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CATALYTIC PROPERTIES OF SURFACES
SITES ON METAL OXIDES AND THEIR
CHARACTERIZATION BY X-RAY PHOTO-
ELECTRON SPECTROSCOPY

R. G. Squires, et al

Purdue Research Foundation

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Metal Oxides and Their Characterization
by X-Ray Photoelectron Spectroscopy

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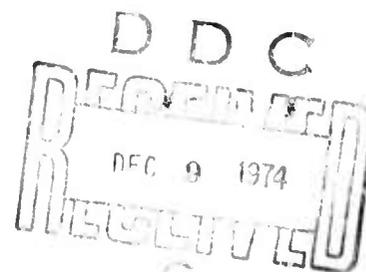
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Catalytic Properties of Surface Sites on Metals
and Metal Oxides and Their Characterization
by X-Ray Photoelectron Spectroscopy

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.

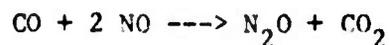
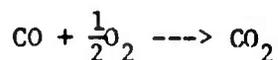
In the course of development of concepts and methodology for characterizing catalysts and understanding the chemical origin of catalytic activity, we plan to expand the scope of our research to include investigation of the catalysis by metals. A new research area for the next year will be the study of selective hydrocarbon synthesis from CO and H₂ 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 oxidation of carbon monoxide and reduction of oxides of nitrogen over chromia catalysts supported on silica is currently under study. One might expect that if two otherwise identical catalysts were prepared with varied dispersions (chromium content being the same), that the reactivity would be different since the active sites, i.e. various stable surface oxidation states, may differ both in number and type. To test this simple hypothesis, a series of catalysts were prepared; series A by chromic acid impregnation and series B by chromium nitrate-oxalic acid complexing. Two series of catalysts with varied amounts of chromium were prepared to insure the existence of a region where the % Cr of both samples overlapped and where the catalyst activity as a function of % Cr could be examined.

The reactions



were studied in the temperature range 160° to 260°C with partial pressure of reactants of approximately $P_{\text{CO}} = .30$ atm and $P_{\text{O}_2} = P_{\text{NO}} = .15$ atm.

The mean average oxidation state was found to be higher after the CO/O₂ or CO/O₂/NO reaction than after the CO/NO reaction. For nearly all catalysts the CO/NO reaction rate was much greater than the corresponding CO/O₂ reaction rate. During the oxidation of CO in the simultaneous presence of O₂ and NO, the NO did not participate in the reaction until nearly all of the O₂ was depleted, and the oxidation state was about the same as when oxygen was the only oxidizing gas. These results verify the findings of Shelef² whose work was on a chromia alumina sample with 10% Cr. No deviations from the above behavior were perceived for any of the catalysts tested; the total selectivity for oxygen was not altered.

The different methods of catalyst impregnation significantly altered both the dispersion of the chromium oxide on silica and the stabilized surface oxidation states following reaction. The oxidation state results correlated well with x-ray photoelectron spectra.

A definite correlation was found between the stabilized surface valency and the relative reaction rate. A lower valency favors a higher rate of conversion of CO by either O₂ or NO.

The relationship between the specific rate of conversion of CO by O_2 (moles/min g Cr) and the % Cr loading was not found to be a monotonic function. The specific rate was high at very low chromium concentration, dropped to a low value, and then increased again as the chromium loading approached 10 weight per cent. There may be a local maximum in rate at about 2-3% Cr. Although similar results have been reported for other systems, this behavior has never been reported for CO oxidation over a chromia-silica catalyst.

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 indicate 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-O₂ 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, $\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$, important in upgrading synthetic natural gas produced from coal, is now underway on ruthenium catalysts. Ruthenium is intriguing because in excess H₂ it has a high specific activity for CH₄ 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.

E. Special Comments

Dr. W. N. Delgass has recently joined the faculty of the School of Chemical Engineering. Dr. Delgass has made significant contributions in the application of ESCA and Mössbauer spectroscopy to catalytic surfaces. His continued research in these areas will be included in the future work of this project.

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I. Introduction

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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 H₂ 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

R. G. Squires
School of Chemical Engineering

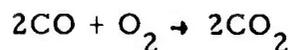
W. N. Delgass
School of Chemical Engineering

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:



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

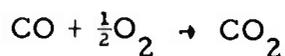
(1) CO and NO reactions on chromia supported on silica: Supported metal and metal oxide catalysts have found wide acceptance in the chemical and petroleum industries. It is not surprising, then, that a great deal of fundamental

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 oxide². 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.

Shelef² 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:



When CO was oxidized in the simultaneous presence of O₂ and NO, very little reduction of NO was found until nearly all of the O₂ 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 covering the physico-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.

(2) Hydrocarbon synthesis over bimetallic clusters: Recent concern over the energy supply has its origin in the relatively sudden realization that the exponentially growing demand for energy is threatening to diverge rapidly from projected supplies. The U.S. Bureau of Mines anticipates that energy demand will double over the next 15 years and triple by the end of the century⁷. While there is great discussion as to precise numbers, it seems generally agreed that oil and gas reserves will dwindle before a new source of energy such as nuclear or solar power can be fully developed and that the resource best suited to fill the energy demand-supply gap is coal, which is abundant within the borders of the U.S.⁸ As pipeline gas now supplies one third of our national energy needs and its use is the fastest growing of all fossil fuels⁹, conversion of coal to substitute natural gas is clearly a problem of immediate national importance. In the longer view, it seems likely that coal will eventually be considered a resource too valuable to be burned, since it can also be converted to feedstocks for the petrochemical industry and thus provide raw material for a variety of chemical products. Since gasification of coal produces a product rich in CO, adjustment of the H₂/CO ratio by the water-gas shift reaction:



can be followed by Fischer-Tropsch synthesis¹⁰ to produce a variety of hydrocarbons by a catalyzed reaction of H₂ and CO.

Recent application of modern catalytic methods to hydrocarbon synthesis have produced surprising results. Vannice has found that the relative methanation activity per surface metal atom for group VIII metals is significantly different than previously accepted¹¹. Differences between these steady state results and the initial rates reported by Dalla Betta¹² using a recirculating batch reactor suggest the importance of careful characterization of the surface and adsorbed species at reaction conditions.

An intriguing aspect of hydrocarbon synthesis from H₂ and CO is the wide range of product distributions obtained over the different group VIII metals. At high H₂/CO ratios Ru is highly selective for methane while at low H₂/CO ratios, it yields high molecular weight waxes¹³. Pd, though relatively low in activity, has high selectivity for methane, while of the group VIII metals Co, Ir and Ru give the highest initial rates for ethylene formation¹¹.

The possibility of catalytically selecting specific synthesis products from the wide range possible is offered by use of multimetallic cluster catalysts, an exciting new development in catalyst research pioneered by J. H. Sinfelt at the Exxon Research and Engineering Company. A commercial catalyst, KX 130, based on this concept, has been recently recognized as an outstanding achievement¹⁴. The general approach, which seems destined for wide spread application, is illustrated in reference 15. In that paper, Sinfelt shows that when Cu is added (up to $\frac{\text{Cu}}{\text{Ru}} = 1$) to 1% Ru or Os supported on SiO₂, the specific activity for ethane hydrogenolysis drops by three orders of magnitude while the specific activity for cyclohexane dehydrogenation remains essentially unchanged. The drastic change in relative activity for the two reactions caused by addition of the second metal suggests that a new degree of selectivity can be built into catalysts by this approach. It also seems clear from the magnitude of the effect seen that the Ru and Cu must have been in intimate contact in spite of the fact that Ru and Cu were present on the SiO₂ in submonolayer quantities and the fact that the bulk phase diagram shows Ru and Cu to be completely immiscible. The latter observation has prompted the term "multimetallic cluster" rather than supported alloy and has been explained on surface

thermodynamic grounds in recent papers^{16, 17}. While the chemical reaction shows the result of the Cu-Ru contact, direct observation of metal-metal contact and detailed chemical investigation of the new material formed has been possible only when one of the metals was iron and the Mössbauer effect could be used for characterization^{18, 19}.

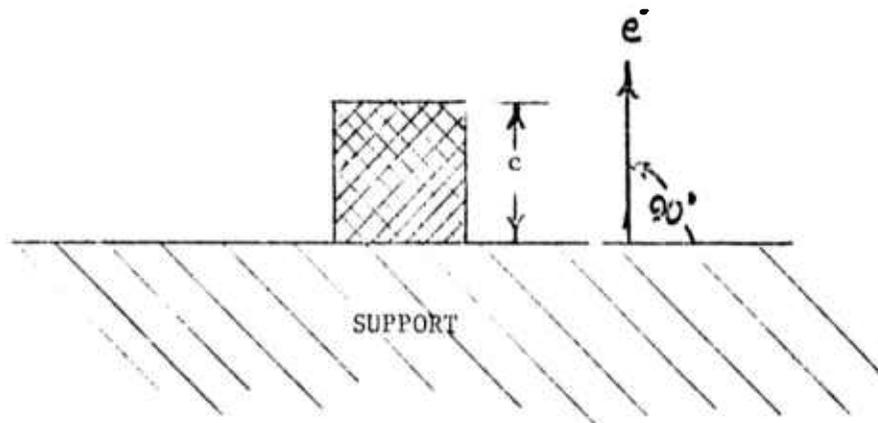
In order to fully investigate the possibility of using multimetallic cluster catalysts for selective hydrocarbon synthesis, it will be necessary to carefully characterize the materials prepared. While the full compliment of experimental techniques available in our laboratories will be used for this purpose, special emphasis will be placed on examination of cluster formation and metal oxidation/reduction chemistry by ESCA and in situ observation of adsorbed species by infrared spectroscopy.

