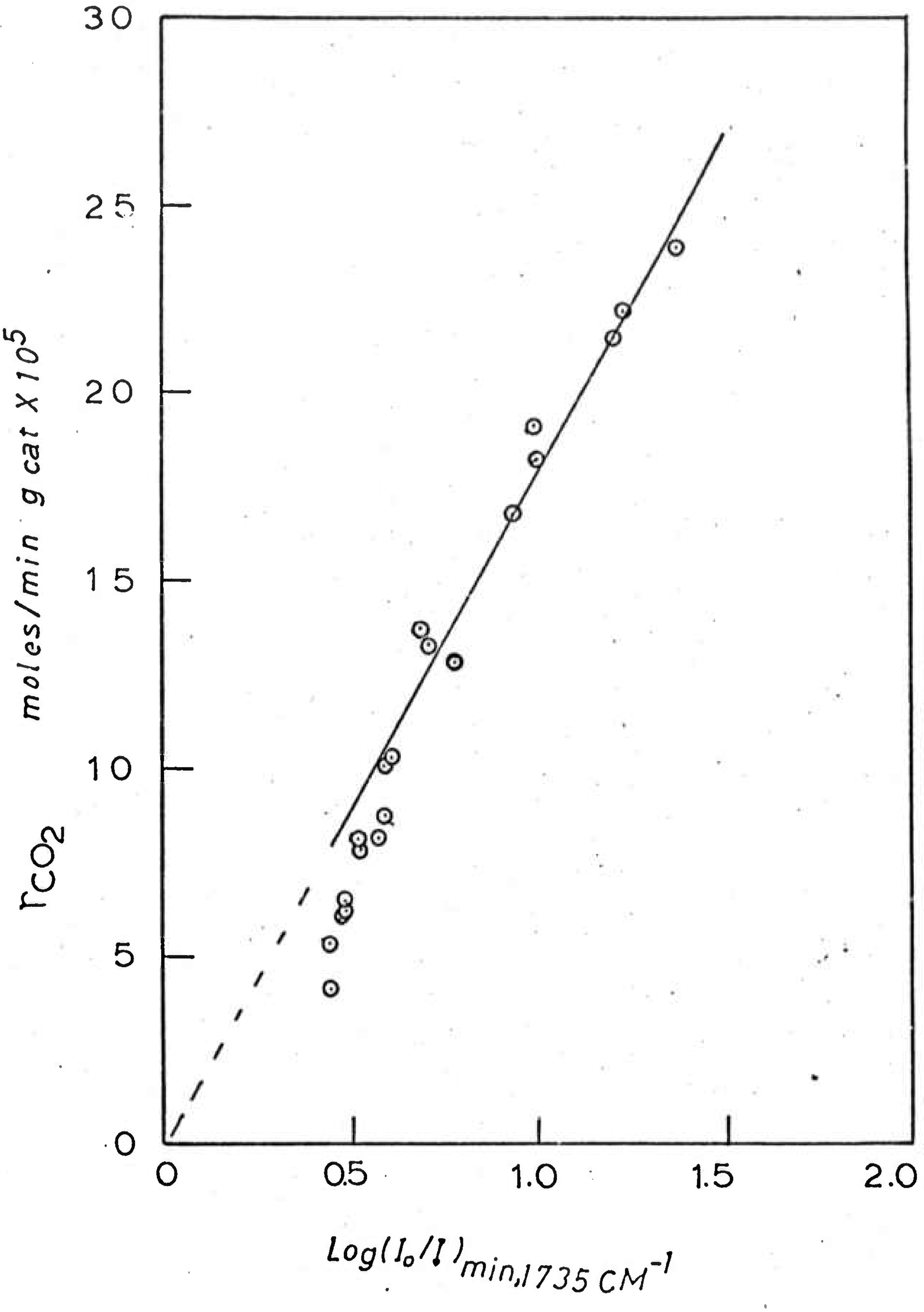

Figure 5. Rate of CO_2 Formation versus log $(I_o/I)_{min}$.

Reaction temperature 250°C, P_{CO} 185 torr, P_{NO} 92 torr. Values of log $(I_o/I)_{min}$ are not normalized.

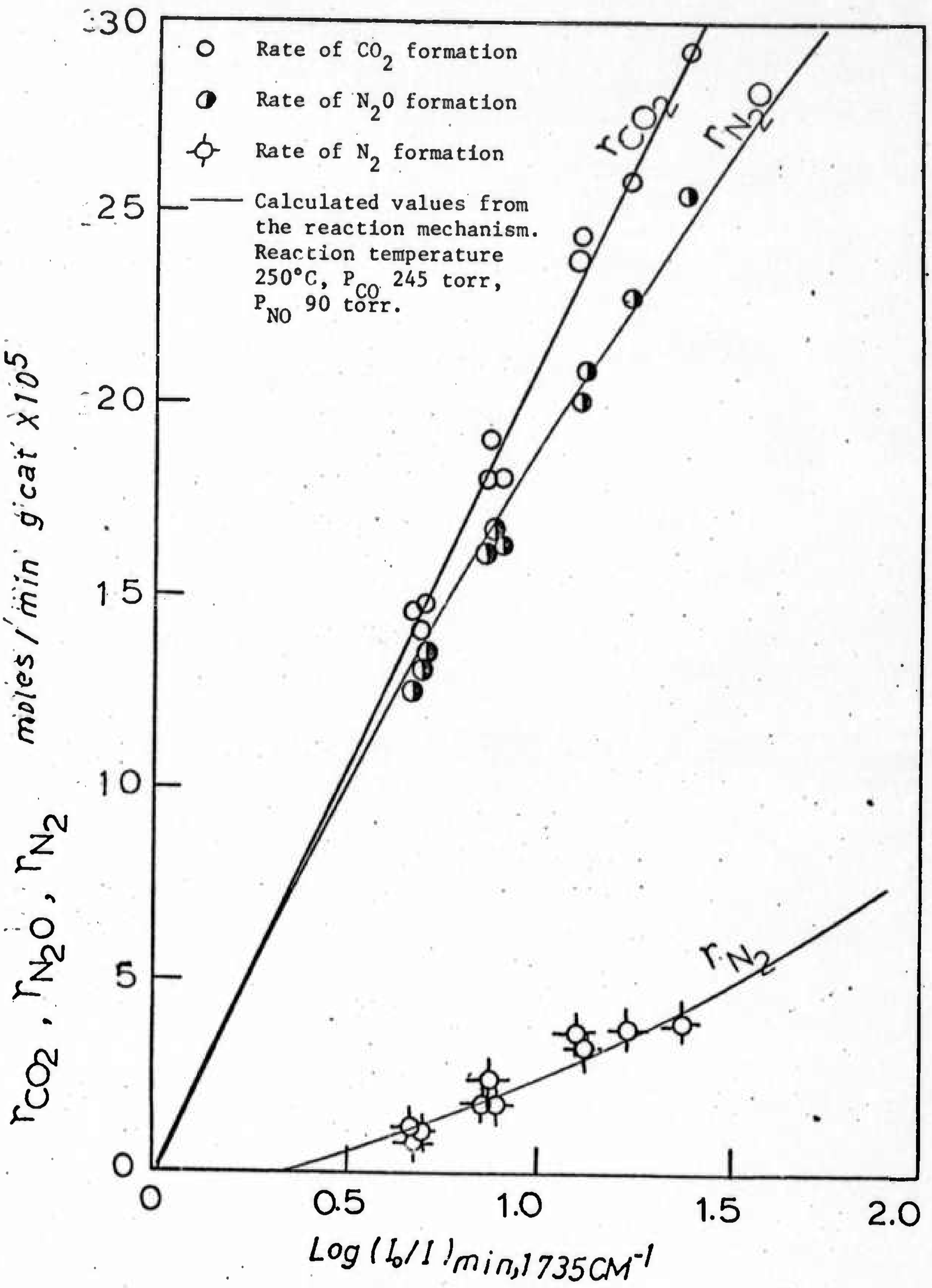

Figure 6. Rates of CO_2, N_2O, and N_2 Formation versus log $(I_o/I)_{min,1735CM^{-1}}$