The use of infrared spectroscopy for the study of adsorbed species is a well recognized technique in catalysis^{20, 21} and has been applied previously to reaction of CO and H₂. Eischens found no evidence for C-OH groups on a silica supported iron surface at room temperature²¹. The room temperature result was confirmed by Blyholder and Neff²², but they found evidence for C-OH groups at 180°C. Adsorption of alcohols on Fe particles in an oil film led to surface alcoxides²³. On nickel, however, no C-OH groups were seen even at 180°C²⁴ and adsorbed alcohols decomposed to give adsorbed CO²⁵. Generalization from these experiments alone is not possible, but they support the feasibility of IR studies of hydrocarbon synthesis intermediates as a function of catalyst and reactant composition.

The general feasibility of catalyst characterization by ESCA has been shown in previous work on this project. Quantitative studies of supported catalysts has also been initiated²⁶ and a summary of results and the potential for study of supported multimetallic cluster catalysts is presented here.

In order to examine the quantitative information in XPS intensity ratios from supported catalyst surfaces, a model for the catalyst structure must be assumed. Initially, the simplest possible model has been used. As shown in Figure 1 the support is taken to be planar, the active material (metal,

MODEL



$$f = \text{fraction of surface area covered by metal} = \frac{w}{c\rho_m A_s}$$

where $w = \text{wt \% metal}$

$\rho_m = \text{metal density}$

$A_s = \text{surface area of support}$

Figure 1

metal oxide, etc.) is assumed to be present on the support in the form of cubes of edge length c . It is further assumed that electrons are emitted at an angle of 90° from the surface plane. An important variable in analysis of this problem is the fraction of support surface area covered by the active species, let's say a metal. This variable, labeled f , determines how much metal is visible on the area of the support projected onto the spectrometer slit system and also controls how much the metal will attenuate the support photoelectron intensity. A simple expression for the ratio of metal intensity to support intensity, I_m/I_s , is given on the top of Figure 2. It includes self-attenuation of metal electrons and shading of support electrons by the metal particles.

As expected, in the limit of monatomic dispersion and low loading, I_m/I_s is proportional to N_m/A_s , the metal loading. It should be noted from equation (2) that the proportionality factor includes the metal-support element cross section ratio, the number density of the support element studied and the inelastic mean free path for support element electrons in the support material. The validity of this expression is demonstrated in Figure 3, showing I_{Na}/I_{Al} versus loading for Na^+ deposited on alumina by impregnation with aqueous $NaOH$. The linearity of this deposition process is supported by the proportionality of CO_2 uptake to Na loading shown in Figure 4. At the high temperature of the adsorption, the uptake of CO_2 molecules per Na atom is less than unity. Nevertheless, the linearity of Figures 3 and 4 is taken as support for the intensity analysis at low loading and high dispersion.

The analysis has been tested further with the Eu/Al_2O_3 system, Figure 5. The filled circles are for Eu on American Cyanamid PHF alumina. In the low coverage region the plot is linear as expected for monatomic dispersion. At the highest coverage, where some agglomeration of the Eu -containing phase must occur since the coverage exceeds an effective monolayer, the point falls off the linear correlation. Analyzing this point by equation (1) gives a particle size for the Eu phase of the order of 10 \AA . The triangles on Figure 5 are for Eu on Harshaw alumina. The low loading sample falls on the linear correlation.

$$\frac{I_m}{I_s} = \frac{I_m^\infty f [1 - \exp(-c/\lambda_m(E_m))]}{I_s^\infty [1 - f(1 - \exp(-c/\lambda_m(E_s)))]} \quad (1)$$

for Na/Al₂O₃

$$c \ll \lambda \quad f \ll 1$$

$$\frac{I_{\text{Na}(1s)}}{I_{\text{Al}(2p)}} = \left(\frac{\sigma_{\text{Na}(1s)}}{\sigma_{\text{Al}(2p)} n_{\text{Al}} \lambda_{\text{Al}_2\text{O}_3}(E_{\text{Al}})} \right) \left(\frac{N_{\text{Na}}}{A_s} \right) \quad (2)$$

- $I_{m,s}^\infty$ = Intensity from an infinitely thick sample of m or s
- $\lambda_x(E_y)$ = Mean free path for inelastic scattering of an electron with energy E_y in material x
- σ = Effective cross-section for production of electrons that will reach the spectrometer detector
- n = Number density of element in support chosen for reference
- N_m = Number of metal atoms per gram of catalysis
- A_s = Support surface area per gram of catalyst assumed equal to BET area per gram of catalyst

Figure 2

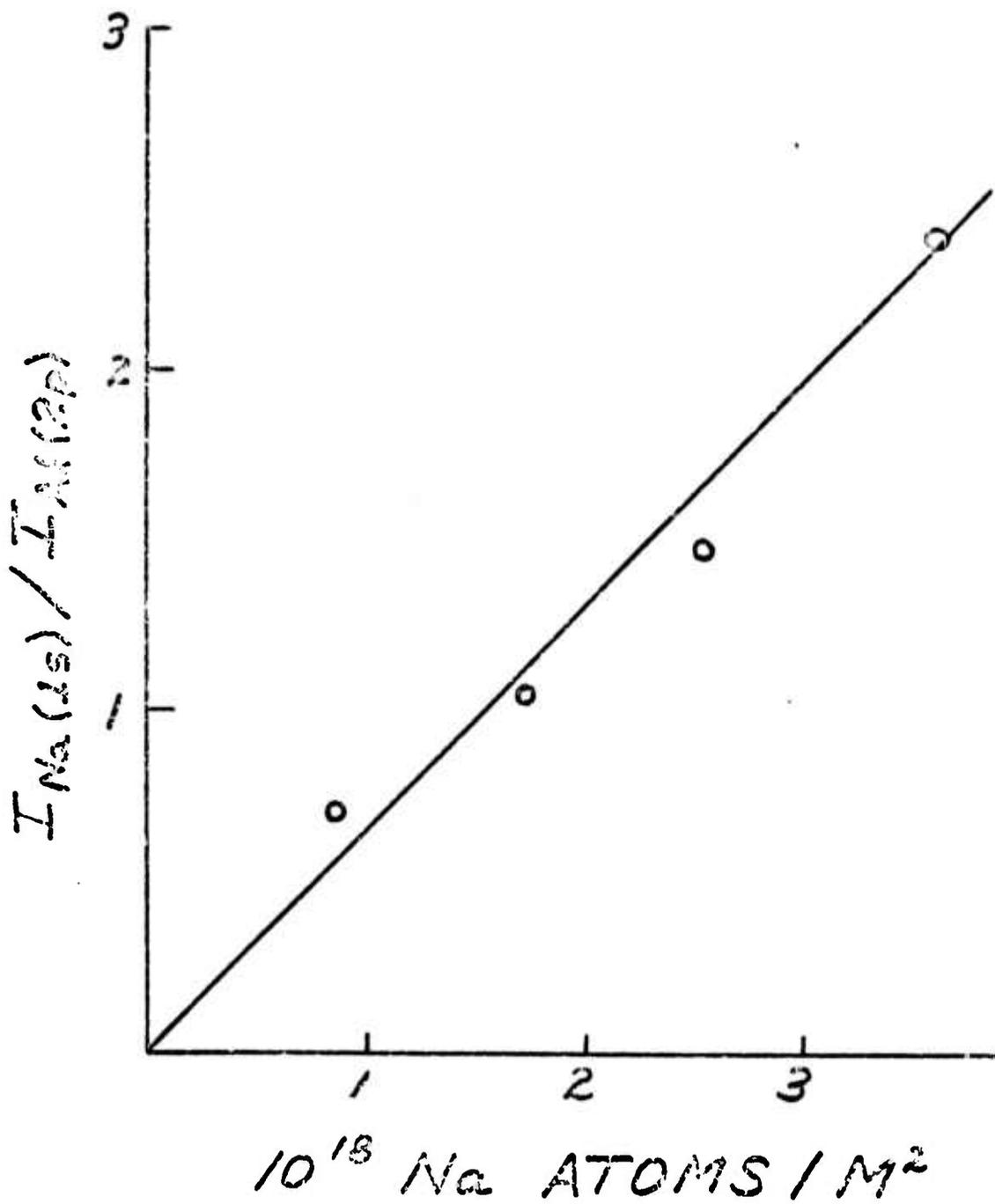


Figure 3

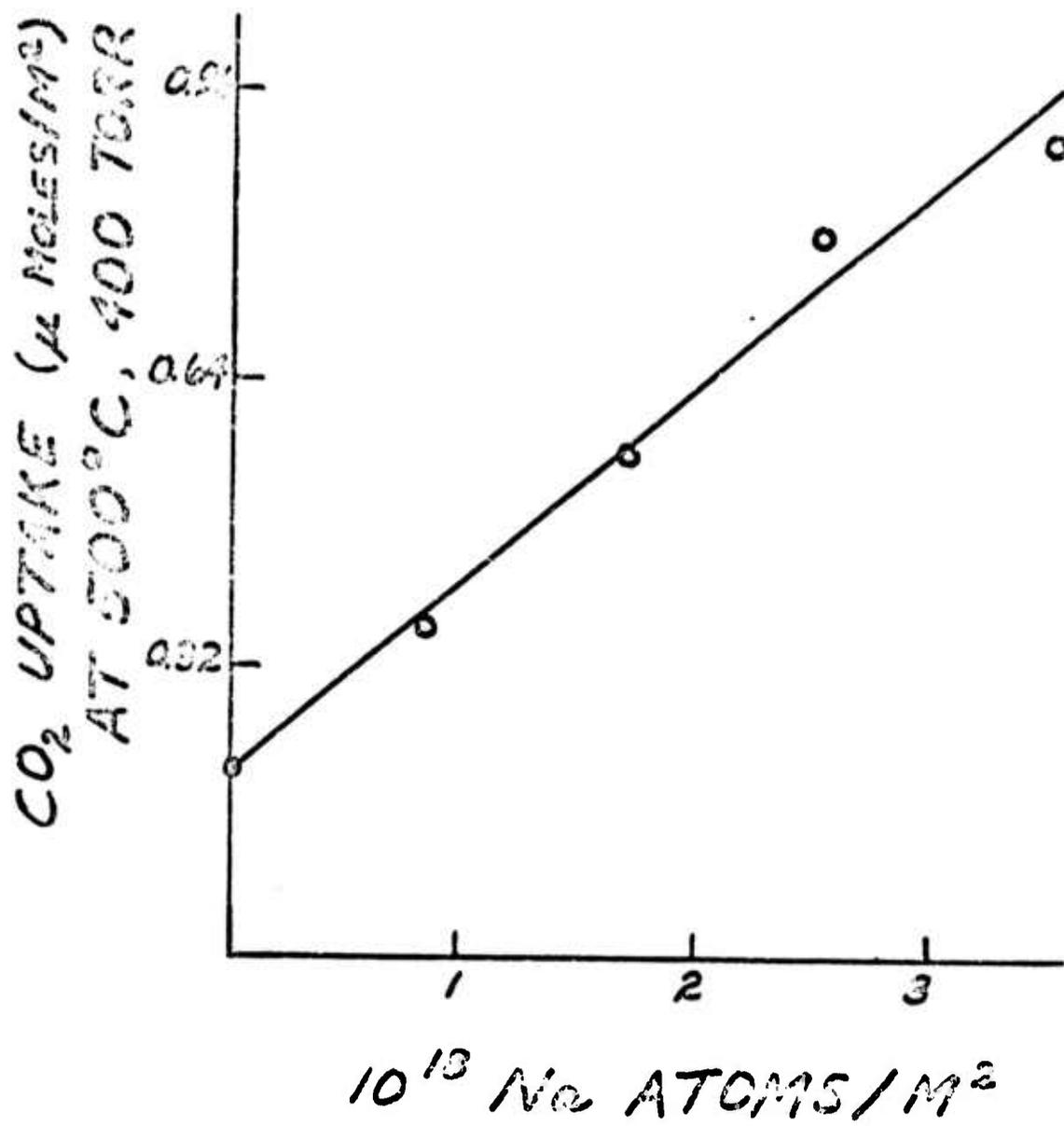


Figure 4

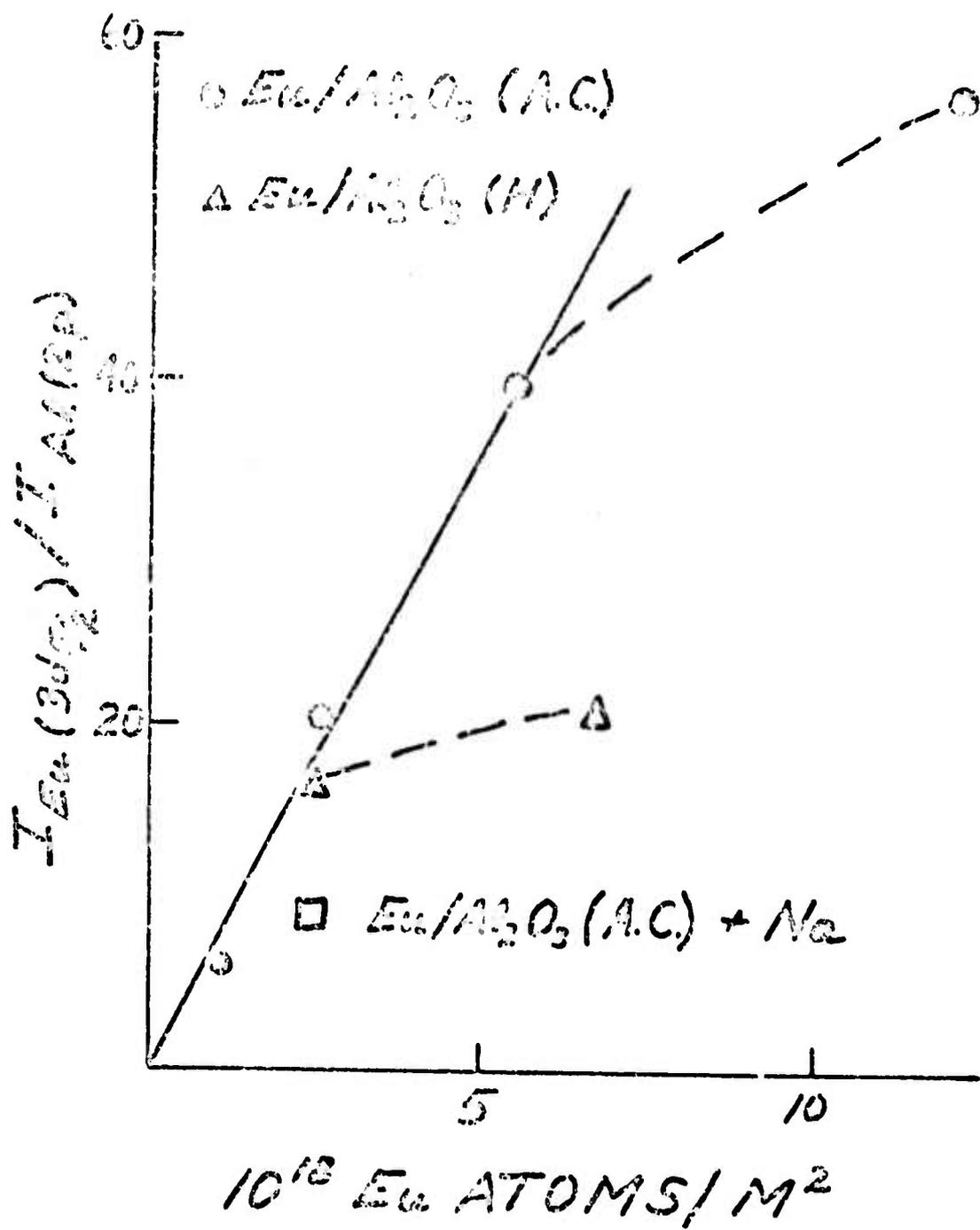


Figure 5

The higher loading sample does not, in spite of the fact that the Eu/Cyanamid alumina plot suggests that it should. This difference can be rationalized by the fact that the Harshaw alumina contains sodium and that the sodium may influence agglomeration of the Eu phase. This suggestion is supported by the observation that when sodium was added by NaOH impregnation to the Eu/ AlO_3 (AC) sample containing 2.5×10^{18} Eu atoms/ M^2 , its intensity ratio after heat treatment fell to the point marked by a \square in Figure 5.

Taken together these data paint a self-consistent picture demonstrating the utility of XPS for quantitative and dispersion analysis of catalysts. A number of improvements of the model are straight forward and are being considered. Since the samples are powders, an average over all electron take-off angles should be made. This would tend to make I_m/I_s higher when f and particle size are high. The use of the parameter f or loading assumes that the distribution of metal is uniform. Capillary condensation or pore exclusion during the genesis of the catalyst could well lead to an inhomogeneous distribution. On the other hand, a good model for the homogeneous case could lead to discovery of the above inhomogeneities by the XPS measurement. This approach also has the advantage that it gives information on agglomeration in the 20 \AA particle size region where x-ray diffraction methods are not reliable. A particularly interesting application of the method will be in the study of supported multimetallic catalysts. At constant A/B ratio but increasing loading of metals A and B, if A and B drop from the monatomic dispersion line together they are likely to be forming a uniform phase. If one metal agglomerates without the other (phase separation), its intensity ratio will drop from the linear relation first. While further work in this area is clearly needed, these results suggest that such efforts will be fruitful.

As has already been pointed out, the chemical shift is also an important parameter for characterizing catalysts. Preliminary work on supported Ru has shown two different oxidation states for Ru in 5% Ru/ Al_2O_3 as received from Engelhard. Presences of multiple-states of Ru is particularly interesting in view of the recently reported dual state behavior of supported Noble metal catalysts²⁷.

3. Accomplishments

(I) Results:

(a) Dispersion and Oxidation States: Two series of catalysts were prepared by different methods with a total range of chromium concentration of from 0.29% to 10.5%. Several types of measurements were performed over these catalysts to elicit further information; oxygen chemisorption (dispersion), x-ray fluorescence spectroscopy, iodometric determination of oxidation state after reaction, x-ray photoelectron spectroscopy (XPS, ESCA), x-ray diffraction, and activity/selectivity measurements for the CO oxidation by O_2 , NO, and by both O_2 and NO simultaneously.

Figure 6 shows the chromium dispersion as a function of catalyst loading. A dispersion greater than 1.0 indicates that the chromia is adsorbing more than one molecule of O_2 per chromium surface atom. It is apparent that although the data may vary widely, at first increasing to dispersion greater than unity, the two catalysts give consistent results. These data can be interpreted as showing a significant difference in dispersion between the A (chromic acid impregnated) and B (chromium nitrate-oxalic acid complexed) catalysts in the region between 0.5% and 3% Cr. The relative amount of surface oxide falls off rapidly after 1.5% Cr for both catalysts.

The results found here indicate that at very low loadings the dispersion is maximum, i.e. unity; however, dispersions much greater than one are also encountered. More importantly is the result that in the intermediate region catalyst A is more dispersed than catalyst B. This result is contrary to what was expected since the B catalysts were prepared in a special manner that has been shown by ESR (electron spin resonance) measurements⁵ to have the greater amount of the dispersed phase.