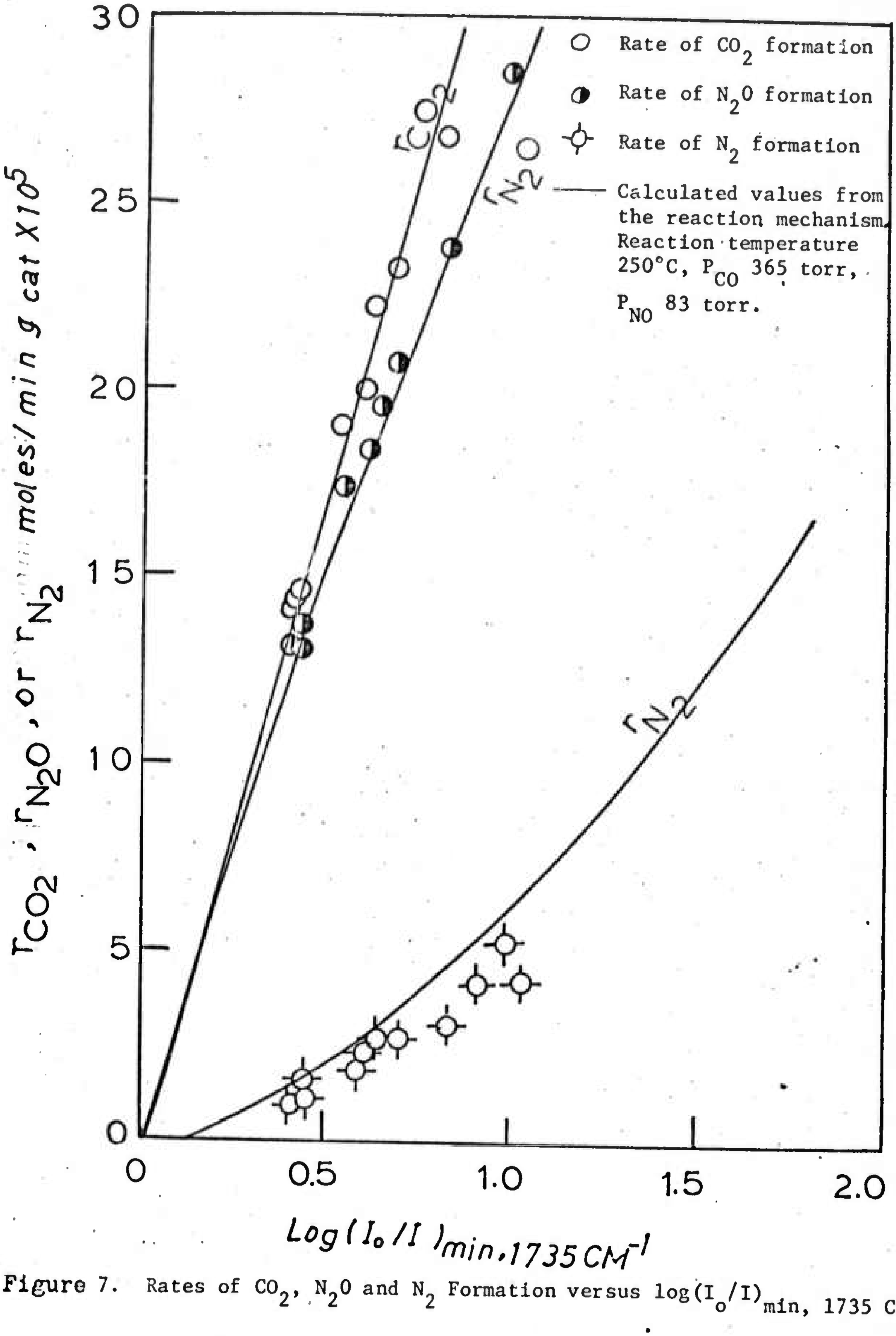

Figure 7. Rates of CO_2, N_2O and N_2 Formation versus $\log(I_o/I)_{min}$, 1735 CM^{-1}

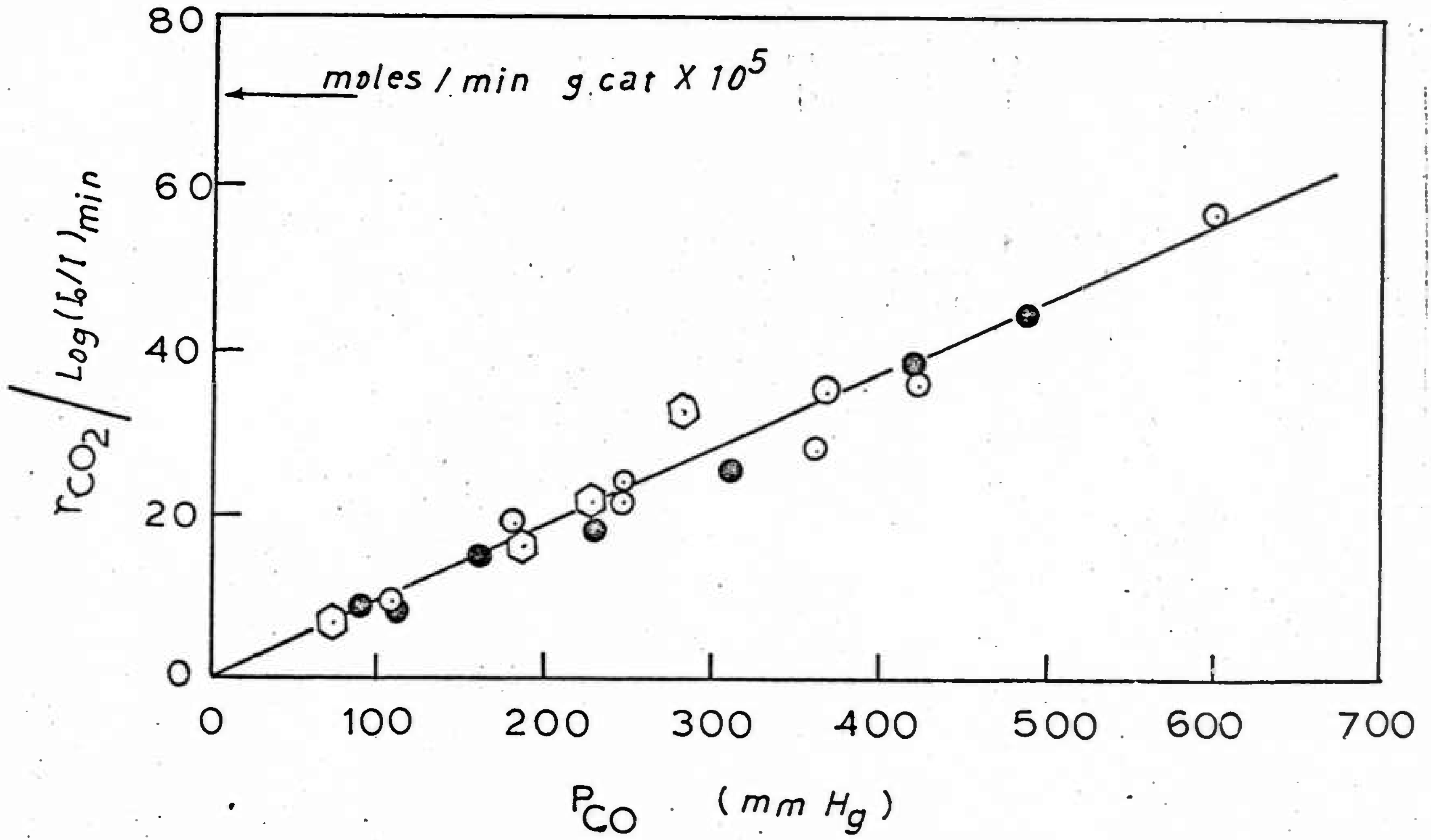

Figure 8. $r_{CO_2}/\log(I_o/I)_{min,1735\ CM^{-1}}$ versus P_{CO}.

⊙ P_{NO} 85 torr, ● P_{NO}/P_{CO} = 0.30,

⬡ P_{NO}/P_{CO} = 0.90, reaction temperature 250°C.

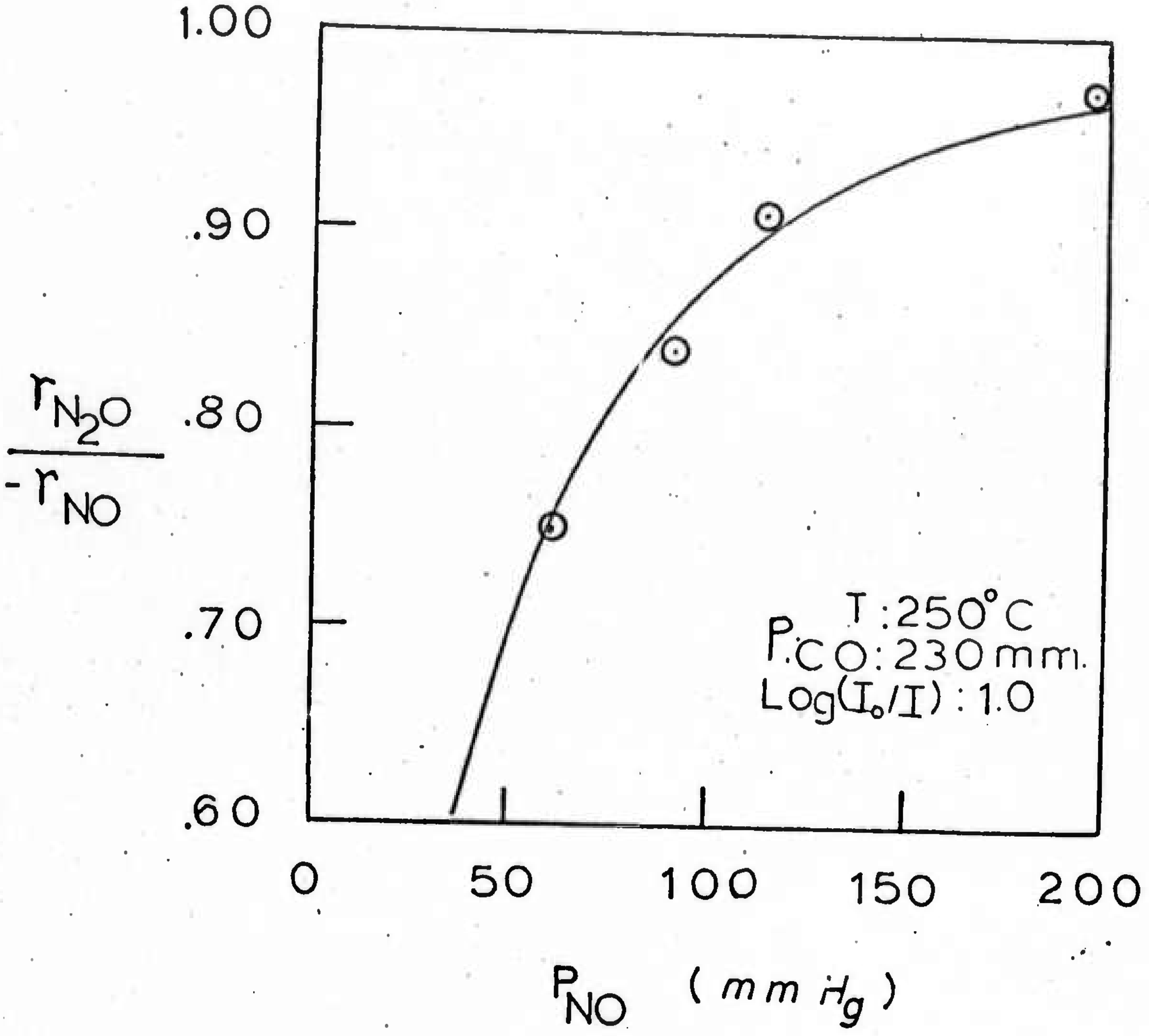

Figure 9. $r_{N_2O}/ -r_{NO}$ versus P_{CO} .

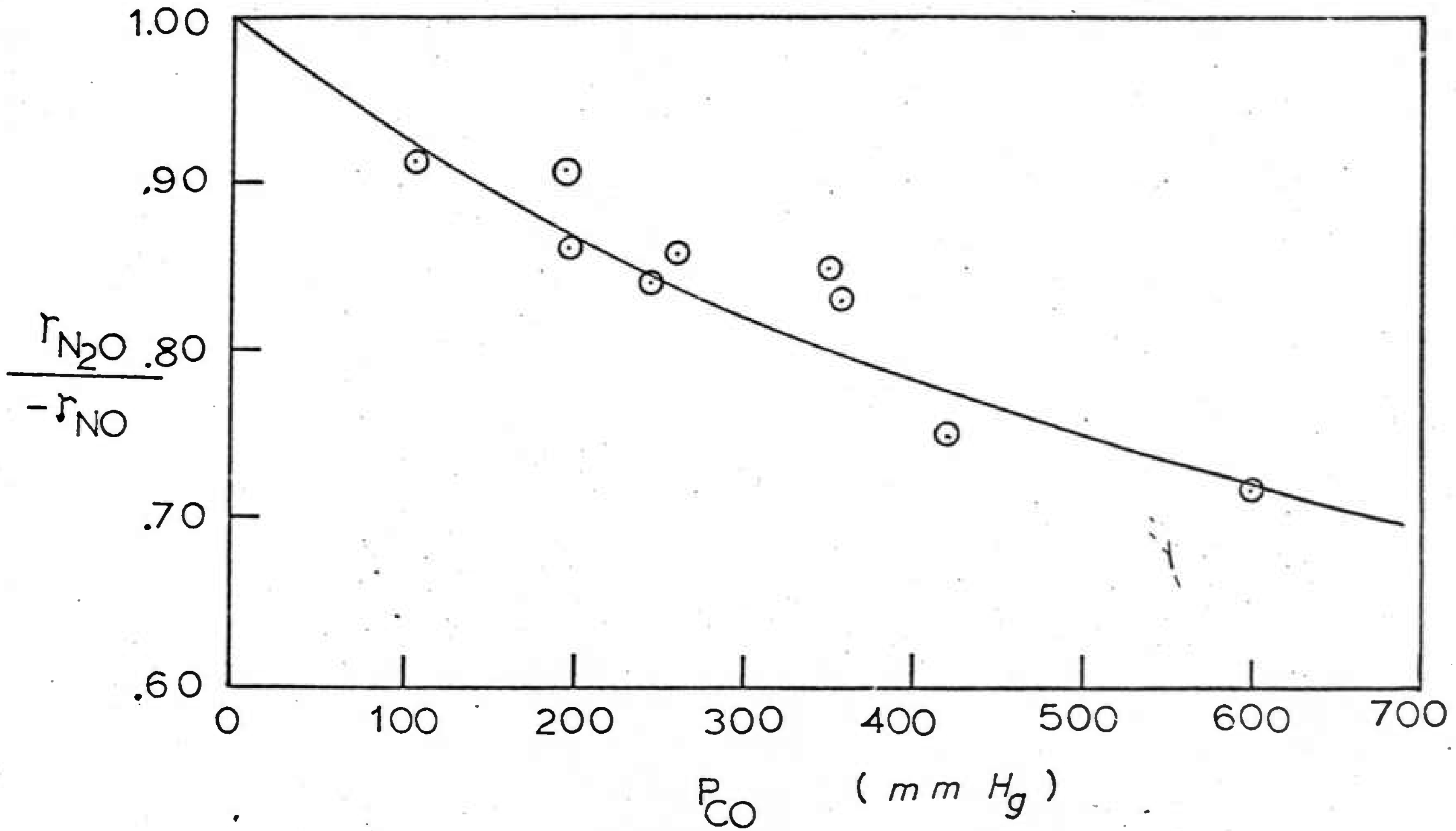

Figure 10. $r_{N_2O}/-r_{NO}$ versus P_{CO}. P_{NO} 85 torr, $\log(I_o/I)_{min,1735CM^{-1}} = 1.0$, 250°C.

nitrous oxide is dependent on the partial pressure of CO as well as NO, and surface concentration of chemisorbed nitric oxide at 1735 cm^{-1}. In general the selectivity decreases as either partial pressure of CO or the surface concentration of chemisorbed NO increases. However, a higher partial pressure of NO leads to a higher selectivity to nitrous oxide if other variables are fixed.

II. Discussion of Simultaneous Infrared and Kinetic Study

A. Catalyst Surface Behavior under Reaction Conditions

During the reaction the catalyst surface is predominantly covered by nitric oxide. No chemisorbed CO and N_2O on the surface are observed. During the course of the experiment the activity decreases accompanied with a decrease in the intensity of chemisorbed NO bands and an increase in the intensity of carbonate bands. Several hours after the reaction the following bands are observed in the spectra (cf. Figure 1 and Figure 2):

1735 cm^{-1}	strong	Chemisorbed NO (Dinitrosyl ligands)
1846 cm^{-1}	strong	
1750 cm^{-1}	shoulder	Chemisorbed NO (Dinitrosyl ligands)
1800 cm^{-1}	shoulder	
1795 cm^{-1}	weak	Chemisorbed NO (mono ligand)

1550 cm^{-1}	medium	bidentate carbonate
1365 cm^{-1}	weak	
1430 cm^{-1}	weak	uncoordinated carbonate
1390 cm^{-1}	very weak	monodentate carbonate
1500 cm^{-1}	very weak	

One day or so after the reaction, the band at 1550 cm^{-1} seemed to increase its width. A broad band at 1620 cm^{-1} and a weak band at 1510 cm^{-1} were observed. It is difficult to assign these two bands, especially for the band at 1620 cm^{-1}. Some species such as adsorbed water, chemisorbed NO_2, and bicarbonate may give rise to a band near 1620 cm^{-1}. Perhaps, the 1620 cm^{-1} is a combination of two or all three of these species (i.e. the shape of this band is not well-defined). However, chemisorbed water is likely to be the candidate, since both the chemisorbed NO_2 and bicarbonate are unstable at 250°C. The 1510 cm^{-1} band can be ascribed to either the monodentate carbonate or the monodentate nitrato complex. Another noticeable change in the spectra is the positive shifts of the bands at 1735 cm^{-1} and 1846 cm^{-1} to 1750 cm^{-1} and 1870 cm^{-1}, respectively. The positive shift of these bands probably is due to the change in surface oxidation state of the catalyst.