The anomaly just mentioned may be explained in terms of the impregnation procedure. While in the present investigation 4 mm diameter silica gel granules were used, in the ESR work micro size non-porous Cab-O-Sil silica was used as the support. It has been shown²⁸ that impregnation of a support with a salt or oxide produces significant concentration gradients in large pellets

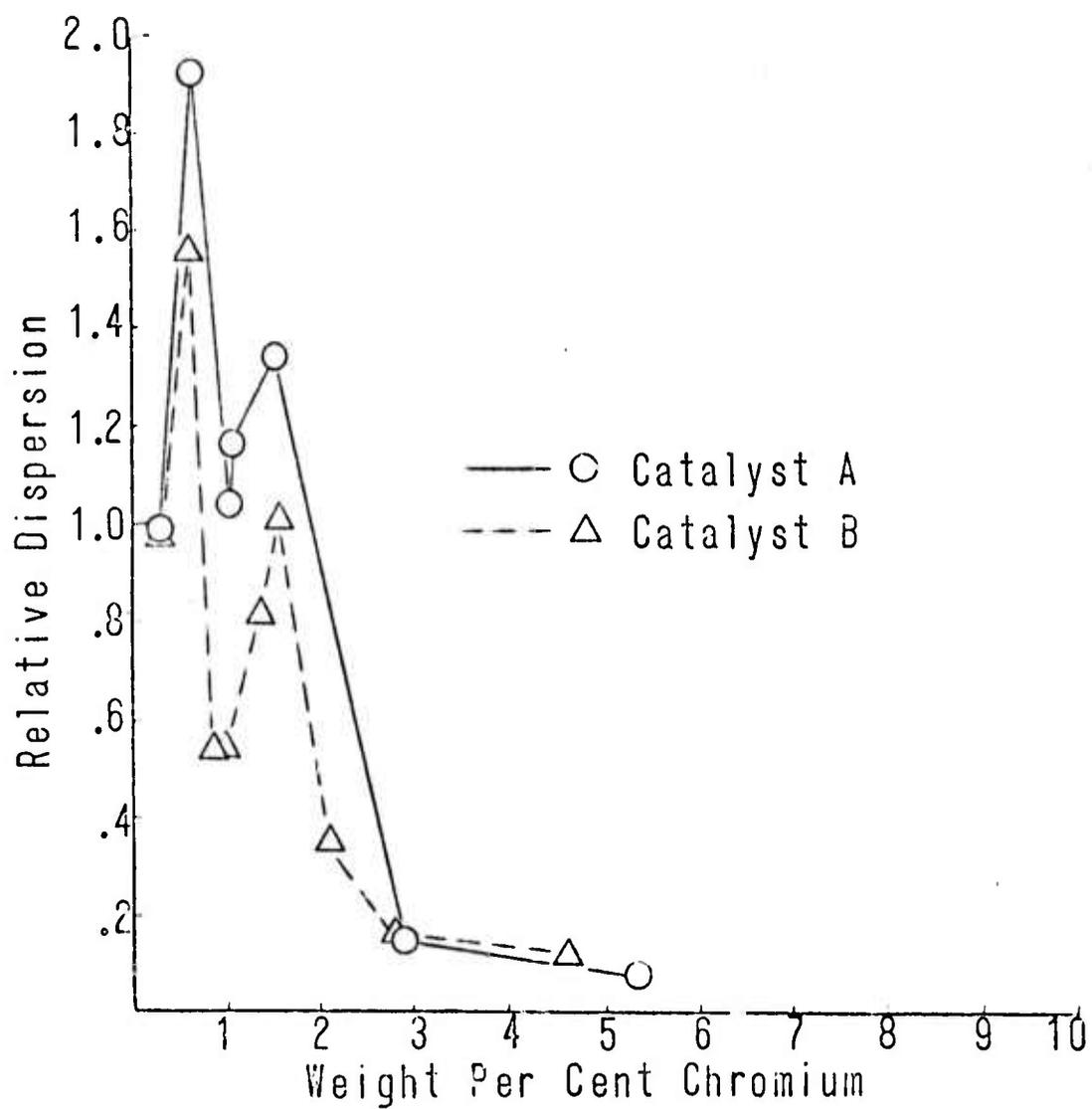


Figure 6 Change in Catalyst Dispersion with % Cr for A and B Catalysts

and that the concentration difference between pellet periphery and center is enhanced by $\text{Cr}(\text{NO}_3)_3$ impregnation (rather than CrO_3) in an alumina support. A visual check of the catalysts used in this study indicates that similar behavior may also be occurring with silica. This was reinforced by x-ray fluorescence spectroscopy of the granules. A considerable heterogeneity in the concentration of chromia was detected.

The catalysts were also analyzed for the mean oxidation state of the chromium that was stabilized during reaction. The results of the iodometric titration of the surface oxide are shown in Figures 7 and 8. The change in mean oxidation state is shown as a function of the % Cr loading for the three different reactions studied; Figure 7 is for the A catalyst (CrO_3 impregnated) and Figure 8 is for catalyst B ($\text{Cr}(\text{NO}_3)_3\text{-C}_2\text{H}_2\text{O}_4$ impregnated).

Significant differences can be seen for the various oxidation states stabilized after each of the reactions. The CO/O_2 reaction always stabilizes a higher chromium valence than the CO/NO reaction. Also the $\text{CO}/\text{O}_2/\text{NO}$ reaction produces a surface with nearly the same oxidation state as when O_2 is the only oxidizing gas, and considering the small differences in partial pressure and experimental error, the two curves could possibly coincide.

(b) Effect of Dispersion on Catalytic Activity/Selectivity: The catalytic activities of the A and B catalysts were determined for the CO oxidation by O_2 , NO, and both O_2 and NO simultaneously. In Figure 9 the absolute rate of CO conversion by O_2 is plotted as a function of Cr loading for 215°C .

The data for CO oxidation by nitric oxide are displayed in Figure 10. The CO/NO reaction rate at 215°C is usually much greater than the rate of oxidation by O_2 . Because of the scatter in data, it is difficult to distinguish significant differences between the A and B catalysts.

An interesting result was found when the relative mean oxidation states were correlated with the relative activities of the A and B catalysts. In Figure 11 the differences in oxidation number and differences in specific activity are plotted together as a function of % Cr. Also plotted on the same

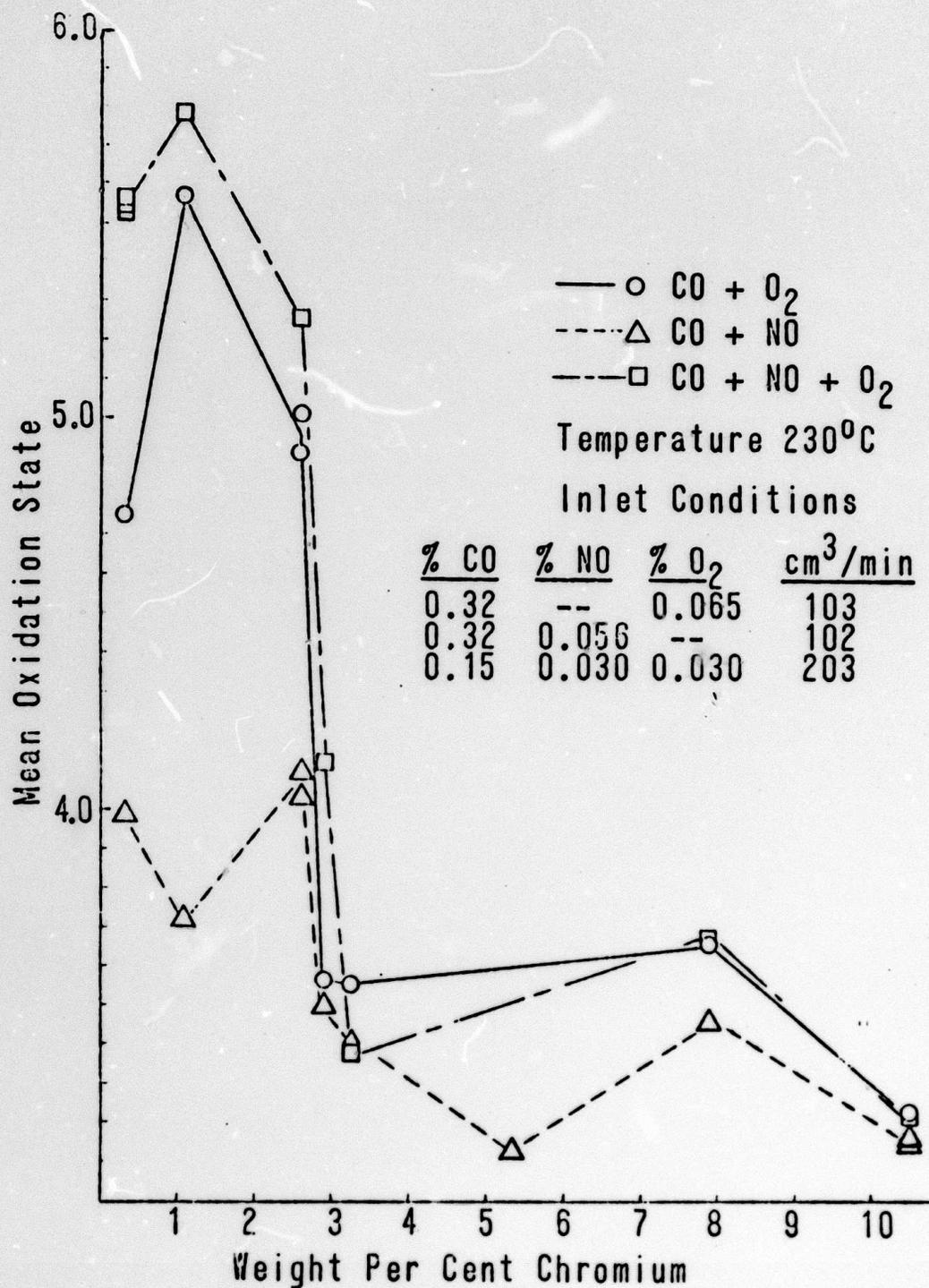


Figure 7 Change in Mean Oxidation State with %Cr and Gas Phase Composition. Catalyst A.