B. Reaction Mechanism

A calcined catalyst has a high activity. The oxygen-covered catalyst is inactive for chemisorption of NO. The presence of CO in the gas phase is necessary for NO chemisorption and for promoting the reaction. During the reaction, the surface is predominantly covered by the chemisorbed NO. It is, therefore, quite possible to treat the chemisorbed NO as the most abundant surface specie. No chemisorbed CO is observed. This implies that either the surface CO concentration is very low or the CO has a very short lifetime on the surface. Since the surface NO concentration can be directly measured from the IR spectra, the surface NO concentration can be treated as a variable. In the present study, it has been found that the rate of CO_2 formation is first order with respect to the surface NO concentration (cf. Figure 3, Figure 5, Figure 6, and Figure 7). Kinetically it implies that the formation of the surface NO is a very fast step while the reaction step of the surface NO is relatively slow. Presumably, the reaction step of the surface CO with gaseous CO to form CO_2 is the rate determining step. The rate of N_2O and N_2 formation are slightly complicated. Both rates are dependent on the partial pressure of CO and NO as well as the surface NO concentration. The distribution of N_2O and N_2 (i.e. selectivity) can be used as a guide to discriminate between possible reaction mechanism. In general, the following trends can be made:

1. The rate of N_2O formation increases with the surface NO concentration and partial pressures of CO and NO.
2. The rate of N_2 formation increases with the surface NO concentration and the partial pressure of CO.
3. The selectivity to N_2O (defined as $r_{N_2O}/-r_{NO}$) increases with the partial pressure of NO if other variables are fixed.

4. The selectivity of N_2O decreases as the partial pressure of CO increases.

Based on the above analyses, a reaction mechanism is proposed:

$$\{*\} + NO \overset{k_1}{\leftrightarrow} \{* - NO\} \qquad (1)$$

$$\{* - NO\} + CO \xrightarrow{k_2} \{* - N\} + CO_2 \qquad (2) \quad \text{RDS}$$

$$\{* - N\} + NO \xrightarrow{k_3} \{*\} + N_2O \qquad (3)$$

$$2\{* - N\} \xrightarrow{k_4} 2\{*\} + N_2 \qquad (4)$$

where $\{*\}$ is active site; $\{* - NO\}$ and $\{* - N\}$ are chemisorbed NO and N on the surface, respectively. The chemisorption of NO is considered to be in the equilibrium, since the reaction of the chemisorbed NO and carbon moxidered is the rate determining step. Based upon the kinetic data that the rate of CO_2 formation is first order in CO partial pressure, a Rideal reaction mechanism is written in Equation (2) for the CO_2 formation step.

An alternative to Equation (3), which could also explain the mechanism of N_2O formation is:

$$\{* - N\} + \{*\} - NO \rightarrow 2\{*\} + N_2O \qquad (3a)$$

The surface NO concentration is independent of NO partial pressure. Therefore the rate of N_2O formation via (3a) is not significant. The data show that the N_2O formation rate is dependent on NO partial pressure.

Another feasible reduction path for N_2 formation is the reaction of CO and N_2O on the surface, i.e.

$$\{*\} + N_2O \rightarrow \{* - N_2O\} \quad (5)$$

$$\{* - N_2O\} + CO \rightarrow \{* - N_2\} + CO_2 \quad (6)$$

$$\{* - N_2\} \rightarrow \{*\} + N_2 \quad (7)$$

or

$$\{*\} + N_2O \rightarrow \{* - ON_2\} \quad (5a)$$

$$\{* - ON_2\} \rightarrow \{* - O\} + N_2 \quad (6a)$$

$$\{* - O\} + CO \rightarrow \{*\} + CO_2 \quad (7a)$$

Adsorption of N_2O on reduced chromia-silica through either the oxygen atom end or the nitrogen end has been reported in IR studies$^{(58)}$. In the present study, the chemisorbed N_2O is not observed by IR during the reaction. The rate of N_2 through the N_2O/CO reaction mechanism is expected to be not significant in the present study.

The rates of CO_2, N_2O, and N_2 formation can be expressed as

$$r_{CO_2} = k_2 [*\text{-NO}] P_{CO} \quad (8)$$

$$r_{N_2O} = k_3 [*\text{-N}] P_{NO} \quad (9)$$

$$r_{N_2} = k_4 [*\text{-N}]^2 \quad (10)$$

where r is the rate of formation, mole/g min

p is the partial pressure, mm Hg

k_2 is the rate constant of CO_2, min^{-1}, mm Hg^{-1}

k_3 is the rate constant of N_2O, min^{-1}, mm Hg^{-1}

[*-NO] is surface NO concentration, mole/g

[*-N] is surface *-N concentration, mole/g

The rate constant of CO_2 formation can be calculated by Equation (11)

$$k_2 = \frac{r_{CO_2}}{[*\text{-NO}]\ P_{CO}} \qquad (11)$$

all [*-N] generated from Equation (2) must be consumed in Equation (3) and Equacion (4), i.e.

$$k_2\ [*\text{-NO}]\ P_{CO} = k_3\ P_{NO}\ [*\text{-N}] + k_4\ [*\text{-N}]^2 \qquad (12)$$

From Equation (12), the surface concentration of [*-N] can be calculated by Equation (13):

$$[*\text{-N}] = \frac{-\ k_3\ P_{NO} \pm \sqrt{k_3^2\ P_{NO}^2 + 4k_2k_4\ [*\text{-NO}]\ P_{CO}}}{2k_4} \qquad (13)$$

[*-N] must be positive. Equation (13) becomes

$$[*\text{-N}] = \frac{-\ k_3\ P_{NO} + \sqrt{k_3^2\ P_{NO}^2 + 4k_2k_4\ P_{CO}[*\text{-NO}]}}{2k_4} \qquad (14)$$

or

$$[*\text{-N}] = \frac{k_3\ P_{NO}}{2k_4}\left(-1 + \sqrt{1 + \frac{4k_2k_4\ P_{CO}}{k_3^2\ P_{NO}^2}\ [*\text{-NO}]}\right) \qquad (15)$$

Substituting Equation (15) into (Equation (9) and Equation (10) yields:

$$r_{N_2O} = \frac{k_3^2\ P_{NO}^2}{2k_4}\left(-1 + \sqrt{1 + 4\ \frac{k_2k_4\ P_{CO}}{k_3^2\ P_{NO}^2}\ [*\text{-NO}]}\right) \qquad (16)$$

$$r_{N_2} = \frac{k_3^2\ P_{NO}^2}{4k_4}\left(-1 + \sqrt{1 + 4\ \frac{k_2k_4\ P_{CO}}{k_3^2\ P_{NO}^2}\ [*\text{-NO}]}\right)^2 \qquad (17)$$

A correlation between absolute surface NO concentration and the intensity of the IR band at 1735 cm^{-1} was not obtained in the present study. The absolute k_2 cannot be obtained. The linear proportionality between the surface NO concentration and IR band intensity (expressed as $\log (I_o/I)_{min}$) is assumed:

$$[\text{*-NO}] = \alpha \log (I_o/I)_{min} \tag{18}$$

where α is a conversion factor, mole/g.

Substituting Equation (18) into Equation (11) yields:

$$k_2 = \frac{r_{CO_2}}{\alpha P_{CO} \log (I_o/I)_{min}} \tag{19}$$

or

$$k_2' = k_2\alpha = \frac{r_{CO_2}}{P_{CO} \log (I_o/I)_{min}} , \tag{20}$$

wherein the rate constant of CO_2,k_2' is used in the analysis of kinetic data. Equation (16) and Equation (17) can be rewritten in terms of k_2':

$$r_{N_2O} = \frac{k_3^2 P_{NO}^2}{2k_4} \left(-1 + \sqrt{1 + \frac{4k_2'k_4 P_{CO}}{k_3^2 P_{NO}^2} \log (I_o/I)_{min}}\right) \tag{21}$$

$$r_{N_2} = \frac{k_3^2 P_{NO}^2}{4k_4} \left(-1 + \sqrt{1 + \frac{4k_2'k_4 P_{CO}}{k_3^2 P_{NO}^2} \log (I_o/I)_{min}}\right)^2 \tag{22}$$

From Equation (20) and either Equation (21) or Equation (22), k_2' and k_3^2/k_4 can be calculated. At 250°C, the averages of k_2' and k_3^2/k_4 are shown in Table I.

Table I. Values of k_2' and k_3^2/k_4 Derived by Fitting the Kinetic Data

k_2'	Avg. absolute relative deviation %	k_3^2/k_4	Avg. absolute relative deviation %
1.27×10^{-5}	3%	1.91×10^{-6}	7.8%

Based on the values of k_2' and k_3^2/k_4 in Table I, some kinetic data are simulated. The calculated data and observed data are shown in Figure 1, Figure 2, Figure 4, and Figure 5. Good agreements are obtained. Numerically the rates of CO_2, N_2O, and N_2 formation can be expressed as:

$$r_{CO_2} = 1.27 \times 10^{-5}\, P_{CO}\, (I_o/I)_{min} \tag{23}$$

$$r_{N_2O} = 9.55 \times 10^{-7}\, P_{NO}^2 \left(-1 + \sqrt{1 + 26.5\, \frac{P_{CO}}{P_{NO}^2} \log\, (I_o/I)_{min}}\right) \tag{24}$$

$$r_{N_2} = 4.78 \times 10^{-7}\, P_{NO}^2 \left(-1 + \sqrt{1 + 26.5\, \frac{P_{CO}}{P_{NO}^2} \log\, (I_o/I)_{min}}\right)^2 \tag{25}$$

The mechanism discussed above is based on the mononitrosyl surface complex (i.e. one chromium ion adsorbs one nitric oxide).

III. Conclusions

1. CO is adsorbed both reversibly and irreversibly on chromia-silica catalysts. The reversibly adsorbed CO gives rise to an IR band around 2200 cm^{-1}. The irreversibly adsorbed CO gives three IR bands at 1550 cm^{-1}, 1430 cm^{-1}, and 1365 cm^{-1}.
2. The IR band at 2184 cm^{-1} of the reversibly adsorbed CO is assigned to weak adsorption of CO on cr^{+3}.
3. The IR bands at 1550 cm^{-1} and 136 cm^{-1} of the irreversibly adsorbed CO are assigned to bidentate carbonate and the band at 1430 cm^{-1} is assigned to uncoordinated carbonate.
4. Nitric oxide interacts with oxidized chromia-silica surfaces giving IR bands at 1565 cm^{-1} and 1620 cm^{-1} at room temperature. The 1565 cm^{-1} band is ascribed to bidentate nitrato complex on the surface. The 1620 cm^{-1} band is ascribed to covalent nitrite.
5. Nitric oxide is chemisorbed on reduced surface giving IR bands at 1750 cm^{-1} and 1876 cm^{-1} at room temperature. The 1750 cm^{-1} and 1876 cm^{-1} are tentatively assigned to dinitrosyl adsorbed on surface chromium ion having an angle of ON-Cr-NO of 126°.
6. During the NO/CO reaction over chromia-silica catalysts, the surface is predominately covered by nitroc oxide. Chemisorbed carbonates are also observed. No IR bands associated with chemisorbed CO and N_2O are detected under reaction conditions.

7. The catalyst can be correlated with the band intensity at 1735 cm^{-1}. The rate of CO_2 formation can be expressed as:

$$r_{CO_2} = 1.25 \times 10^{-5} P_{CO} \log (I_o/I)_{min,1735\ cm^{-1}}$$

and the rates of N_2O and N_2 formation can be expressed as

$$r_{N_2O} = 9.55 \times 10^{-7} P_{NO}^2 \left(-1 + \sqrt{1 + 26.5 \times \frac{P_{CO}}{P_{NO}} \log (I_o/I)_{min,1735\ cm^{-1}}}\right)$$

$$r_{N_2} = 4.77 \times 10^{-7} P_{NO}^2 \left(-1 + \sqrt{1 + 26.5 \times \frac{P_{CO}}{P_{NO}} \log (I_o/I)_{min,1735\ cm^{-1}}}\right)^2$$

8. Under the reaction conditions, the chemisorbed NO gives rise to IR bands at 1735 cm^{-1}, 1795 cm^{-1}, 1846 cm^{-1}, and two shoulders at 1750 cm^{-1} and 1760 cm^{-1}. Two bands at 1735 cm^{-1} and 1795 cm^{-1} and two shoulders at 1750 cm^{-1} and 1860 cm^{-1} are ascribed to dinitrosyl adsorbed on two types of chromium sites. The 1735 cm^{-1} band and 1846 cm^{-1} are associated with the chromium sites having a high oxidation state. The shoulders at 1750 cm^{-1} and 1860 cm^{-1} are associated with the chromium sites having a low oxidation state. The weak band at 1795 cm^{-1} is ascribed to mononitrosyl adsorbed on chromium ion.

9. The surface chromium ions having a high oxidation state are the active sites for the reaction. The deactivation of the catalysts may include the reduction of the surface, formation of stable carbonates and adsorption of water on the active sites.

4. Proposed Research

It is recommended to

(1) Perform chemisorption of NO isotopes with IR. The frequency shifts due to the presence of isotopes can be used to discriminate between the assignments of the chemisorbed IR bands. If NO is adsorbed in the mononitrosyl structure both 1876 cm^{-1} and 1750 cm^{-1} bands become doublet after adsorption of 50% - 50% ^{15}NO - ^{14}NO mixture. If NO is adsorbed in the dinitrosyl structure, this two bands are expected to split into three bands after the adsorption of NO isotopes.

(2) Perform additional simultaneous spectral and reaction kinetics experiments at higher temperature such as above 350°C. This data can be used to test the validity of the deactivation mechanism by the formation of stable carbonates. At such high temperature, the carbonates are unstable. Their poisoning effects become insignificant to the reaction.

(3) Modify the existing cells so that the <u>in situ</u> pretreatment (at 500°C) can be performed. This can minimize the possibility of adsorption oxygen or water during the transportation.

(4) Obtain spectral isotherms of nitric oxide adsorbed on the catalysts for which the amount (weight) of adsorbed nitric oxide is determined. This can provide the necessary information for the calculation of absolute reaction rate constant of CO_2 formation.

(5) Perform additional simultaneous spectral and reaction kinetics experiments on previously carefully reduced samples (i.e. progressive reduction of the sample by CO or H_2 and evacuation at progressively higher temperature). This data can be used to discriminate the deactivation mechanisms between the change of the surface oxidation state and formation of stable carbonates.

(6) Study the NO/CO reaction over low chromium content catalysts. The data can be used to elucidate the role of the mononitrosyl complex (i.e. the 1795 cm^{-1} band). The intensity of this band has been reported to be dependent on the chromium contents. In the present study the 1795 cm^{-1} band is very weak (10% Cr). It is expected that the 1795 cm^{-1} will develop when low chromium content catalysts are applied.

(7) Systematically study the chemisorption of NO by the ESCA (Electron Spectroscopy for Chemical Analysis). The ESCA has a potential ability to identify Cr^{+3} and Cr^{+6}. The ESCA study is being used in the Purdue University Chemistry Department to study surface phenomena. The ESCA data may provide the absolute oxidation state of the two types of chromium site.

Hydrocarbon Synthesis Over Bimetallic Clusters

Hydrocarbon synthesis over bimetallic clusters: The wide range of products obtained over Ru catalysts as a function of H_2/CO feed ratio and the proven cluster formation in the Ru-Cu/SiO_2 system strongly suggest Ru catalysts as the starting point for development of multimetallic cluster catalysts for selective hydrocarbon synthesis. Initial catalyst preparations will include Ru, Ru/Cu- as a test case for which cluster formation is known, Ru/Fe- to emphasize synthesis and allow characterization by Mossbauer spectroscopy, Ru/Ir- to improve dispersion and accentuate olefin production, and Ru/Pd and Ru/Ni- to limit synthesis and accentuate methane formation. Both SiO_2 and Al_2O_3 will be used as supports to test the importance of support interactions. For initial experiments the Ru loading of the catalysts will be held at 1 wt % and the atom ratio of added metal varied. The recent work of Taylor shows that the intriguing differences in activity of the reduced and oxidized forms are most pronounced at metal loadings on alumina of less that 1 wt %. We will pursue the possibility of producing unusually active catalysts by special pretreatment and stabilizing them by adjustment of catalyst composition. Ru loadings as low as 0.1% will be used in this phase of the work if warranted. All catalysts will be characterized by selective chemisorption of H_2 and CO, ESCA, and Mossbauer spectroscopy where appropriate.