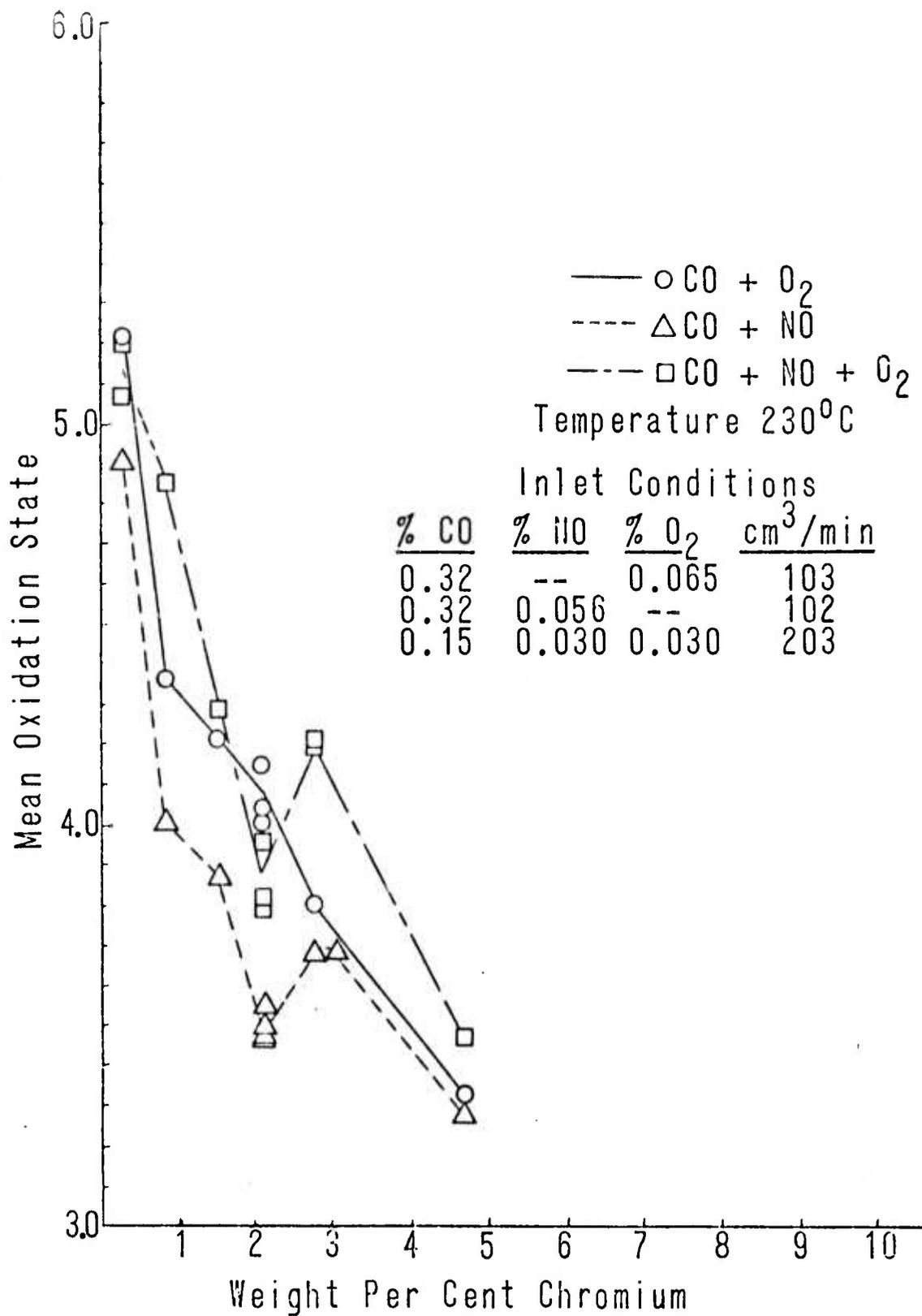


Figure 8 Change in Mean Oxidation State with %Cr and Gas Phase Composition. Catalyst B.

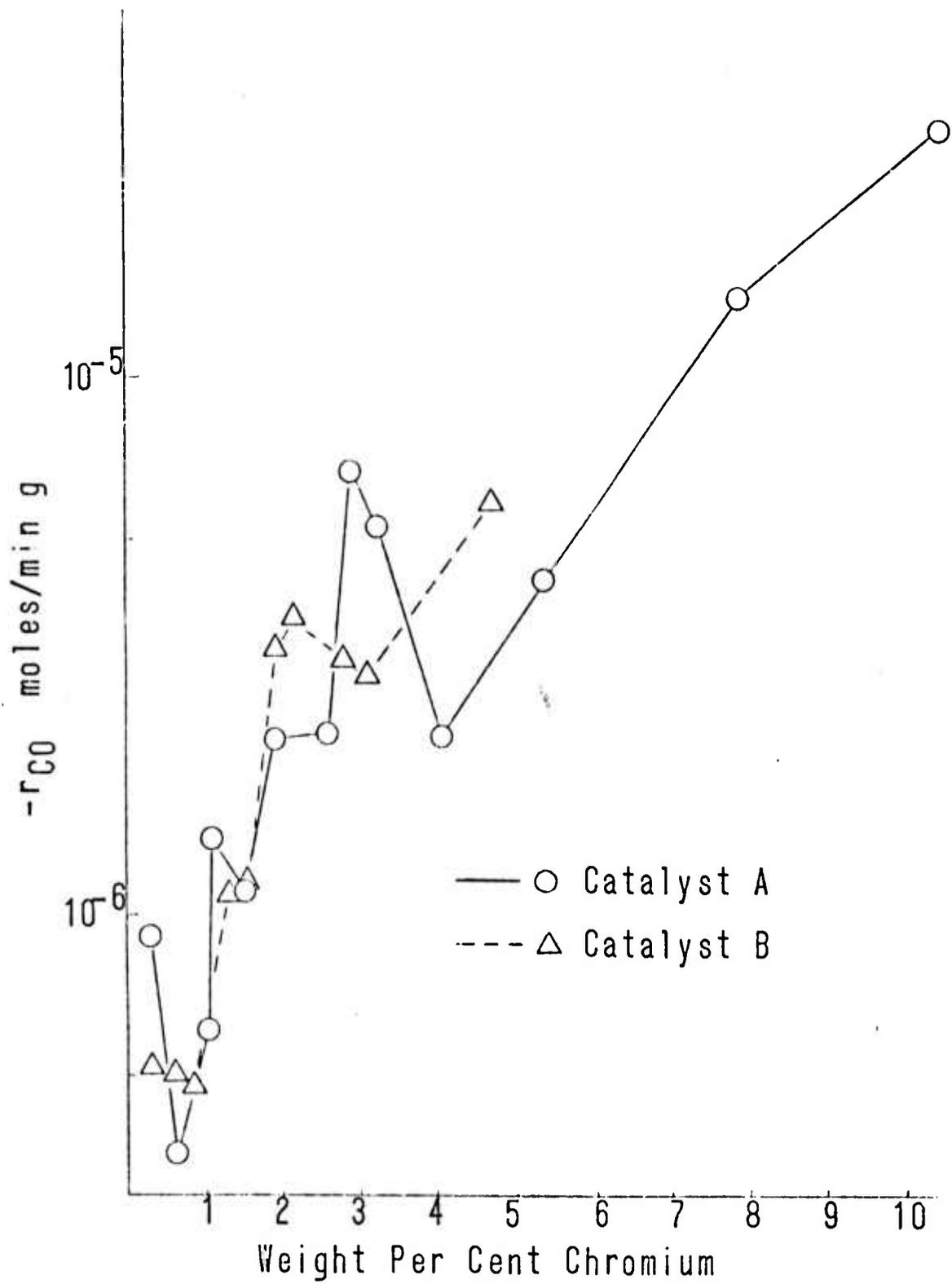


Figure 9 Change in Absolute Reaction Rate with %Cr for A and B Catalysts. CO Oxidation by O_2 , $215^\circ C$.