The detailed kinetics of the synthesis reaction will be studied with a Union Carbide gradientless reactor with mass spectral analysis and with a differential flow reactor with gas-chromatographic analysis. Reactions will be run at one atmosphere pressure with an H_2/CO ratio of 0.5 to 4 with Ar or He diluent added for partial pressure dependence studies. The temperature range will be 200-400°C with most work being done at 250°C. Special attention will be paid to detection of both ethane and ethylene to monitor olefin formation. Hydrocarbons with more than 5 carbon atoms will not be analyzed explicitly. Coupling between the catalyst characterization and the kinetic results will be made more specific by use of in situ IR during the synthesis reaction. These reactions will be run at 250°C and below in a specially constructed IR cell in which the IR wafer will act as the catalyst in a recirculating differential flow reactor with gas-chromatographic analysis. The cell and reactor system are already available and, as mentioned, have been used to advantage in the study of CO and NO reactions over supported chromia. In these experiments we will be looking for oxygenated hydrocarbon intermediates and evidence for growing hydrocarbon chains on the catalyst surface. Significant coking of the catalyst will be followed by ESCA as well as by IR. Coupled with the kinetic analysis, the IR results will be particularly important in identifying kinetically significant changes in surface chemistry and in guiding formulations of new catalyst materials.

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Characterization of Surface States by ESCA

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1. Objective

Our proposed research encompasses the continuing development of electron spectroscopy (ESCA) as a technique to determine surface chemical structure as it relates to heterogeneous catalytic and electrochemical reaction mechanisms. We are particularly concerned with the behavior of clean metal surfaces, prepared under ultra-high vacuum ($\sim 10^{-10}$ torr) conditions, after exposure to active gases (O_2, CO, NO, etc.). The major purpose of these experiments will be to characterize the oxidation state of all the stable surface species with a special emphasis on those possessing unusual oxidation states. With a backlog of information of this type we plan to compare these results to samples actually exposed to reaction conditions, be they catalysts or electrodes used in electrocatalytic processes. We feel very strongly that one of the primary advantages of the ESCA technique is that useable data can be obtained not only on "clean" systems prepared at 10^{-10} torr but also on "dirty" systems prepared under reaction conditions, such as the chromia/silica catalyst system. The possibility of "bridging the gap" between these two situations is most exciting to researchers in the catalysis field. Since these complex surfaces must determine the course of most heterogeneous reactions, the ability to characterize these species will have a tremendous impact in identifying the active molecules in many catalytic processes. In addition, the efficiency and reliability of battery power systems and fuel cells depend greatly on the materials character of the electrodes. The dynamic stability of these materials will clearly be related to the types of any unusual species which may form on the electrode surfaces.

2. Background and Technical Need

The proposed plan of research encompasses the development of the ESCA technique to determine heterogeneous catalytic and electrochemical reaction mechanisms. The first phase of the work has been concerned with the interaction of clean metal surfaces with gases and metals using samples prepared under ultra high vacuum ($\sim 10^{-10}$ torr) conditions. The major purpose of these experiments has been to characterize all the stable surface species with particular emphasis on those possessing unusual oxidation states. These studies will now be applied to the characterization of samples more directly related to the actual environment of the catalyst or the electrode. This second phase includes the correlation of the steady state surface behavior as observed by XPS with any catalytic activity. In addition, we plan to study reactions of unusual importance to fuel cell technology and to fundamental corrosion mechanisms. Emphasis will be placed on systems which affect the electrode surface, such as oxidation and adsorption processes, so that the chemical structure of products can be determined.

Paralleling these studies will be an attempt to correlate the changes in metal core binding energies with change in oxidation state for derivatives of certain key metals which show catalytic activity. Included in our studies will be derivatives of rhodium, rhenium, ruthenium and molybdenum, all of which find use as important components for certain heterogeneous catalysts. In these instances, these species will not be generated <u>in situ</u> but rather will be synthesized outside of the spectrometer and then subjected to ESCA studies. The object here is to generate species of known stoichiometry and molecular structure in order to make a detailed correlation of metal core electron binding energies with structure. This will be of help in our identification of species which are subsequently generated <u>in situ</u> during catalysis.

All ESCA measurements will be made on an existing Hewlett-Packard 5950A Spectrometer. This instrument utilizes monochromatic Al K_α X-ray obtained from a quartz crystal disperser as well as a multi-element detection scheme. The enhanced resolution and sensitivity of this configuration is vital for interpretation of complex spectra which have overlapping bands. For example, the Au $4f_{7/2}$ peak on this instrument has a F.W.H.M. of about 0.8 eV. Without the crystal disperser, as is the case with all other commercial instruments, this value rises to ~1.2 eV. Since chemical shifts on the order of 0.5 eV need to be discerned on peaks which are overlapping, the use of the Hewlett-Packard system is absolutely essential to perform these experiments.

The x-ray generator and electron analyzer are isolated from a sample treatment chamber by a high vacuum gate valve. This chamber is then pumped separately with two 30 l/sec noble ion pumps and a 350 l/sec titanium sublimator pump. The sample itself is placed on a probe which can be pushed through a set of sliding teflon seals into this chamber and into the analyzer for special analysis. The sample chamber is equipped with a cross-probe for <u>in situ</u> evaporation, a leak valve for introducing needed gases as well as an argon ion gun. The temperature of the sample can be set from -180°C to 350°C, as indicated by a platinum resistance thermometer, by heating a filament implanted underneath the sample or by passing cooled N_2 gas through the sample probe tip.[1]

We have added several important additions to this system to expand its versatility for surface studies. First, although the system is essentially compatible for ultra high vacuum, the sliding seal arrangement for the sample probe is not satisfactory. An external chamber was built around the sample inlet with a controlled atmosphere of pure argon. This procedure allows direct transfer of samples from this "dry box" into the instrument without exposure to air or water. To attain pressures of 10^{-10} torr, a bake out oven was built around the instrument and it could be heated to 150°C for removal of residual water. A residual gas analyzer has been installed and is able to monitor the residual gas level.[2]

Three types of sample treatments are available using the above scheme:

(1) "Clean" surfaces can be exposed to low levels of background gases (to 5×10^{-6} torr) during x-ray analysis. This procedure is particularly useful for observing the initial stages of surface coverage.[3,4]

(2) Samples can be extensively exposed to higher pressures in the treatment chamber (up to atmospheric pressure) but the gas must be removed during spectral analysis.

(3) Gross perturbations, such as electrochemical or catalytic reactions, can be carried out in the external dry box sample chamber although the spectra must be recorded in vacuo.[5]

3. Accomplishments

The major thrust of this research has been to identify the presence of various oxidation states on metal and metal oxide surfaces. We have proceeded to characterize these systems by first beginning with the evaporated metal films.[4,5,6] After exposure to various active gases, the formation of surface compounds is then observed by following the chemical shift of the core photoelectron lines. During these studies we have made the important discovery that predictable chemical changes can be induced by bombardment with high energy (~ 1 keV) inert gas ions.[2] The procedure is being developed as a surface analysis method and as a technique for generating unusual surfaces. In order to fully identify catalytically active species which may be generated in the course of a reaction, it is essential to be able to eliminate the possibility that (a) binding energy shifts could be arising from undesired surface charging effects and (b) that peak shapes may be affected by so-called "multiplet splittings." Accordingly work was carried out to understand as fully as possible these two phenomena as they relate to our catalytic studies. With these model systems beginning to be understood, a number of studies on real catalysts, most notably chromia, have been commenced with the objective of correlating the actual species present on the surface with their observed catalytic activity. Other applications of this approach to surface analysis have been demonstrated by characterization of oxides on anodized electrodes. Specific details of our accomplishments are now presented in more detail:

(1) The nickel-oxygen system: An extensive study has been completed by exposing evaporated Ni films to various concentrations of oxygen at various

temperatures.[1] The spectra of metallic Ni, NiO and Ni_2O_3 were characterized from samples prepared directly in the spectrometer. The Ni_2O_3 species, a cation defect structure of NiO, could be distinguished from an authentic $Ni(OH)_2$ from both the XPS lines and the Auger transitions. The Ni_2O_3 was found to be present on most nickel-oxygen surfaces except those prepared by exposing Ni to air for many hours at high temperature (> 600°C), indicating that the stability of Ni_2O_3 decreased as the temperature increased. Our results present the first direct spectroscopic evidence for Ni_2O_3 and point to some significant consequences to catalytic studies. For example, we have found that CO adsorbs more readily on an Ni_2O_3-rich surface than on an NiO-rich surface.