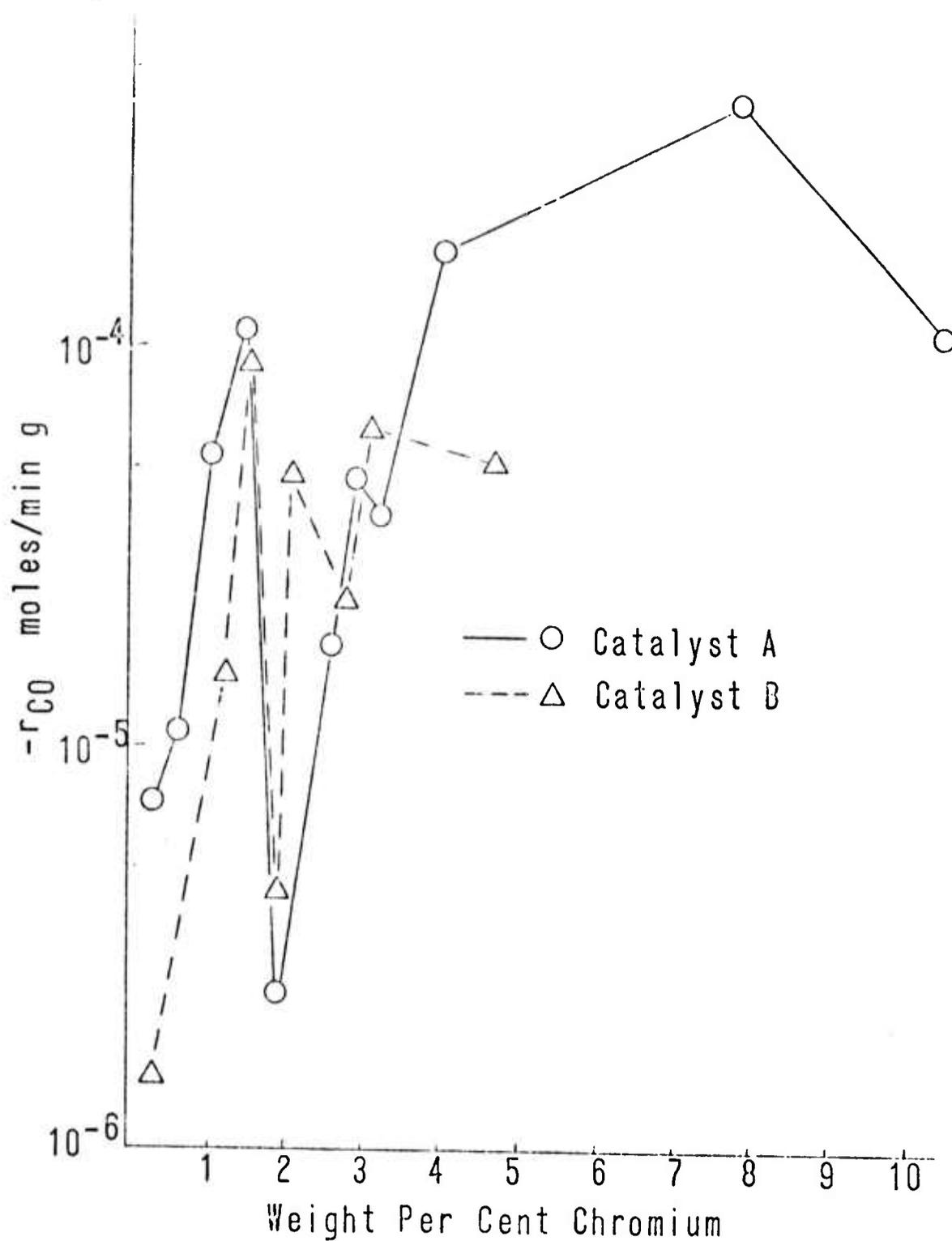


Figure 10 Change in Absolute Reaction Rate with %Cr for A and B Catalysts. CO Oxidation by NO. 215° C.

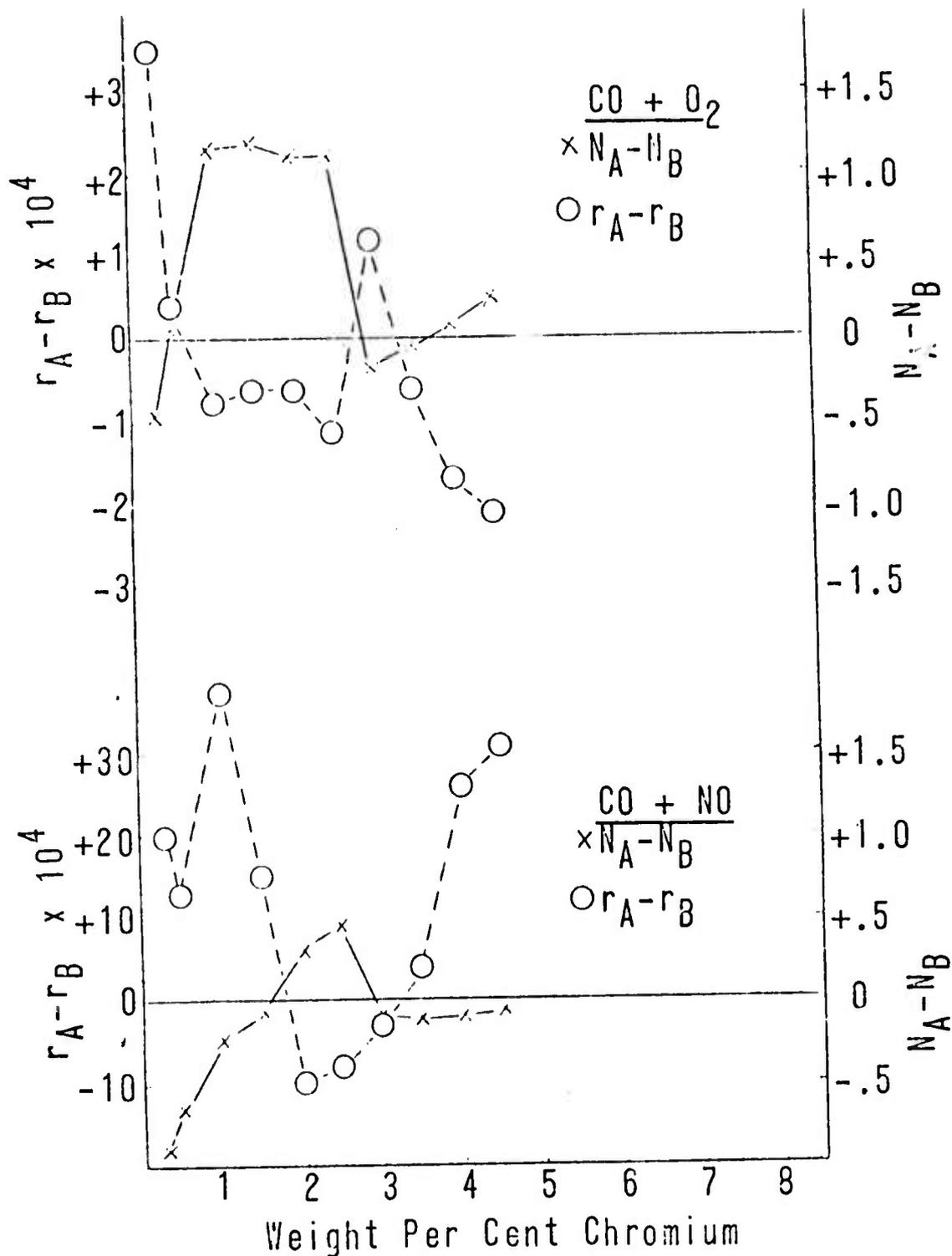


Figure 11 Relationship between the Relative Mean Oxidation States and Relative Specific Activities for A and B Catalysts.

figure are similar data for the CO/NO reaction. It is apparent that the catalyst stabilizing the lower oxidation state is the one with higher activity for CO oxidation. This holds very closely for both reactions notwithstanding the differences in temperature for the nitric oxide plot.

(2) Discussion: Although the oxidation of CO by nitric oxide has a higher negative free energy as compared to O_2 , whenever the two gases are present simultaneously over the chromia-silica catalyst, the NO is not able to participate in the reaction until the O_2 is nearly depleted. This apparent selectivity for oxygen was not altered by changing dispersion or stabilized oxidation states. The O_2 predominated regardless of which catalyst impregnation procedure was used or the amount of Cr loading. The results of the present work verify the findings of Shelef².

The research objectives listed earlier have been met, and they will be discussed here in light of the experimental results and the literature. Both the dispersion of the metal oxide on silica and the stable surface oxidation state stabilized during reaction have been altered by the two methods of catalyst preparation. Measurement of the BET surface area by low temperature N_2 adsorption has indicated that significant shrinkage of the total catalyst surface area accompanies the catalyst impregnation.

The CO oxidation by NO is found to be nearly always much faster as compared to O_2 . This agrees well with the literature². What has never been reported, however, is that the stable surface oxidation state does indeed affect the reactivity of the catalyst. The lower relative surface valence favors higher activity for both reactions. A selectivity affect for the separate reactions was not readily apparent since the CO/NO activity varied over a much wider range than the CO/ O_2 activity, and therefore the ratio of specific activities follows much the same curve as does the CO/NO specific activity when plotted versus % Cr.

A selectivity change could not be seen in the competitive oxidation of CO by NO and O_2 ; the oxygen always predominated setting the oxidation state

at a high value and yielding a reaction rate close to that observed when O_2 was present as the only oxidizing gas.

The relationship between activity and % Cr is very complex. At low concentrations, where all of the Cr atoms are on the surface, the specific activity for CO/O_2 was high. It decreased upon further loading and then increased again as the loading approached 10%. There may also be a maximum in the activity at around 2-3% Cr. Although there is enough theoretical basis^{29, 30} to support this behavior, the experimental data do not characterize this region well enough for concrete conclusions. As might be expected, the CO/NO reaction showed similar behavior but over a much wider range of activity.

Although the stable surface oxidation state has been shown to depend on the catalyst preparation method and that this has a significant affect on reactivity of the catalyst, it has been concluded that a priori control of the stabilized oxidation state to produce specified activity and selectivity characteristics would be difficult because of the sensitivity of the surface to early heat treatment. Further work along these lines is necessary and looks promising for supported metal oxide systems in general.

It should be pointed out that in meeting these objectives many different tools common to catalytic research have been used. These tools have a two-fold purpose; the addition of structural information necessary for characterization and understanding of the catalyst and the capability to fully point out the complexities of the system and limitations of other tools.

Oxidation state studies by iodometric titration can yield only average oxidation states of the surface and/or bulk. ESCA, on the other hand, is capable of yielding qualitative data on the distribution of the surface valencies.

Dispersion data can be obtained in several different ways. ESR work, although part of a previous study, was referred to when discussing the relative amounts of dispersed and bulk phases of chromia. Oxygen chemisorption was used as part of a separate study to determine relative dispersion of the active surface on the silica support. The results can be interpreted as the relative availability of the surface oxide. X-ray fluorescence spectroscopy was also

used in conjunction with this project. The results emphasized that there are gross heterogeneities in dispersion through the catalyst pellet.

Activity measurements, the essence of catalytic research, are necessary in order to determine the behavior of the catalyst during reaction. In this way the effects of the catalyst characterization variables, i. e. preparation method and resulting oxidation states, etc., can be analyzed. A recycling differential reactor, capable of eliminating heat and mass transfer gradients at the catalyst periphery was used to insure that intrinsic kinetics were measured.

Results of in situ infrared work, part of still another project measuring chromia-silica activity and simultaneous adsorption of reactants and products, were used in determining that oxygen was indeed a poison for the reaction. When NO and O₂ were present in a reaction mixture with CO, chemisorption of NO and CO were not detected. A layer of oxygen covered the surface.

The ESCA work has indicated that there is a qualitative correlation between the surface oxidation state following reaction and the mean oxidation state determined iodometrically. A large change in the catalyst surface was also seen by ESCA after the sample was heated to 400°C and 500°C. These changes could be due to possible incomplete conversion of hexavalent to trivalent chromium or to the incomplete transformation to crystalline α -Cr₂O₃ at 400°C. X-ray diffraction work can help in this determination.

In short, this investigation has, through the use of various tools, been able to detect, if not characterize, the complexities leading to the nature of the activity and selectivity of the chromia-silica catalyst. Specifically, the alteration and measurement of surface oxidation states stabilized during reaction; the determination of the relationship between the specific activity for CO oxidation by O₂ and % Cr between 0.29% and 10.5%; and the characterization of the relationship between relative activity and stabilized oxidation states for oxidation of CO by both O₂ and NO, are contributions that are unique to this study.

4. Proposed Research

(1) Chromia: The overall research program is continuing. ESCA is being used in the Purdue University Department of Chemistry to study surface phenomena of the supported chromium oxide. Dispersion and surface area measurements and x-ray diffraction work are continuing as part of a Masters project in Chemical Engineering. A simultaneous reaction and infrared study is also in progress.

The ESCA work looks very promising. A systematic study should be made to determine the effects of early heat treatment and catalyst impregnation procedure on the oxide surface. Iodometric titration for the higher oxides and x-ray diffraction to determine crystal structure will complement this study.

The dispersion studies have demonstrated that the catalyst is sensitive to heat treatment and to the impregnation procedure. A detailed study to produce very nearly homogeneous pellets would be helpful. This could be achieved by using weak solutions and smaller pellets. The pellets could be vacuum dried and the impregnation repeated until the desired concentration is reached.

In situ infrared studies of the CO-NO reactions will be continued to determine the mechanism of catalyst deactivation. Preliminary results indicate that significant changes in surface concentrations of the adsorbed species occur during the deactivation process. Studies aimed at correlating this change in activities with the concentrations of surface species are currently in progress.

(2) 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/SiO₂ 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 Mössbauer 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 than 1 wt %. We will pursue the possibility of producing unusually active catalysts by special pre-treatment 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^{31} , ESCA, and Mössbauer 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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III. 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 in situ 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 in situ 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 in situ 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 tip¹.

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 level².

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 vacuo⁵.

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 ions². 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

temperatures¹. The spectra of metallic Ni, NiO and Ni₂O₃ were characterized from samples prepared directly in the spectrometer. The Ni₂O₃ 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 Ni₂O₃ 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 Ni₂O₃ decreased as the temperature increased. Our results present the first direct spectroscopic evidence for Ni₂O₃ and point to some significant consequences to catalytic studies. For example, we have found that CO adsorbs more readily on an Ni₂O₃-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 μamp/cm² 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^0 value. All oxides with $-\Delta G_f^0$ below 120 kcal/mole were reduced by exposure to Ar⁺ ions while those with $-\Delta G_f^0$ 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:



and



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 levels². 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 energy⁷. 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 SiO₂ versus pure Au is +1.1 eV but the matrix shift, estimated from implanting Ar in Au and SiO₂, 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 relaxation 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 clusters⁸.

(4) Identification and interpretation of the origin of shake-up phenomena in 3d⁰ 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 d¹⁰ systems, such as ZnF₂ and CuCl^{11,12}, nor d⁰ systems, such as TiO₂ or V₂O₅¹¹, exhibit satellites in this same energy range. It was also indicated in the paper by Rosencwaig¹¹, 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 $\text{Sc}_2(\text{C}_2\text{O}_4)_3 \cdot 6\text{H}_2\text{O}$, 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 $3d \rightarrow 4s$ transitions, so that an alternative assignment is clearly required. Since $3p \rightarrow 4s$ excitation is not feasible, the most attractive possibility is in terms of a monopole charge transfer transition (ligand \rightarrow metal 3d), an assignment which was originally proposed by Kim⁹, as an alternative to $3d \rightarrow 4s$ 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 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) activation; (d) reaction. The catalysts have been studied in the form of pressed discs, containing between 5 and 15% chromium. At the present time we are just finishing 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 500°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.

(6) XPS studies of electrode surfaces: From the above accomplishments, it is clear that various oxides can be identified on a variety of surfaces. We have, therefore, attempted to study the surface chemistry of oxides formed

by anodizing various electrode materials in acidic aqueous solutions. On gold, a film of hydrated Au_2O_3 or $\text{Au}(\text{OH})_3$ was observed which varied in thickness up to 30 \AA at 1.9 eV versus SCE applied potential¹³. Hydrated IrO_2 or $\text{Ir}(\text{OH})_4$ was also observed on the IR electrode and a correlation was attempted between the coulometric data and the thickness of the IrO_2 film measured, using XPS data¹³. This correlation was successfully completed by measuring the intensity ratio between the IrO_2 and Ir metal to obtain the oxide thickness from XPS data. The thickness from coulometric measurement was obtained by measuring the charge required to strip off the oxide after XPS analysis.

4. Proposed Research

The major thrust of this research is to identify the presence of various oxidation states on metal and metal oxide surfaces. This emphasis will include a correlation of results to ongoing catalytic testing projects as well as fundamental electrochemical studies of heterogeneous electron transfer reactions. In addition, we hope to find ways to maximize desirable surface conditions for maximum reactivity, using ESCA to monitor the success of any new synthetic methods. In this section, then, the general scheme will be presented as related to both the catalysis and electrochemistry programs.

(1) Ion bombardment studies of metal and metal oxide surfaces: The use of ion beams presents an intriguing opportunity for preparation and characterization of new catalyst surfaces. Since ESCA measurements are sensitive to different oxidation states of an element and since ion bombardment can potentially enable us to analyze in depth composition of oxidation states, we need to understand the various complications ion bombardment would add to the chemistry and, hopefully, to gain further insight into the mechanism of interaction of these ions with solid surfaces. However, we feel that even if the details of the ion-surface interaction cannot yet be fully understood, that if the chemical alterations which occur can be predicted in a systematic fashion, the approach will take on new meaning.

There are a number of factors to be examined to optimize the preparative value of this approach and to be able to use bombardment methods as an aid to ESCA studies. The significance of the 120 kcal cutoff energy is not yet clear although we suspect that it closely relates to the distribution of energy between the lattice and the sputtered surface atoms and the reflected argon species. We plan to study a wide variety of metal-oxygen systems as a function of the incident ion kinetic energy over the range of several eV to several keV to attempt to alter this 120 kcal cutoff value. In some cases, we plan to investigate any chemical changes which may occur as a function of the temperature of the sample since dramatic temperature effects have been observed previously. By bombarding NiO with O_2^+ , the surface concentration of Ni_2O_3 , the cation defect NiO structure, was 100% at $-80^\circ C$, 40% at $20^\circ C$, and 5% at $200^\circ C$ ¹. Other workers have also observed variations of the sputtering yield of certain oxides with temperature indicating involvement of a thermal rather than a direct collision mechanism. An understanding of these kinds of variations is basic and crucial to our overall scheme.

The other factor of interest in these studies is the chemical nature of the bombarding gas. In preliminary work, we have found that PbO bombarded by He^+ readily reduces to metallic Pb. This observation is significant in that ion scattering spectrometric studies of PbO surfaces by He^+ bombardment have failed to detect an oxygen signal¹⁵. Bombardment with Xe^+ , however, causes no observable change in the surface composition. The explanation for this variation is not yet clear but if reduction occurs by direct collision, the maximum energy transfer occurs to the atom with a mass similar to the bombarding ion. Thus, for PbO, He^+ might preferentially remove oxygen while Xe^+ might preferentially remove Pb. Thus, certain results point to a thermal sputtering mechanism while others suggest the process is mainly collisional in nature. The real situation indeed will depend on the physical and chemical structure of the substrate and in some cases may involve both mechanisms, as suggested by Kelly¹⁴. Clearly, a number of other factors must be involved and need to be investigated and taken into account, including

the ionization potential and/or degree of ionization (e.g., Ar^+ versus Ar^{++}) of the bombarding gas, the range of the bombarding gas in the oxide substrate and any additional chemical or thermodynamic factors which may be relevant.

The presence of these rather extensive ion-induced surface reactions certainly puts a damper on using ion bombardment methods for profiling the concentration of oxidation states as a function of depth into the sample. When the direct sputtering of the oxide dominates over the reduction process, however, certain inferences regarding its special distribution may be possible. The presence of these conditions can be checked by measuring the thickness of the altered layer using ESCA and comparing it to the sputtering yield of the metal or metal oxide. We have already shown that for PdO and NiO after ion bombardment, sputtering is the primary process² and could qualitatively be used to monitor the composition of the various oxygen species as a function of depth in the sample. We hope to generalize these initial findings to evaluate the possibilities of profiling oxidation states and to gain further insight into the mechanism of the bombarding process.