(2) Ion-bombardment of metal-oxygen surfaces: Bombardment of surfaces with inert gas ions has long been recognized as a method for cleaning surfaces via sputtering of surface impurities. Since XPS measurements give chemical surface information, added impetus is given to developing these methods in profiling oxidation states and in preparing well-characterized surfaces.

We have completed several initial experiments related to these objectives using a rather crude ion gun without mass filtering and limited in its energy range.[1,2] The first series of experiments involve ion bombardment with a $10 \mu amp/cm^2$ flux of 400 eV Ar^+ ions onto a series of pure metal-oxides either prepared as powders or by oxidizing the corresponding metal in air at high temperature. After examining nearly 50 oxides, we find that many systems show reduction from a higher oxide to the metal or to a lower oxide due to a preferential loss of oxygen. We have found, without exception, that a correlation exists between the propensity of the oxide to lose oxygen and its room temperature ΔG_f^o value. All oxides with $-\Delta G_f^o$ below 120 kcal/mole were reduced by exposure to Ar^+ ions while those with $-\Delta G_f^o$ above 120 kcal/mole were stable to this exposure. In the case where higher oxides are found to be reduced, the reaction proceeds through a stable intermediate oxide. For example, with the tungsten-oxygen system, WO_3 can be reduced to the metal via WO_2 as follows:

$$WO_3 \longrightarrow WO_2 + \tfrac{1}{2}O_2 \qquad \Delta G^o = 64 \text{ kcal/mole} \qquad (1)$$

and

$$WO_2 \longrightarrow W + O_2 \qquad \Delta G^o = 118 \text{ kcal/mole} \qquad (2)$$

Other systems including PbO_2, MoO_3, and Fe_2O_3 behave similarly. On the other hand, oxides like Ta_2O_5, Al_2O_3, and SiO_2 have no stable intermediate form and are thus stable to reduction by ion bombardment.

The fact that radiation of this sort directed onto a solid surface can alter the composition presents an intriguing prospect for preparation of possibly unusual materials. Additional work supports this contention. We have found that in the Mo-oxygen system, for example, MoO_3 is reduced to MoO_2 after Ar^+ bombardment although a large concentration of a defect MoO_x structure, where $2 < x < 3$ can be seen with ESCA at intermediate Ar^+ dose levels.[2] A further example, is the production of Ni_2O_3 on NiO by O_2^+ bombardment, suggesting a new synthetic method for preparing catalytically active surfaces.

(3) Chemical shifts due to matrix effects: Several initial studies have been completed which indicate the environment of support metals can effect the measured binding energy.[7] We have prepared a number of "ion-implanted" systems by "knocking" surface atoms into metal and metal-oxide matrices using Ar^+ ion bombardment. Core level binding energies of Au in SiO_2, Pt in graphite, Au in Ag, and Ag in Au prepared in this manner have been measured and compared to values for the bulk species. Their shifts, referenced to the Fermi level, are interpreted to consist of a matrix shift resulting from differences in crystal field potential, relaxation energy and work function as well as a chemical shift due to difference in valence electron density. By estimating the matrix shift using implanted Ar in the related pure materials we can isolate

the chemical shift from the observed binding energy shift. In all cases studied, the matrix shift is greater than the chemical shift and its contribution to the binding energy shift is in the opposite direction. For example, the measured 4f binding energy shift for Au in SiO_2 versus pure Au is +1.1 eV but the matrix shift, estimated from implanting Ar in Au and SiO_2, is -1.4 eV giving a net chemical shift of -0.3 eV. This result suggests the implanted gold species really looks more like atomic Ar rather than a higher oxidation state of Au which one might infer without taking into account the matrix terms. Similar results are observed for Pt in graphite. In this case the Pt $4f_{7/2}$ value is shifted to higher binding energies almost continuously as the bombardment time increases, suggesting a large variation in possible configurations of Pt atoms as the concentration of Pt decreases below the monolayer coverage range. One may speculate, in fact, that as the size of the Pt cluster in the surface region decreases to some critical value, the number of electrons available to the conduction band is limited and the relazation energy due to polarization of the final hole state decreases. Alterations in the d-band structure of atomically dispersed Ag on graphite support this claim and indicate that the approach may be available in estimating the particle size of these small metal clusters.[8] We are presently undertaking similar studies on the valence level spectra of Hg and Au implanted in SiO_2 in order to determine the influence of the matrix on the metal atom electronic structure.

(4) Identification and interpretation of the origin of shake-up phenomena in $3d^0$ systems: In order to definitively identify the metal oxidation states which are present on a metal oxide surface, it is essential to distinguish peaks due to different metal oxidation states from those due to such phenomena as "shake-up".[9,10] For the first

transition series such satellites, within 12 eV of the metal 2p binding energies, have usually been attributed to 3d → 4s transitions accompanying the primary photoionization.[11,12] Support for this assignment comes from the observation that apparently neither d^{10} systems, such as ZnF_2 and CuCl, [11,12] nor d^0 systems, such as TiO_2 or V_2O_5,[11] exhibit satellites in this same energy range. It was also indicated in the paper by Rosencwaig,[11] that scandium (III) has no such satellites, although it was not made clear whether a specific scandium (III) compound was in fact studied. In our studies, we found that satellites are located in this energy region for Sc_2O_3 and $Sc_2(C_2O_4)\cdot 6H_2O$, so that a partially occupied 3d shell not necessarily be a prerequisite for satellite formation. Our results suggested that an investigation of other d^0 systems would be desirable, and in particular, a careful reexamination should be made for satellite peaks in the spectra of such d^0 systems as TiO_2 and $SrTiO_3$, These investigations have been carried out and related satellite peaks observed. For d^0 systems, these satellites cannot arise from 3d → 4s transitions, so that an alternative assignment is clearly required. Since 3p → 4s excitation is not feasible, the most attractive possibility is in terms of a monopole charge transfer transition (ligand → metal 3d), an assignment which was originally proposed by Kim,[9] as an alternative to 3d → 4s excitation, for the 5 - 10 eV satellites in the 2p electron spectra of the 3d transition metal ions. We can exclude the possibility that these peaks are due to energy-loss phenomena.

(5) Chromia/silica Catalysts. - ESCA studies on the chromia/silica (Cab-O-Sil) catalyst have been carried out in order to determine the chemical species present on the surface of the catalyst during its reaction with gaseous non-metal oxides - specifically CO and NO. We have planned to monitor the catalyst throughout the following stages: (a) preparation; (b) calcination; (c) reaction. The catalysts have been studied in the form of pressed discs, containing between 5 and 15% chromium. At the present time we have finished our studies of the catalyst at the calcination step. Measurement of Cr 2p, Si 2p and O 1s binding energies show that over the temperature range 300 to 600°C there is a change in chromium oxidation stage from Cr(VI) below 400°C to Cr(III) almost exclusively above 500°C. At 500°C we have evidence for a very rapid and dramatic change in the dispersion of the chromium, the concentration at the surface being at a maximum at this point. At ca 515°C this change is reversed and the ESCA becomes identical to those exhibited by samples calcinated just below 500°C.[13]

Work is currently in progress on studying the changes which occur upon reacting CO, NO and CO-NO mixtures with these catalysts. A sample calcinated at

300°C and exposed to CO for 4 hrs. showed different changes from the non-calcinated catalyst. The Cr 2p peaks were narrower and shifted to a slightly lower binding energies compared to the calcinated only sample. The O 1s peak was not only shifted to a lower binding energy but now appears as a doublet. The Si concentration at the surface was considerably reduced. Also, in all cases, very little CO concentration was detected on the surface.

Remaining work will include similar treatments of the samples calcinated at 400°C, 500°C, and 550°C.

(6) Heavy Transition Metal Catalysts. - Paralleling the studies described in section (a), we have attempted to correlate the changes in metal core binding energies with change in oxidation state for derivatives of certain key metals which show catalytic activity. During the past year we have concentrated our attention upon derivatives of rhenium, an element which finds use as an important component of certain heterogeneous catalysts. In these studies the derivatives have not been generated *in situ* but rather have been synthesized outside of the spectrometer and then subjected to ESCA studies. The object here is to generate species of known stoichiometry and molecular structure in order to make a detailed correlation of metal core electron binding energies with structure. This will be of help in our identification of species which are subsequently generated *in situ* during catalysis.

Studies previously carried out in these laboratories on the oxidation states of rhenium[14,15] showed that while there is little difference between the 4f binding energies of Re^{2+}, Re^{3+}, Re^{4+} and Re^{5+}, the highest oxidation state Re^{7+} exhibits related binding energies which are ~2eV higher than those of the former group. The magnitude of this shift for Re^{7+} is such that the interconversion between Re^{5+} and Re^{7+}, for example, can be readily followed by ESCA and this may prove to be of use in establishing the mechanism of certain rhenium catalysts.

In making comparisons of core electron binding energies between transition metal complexes in different oxidation states, account must be taken of changes in coordination number and structure type. Since it is often impossible to keep these features unchanged as the metal oxidation state is varied, a meaningful interpretation of metal core binding energy shifts can become rather difficult. In our studies of the X-ray photoelectron spectra of complexes of the heavy transition elements such considerations are particularly important since charge variations occur at rather large metal centers and consequently binding energy shifts are proportionately smaller than those observed for the lighter elements.

We have recently synthesized and structurally characterized[16,17] a series of dinuclear tertiary phosphine complexes of rhenium of stoichiometry $Re_2X_5(PR_3)_3$ and $Re_2X_4(PR_3)_4$ (X = Cl or Br) which have closely related structures to the rhenium(III) dimers of the type $Re_2X_6(PR_3)_2$. We have investigated the ESCA of these complexes and have discovered some striking differences in rhenium binding energies.[18]

The rhenium $4f_{7/2}$ binding energies occur in the range 40.9 to 42.7eV and reveal a clear dependence upon the <u>formal</u> metal oxidation state: 40.9-41.2eV for Re(+2); 41.5-41.8eV for Re(+2.5); 42.2-42.7eV for Re(+3). The magnitudes of these energies shifts are significantly greater than those observed in our earlier studies on rhenium complexes.[14,15] This we attribute to the structural similarity within the present series of complexes, wherein the replacement of halide by tertiary phosphine ligands occurs in a systematic and regular fashion.

The FWHM values for the rhenium 4f binding energies of the paramagnetic complexes $Re_2X_5(PR_3)_3$ are greater than comparable data for diamagnetic $Re_2X_6(PR_3)_2$ and $Re_2X_4(PR_3)_4$. The obvious explanation for this broadening effect is either that it reflects the occurrence of 'multiplet splittings', or that it arises from the presence of two dissimilar rhenium environments within these dinuclear species.

We favor the latter explanation since no such broadening effects arising from 'multiplet splittings' are observed with the paramagnetic complexes $ReCl_4(PPh_3)_2$ and K_2ReX_6.

In explaining the rhenium 4f binding energy chemical shifts within the series $Re_2X_{6-n}(PR_3)_{2+n}$, it is tempting to conclude that the variation in binding energies is simply a reflection of differences in the initial state charge distributions, with the order being $Re_2X_6(PR_3)_2 > Re_2X_5(PR_3)_3 > Re_2X_4(PR_3)_4$. While this may be true it is also quite likely that final state relaxation effects enhance this trend. Although the treatment of relaxation effects is much more complicated for the condensed than the gaseous phase, it is perhaps reasonable (to a first approximation) if we ignore secondary intermolecular interactions for the series of insulators $Re_2X_{6-n}(PR_3)_{n+2}$. Certainly, crystallographic data for $Re_2Cl_6(PEt_3)_2$ and Re_2Cl_4-$(PEt_3)_4$ supports such a premise. In studies by Martin and Shirley[19] on the binding energy shifts in simple aliphatic alcohols, it was found that the relaxation energy (E_R) increased with the molecular size of a substituent group, thereby resulting in a decrease in observed binding energy at the oxygen atom. Applying such an argument to $Re_2X_{6-n}(PR_3)_{n+2}$ would imply that as the halide ligands are progressively replaced by the larger tertiary phosphines the relaxation energy should increase, since the latter ligands are more able to effectively distribute excess positive charge. In other words, both differences in initial state charge distributions and final state relaxation effects probably contribute (in the same sense) to the observed rhenium 4f binding energy shifts. At the present time it is clearly impossible to unravel the relative magnitudes of these different contributions to the overall binding energy shifts for these particular complexes.

We have just developed a new and convenient procedure for the synthesis of unknown metal halide phases β-MoX_2 (X = Cl or Br) by reaction of the solid metal acetates with the gaseous hydrogen halides.[20] These materials are structurally different from the α-phases which possess the Mo_6X_{12} cluster structure. Since these species are likely to have activity as heterogeneous catalysts, we hope to develop a procedure for synthesizing them on alumina and silica supports. ESCA studies will be applied to the characterization of these new materials and their reactions with small molecules such as CO, NO and N_2 will be investigated.

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Electrode Reaction Studies: Role of Surface Oxides on Cathode Surface of Hydrogen-Oxygen Fuel Cell

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Objectives:

The main objective of this investigation has been to clarify the phenomena that occur on the surface of the cathode used in a hydrogen-oxygen fuel cell in which dilute solutions of KOH are used as the electrolyte. Previous Purdue investigations (1-5) have indicated that adsorption of oxygen on the platinum cathode (or actually the formation of platinum oxides) was occurring at least when the cathode was rested, at which time the platinum cathode was allowed to equilibriate with an oxygen atmosphere or with an oxygen-saturated electrolyte. At start-up when the circuit is closed (allowing the cell to start generating electricity), large currents result for the first 20-60 seconds. These high initial currents are caused in part by the high concentrations of oxygen on or in the boundary layer of the electrolyte surrounding the portion of the cathode submerged in the electrolyte. One of the purposes of the present project was to clarify the manner in which oxygen is adsorbed or reacted on the platinum cathode.

Experimental Approach Used:

In the fuel cell being used, flat-plate-type cathodeswere used. These cathodes can be partially or completely immersed in the electrolyte. By changing the height of the cathode, the submerged area can be varied. In such a cell, the current densities in the portion of the cathode near the meniscus (close to where there is a triple interface of electrolyte solution, oxygen gas, and platinum cathode) are much greater than in the portions of the cathode that are submerged. A reference electrode is used so the polarization of the cathode can be measured (and changed if desired by suitable equipment) as the cell is used. The anode used was also constructed of platinum. In the present investigation, special attention was given to the regions of the cathode close to the meniscus.

Earlier Purdue investigators (3,5) in their studies of current surges at start-up had in all cases emphasized those portions of the cathode that were submerged in the electrolyte. Essentially no attention was given to the phenomena or type of currents obtained in the regions of the cathode (or anode) close to the meniscus. The earlier investigators found that the current in the submerged portion of the cathode was essentially controlled by transfer and/or diffusion of the oxygen through (or in) the electrolyte. One would postulate that in the meniscus region that oxygen transfer would be less controlling whereas surface electrochemical reactions would be more controlling.

Results:

Key findings made in the last six months are as follows:

1) Start-up currents for the meniscus do begin at fairly high values and do decrease to steady-state values after 20-30 seconds. These results indicate that adsorption of oxygen in this portion of the cathode and of oxygen adsorption in the meniscus are factors of importance.

2) Start-up and steady-state results are both affected by the concentration of the KOH electrolyte solution in the 0.5-5.0N range. The results are hard to interpret in detail because each of the following change as the concentration of the electrolyte is changed.

(a) Solubility of oxygen in electrolyte is changed.

(b) Viscosity of electrolyte. At steady-state operation, convection currents (resulting from minute thermal gradients, vibrations in laboratory, etc.) become important and viscosity of course affects the degree of convection obtained.

(c) Surface tension of the electrolyte that affects the shape of the meniscus.

(d) The concentration of hydroxyl ions (that are transferred between the electrodes of the fuel cell).

It is thought that each of the above has a significant effect on the currents produced.

3) ESCA analysis of platinum cathodes seems to indicate that significant differences occur as the cathode is rested and as the cathode is used during start-up (as steady-state operation is approached). Only preliminary results have been obtained to date, but the location of the platinum oxide peaks has apparently shifted indicating differences in the strength of the Pt-0 bonds formed. The approximate amount of adsorbed (or reacted) oxygen on the surface may however not change.

<u>Future Plans</u>:

The results to date have been very encouraging, and considerable more attention needs to be given to ESCA analysis of the platinum cathodes. Additional analyses will be made of cathodes in order to clarify how the surface oxides change with time of operation of the cathode, and with the location of the site on the cathode relative to the meniscus.

Additional data need to be obtained to clarify further the complicated relationship between the several factors that control the levels of currents generated; these factors include the resistances to transfer of oxygen to the cathode, transfer of hydroxyl radical, other transfer steps, etc. and of the resistances to the surface electrochemical steps. The ESCA results should prove most helpful in clarifying the electrochemical reactions.

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