(2) Application of ESCA to analysis of electrode surfaces: Aside from the information presented in section 3, a great deal of additional data suggests the powerful impact this technique will bring to bear on elucidating electrochemical mechanisms. We have already demonstrated that the oxidation state of passivated electrodes can be easily determined and we will continue this approach by studying additional systems. The Ni - Cd electrode represents an excellent candidate since not only can the formation of Ni and Cd-oxides be monitored with applied electrode potential, but the relative surface concentration of Ni and Cd can be determined. The background work needed to characterize this system has been completed since the surface chemistry of both Ni-oxygen and Cd-oxygen have been thoroughly investigated using clean systems.

These same concepts will be used to study the types of interactions involved in adsorbed molecular layers with a special emphasis on the under-potential deposit of adatom species¹⁶. These processes may be of particular

importance in many corrosion reactions. Bruckenstein has reported the most recent electrochemical results for Ag^+ deposition on platinum at underpotential¹⁷. A LEED study¹⁸ and a specular reflection study¹⁹ have also been undertaken to understand this phenomenon. We plan to measure the binding energies of the adatom layers using ESCA and to measure their optical constant using IRS. These evaluations should point to the nature of the interaction involved in the adsorption since extensive charge transfer from Pt to Ag^+ will result in near metallic optical properties with ESCA binding energies very similar to the pure metal. The existence of such species as $\text{PtO} \cdot \cdot \cdot \text{Ag}$ or $\text{Pt} - \text{Ag}^+$ could readily be resolved. A variety of other metal ions (e. g., Bi^{3+}) may exhibit interesting amalgamation characteristics²⁰.

The fundamental nature of the ESCA chemical shift also suggests a possible approach to evaluating the magnitude of the underpotential effect. As discussed earlier, the chemical shift can be thought of as containing a chemical term, a relaxation term, a work function term and an initial state potential term. The net chemical shift of a thin metal film deposited on a different substrate would then consist of the sum of all these effects. In the electrochemical cell, a very similar picture can be developed. As a metal ion approaches an electrode at a given potential, the driving force for adsorption and reduction of the ion consist of a number of factors. First, the work function difference between the electrode material and the ion has been shown to be an important factor. Secondly, the possibility for alloy or oxide formation can contribute an additional amount of energy. And finally, the metal ion positive charge can be polarized by the conduction electrons in the metal in a fashion exactly analogous to the extra-atomic relaxation effect observed during photoemission. Thus, the contributing factors which drive an ion to be deposited at underpotential are similar indeed to the factors which contribute to the chemical shift of one metal thin film deposited on a second substrate. We plan, then, to correlate the ESCA chemical shift of thin metal films to the underpotential magnitude of the deposit for a variety of systems with the goal of obtaining a more fundamental understanding of this important phenomenon.

(3) ESCA studies of chromia catalyst surfaces: Work on chromia catalysts will be pursued in the immediate future. As we have described in the Accomplishments section the ESCA spectra of the chromia/silica catalyst have been monitored during its preparation and calcination steps. To complete this particular study we will carry out related investigations of the catalyst during its activation in reducing (CO) and oxidizing (O₂) atmospheres. Finally, its behavior when exposed to the gaseous oxide mixture NO + CO + O₂ will be studied. With this completed ESCA information then available, correlations will be made with the kinetic measurements and in situ infrared spectral studies of Professor R. G. Squires. Since the ESCA techniques enables us to monitor not only the average oxidation state, but the distribution of Cr²⁺ to Cr⁶⁺ surface sites during adsorption and reaction, this will hopefully enable us to determine which surface site participates in the catalytic reaction. For instance, if the oxidation of CO and simultaneous reduction of oxides of nitrogen that is desired in catalytic automobile exhaust systems requires two different oxidation states, knowledge of which states are important in each reaction would be important for optimal catalyst design. An additional important investigation which should be pursued is a study of the effect of catalyst preparation upon its activity. Accordingly, in addition to the chromic acid (Cr⁺⁶) impregnation method which we have used up to the present time, we will also use the chromium nitrate (Cr⁺³)-oxalic acid procedure. ESCA measurements will be made on this system to compare the chromium dispersion and binding energy shifts with those of the chromic acid impregnated catalysts.

ESCA studies will also be made on other systems which catalyze the reactions between gaseous oxides of the non-metals. For instance, it has recently been discovered that non-aqueous solutions of the rhodium and ruthenium compounds RhCl₃·xH₂O and Ru(NO)₂[P(C₆H₅)₃]₂ catalyze the reaction 2NO + CO → N₂O + CO₂²¹. We plan to investigate the ESCA spectra of RhCl₃·xH₂O dispersed on silica and/or alumina in the hope of obtaining a suitable heterogeneous catalyst for this same important reaction.

We have just developed a new and convenient procedure for the synthesis of unknown metal halide phases (e. g. β - MoCl_2 and RhX_2 ($\text{X}=\text{Cl}$ or Br) by reaction of the solid metal acetates with the gaseous hydrogen halides²². 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, by first impregnating these latter materials with the appropriate metal acetate and then generating the halide by reaction with the gaseous hydrogen halides. 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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IV. Electrode Reaction Studies Role of Surface Oxides on Cathode Surfaces

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1. Objective

Preliminary results have shown that x-ray photoelectron spectroscopy (XPS or ESCA) will provide valuable information that will be useful for clarifying the mechanism of electrochemical reactions occurring on the platinum cathode of a low-temperature hydrogen-oxygen fuel cell. The amounts of platinum oxides on the cathodic surface was found to change as the fuel cell was operated. When dilute KOH is used as the electrolyte, oxygen reacts at the cathode with water forming hydroxy ions and releasing electrons. The hydroxy ions migrate to the anode where they react with the hydrogen and electrons to form water. The cathodic reaction obviously involves some type of chemisorption and dissociation of the oxygen molecule. Probably the platinum oxides that are measured on the cathodic surface are intermediates in the electrochemical sequence. Determining the composition of the surface of the cathodic surface will almost certainly be a valuable tool in suggesting techniques for the better understanding of very possibly improved operation of fuel and other electrochemical devices.

(1) Previous fuel cell research at Purdue University: Fuel cell research^{1, 2, 4, 8} conducted under the direction of the author has shown that at least two factors are of importance in controlling the rate of current generated by a fuel cell.

The first factor is the diffusion of oxygen to the cathode and of hydrogen to the anode. Such diffusion steps are often if not always rate controlling steps in the overall complicated sequence of events occurring in a fuel cell. Such a sequence certainly includes dissolving the oxygen in the electrolyte near the cathode, dissolving the hydrogen in the electrolyte near the anode, diffusion of the oxygen to the cathode, diffusion of the hydrogen to the anode, chemisorption and dissociation of both the oxygen and the hydrogen on the cathode

and the anode respectively, surface reactions, transfer of ions between the cathode and anode, and diffusion of water from the electrode at which it is formed. Studies with both the cathode and anode of fuel cells using either dilute KOH or dilute sulfuric acid as the electrolyte have confirmed the importance of the diffusion of both hydrogen and oxygen to their respective electrodes. Models based only on molecular diffusion of the dissolved fuel (oxygen or hydrogen) have been found to predict experimental data for the immersed portion of electrodes with good accuracy.

Purdue investigations have also shown that the character and previous treatment of the platinum electrodes used have significant effects on the current fluxes obtained. For example, roughening of platinum foil by means of platinizing techniques has been found to increase significantly the current fluxes generated in the region of the triple interface between the gas phase (gaseous fuel), the liquid electrolyte, and the solid electrode. Furthermore, allowing a cathode to equilibrate at open-circuit conditions with an electrolyte saturated with oxygen results in a cathode that produces very large current fluxes immediately after the circuit is closed. A similar finding also occurs for an anode contacted with an electrolyte saturated with hydrogen.

The above findings strongly imply that a large surface area (increased by microscopic roughness) and a surface "saturated" with oxygen in the case of a cathode (or with hydrogen in the case of an anode) are desired. There is definitely a need to test the above postulates, and ESCA measurements should be most helpful. In regards to ESCA measurements, it has been found in our preliminary investigations (conducted since June 1974) that the ratio of the oxygen to platinum ESCA peaks vary from about 1.7 to 3.3 after various specified operations of the cell. Clearly ESCA will give quantitative values relative to the surface compositions in the cathode.

2. Proposed Research

Preliminary results have demonstrated that significant differences of the concentration of surface oxides or of adsorbed oxygen present on a platinum

cathode are occurring as the fuel cell is used. However, considerable more data are needed in order to relate these surface compositions to various phenomena noted during fuel cell operation. In particular, ESCA data will be obtained for the platinum cathode as a function of the following variables:

(a) Time after start-up of the cell (during which time the current decreases rapidly). During open-circuit of the cell, it is thought that oxygen is chemisorbed on the surface; then when the circuit is closed, the concentration of adsorbed oxygen on the surface probably decreases and approaches a dynamic steady-state value.

(b) Position of the cathodic surface relative to the triple interface between oxygen, electrolyte, and solid cathode. In the region of the interface, oxygen transfer to the cathodic surface is relatively fast as compared to transfer in the portion of the cathode immersed significantly below the electrolyte surface. The concentration of surface oxides may then vary significantly with the cathodic position.

(c) Temperature.

(d) Imposed potential likely has some effect on the kinetics of the surface reactions and indirectly on the concentration of surface oxides.

(e) Roughness of the cathode.

Knowing the types and concentrations of surface oxides promises to be most helpful in clarifying the basic cathodic mechanism. This information will further clarify how important imposed potentials are in affecting the reactivity (or activity) of various platinum oxides in fuel cell operation and possibly also for various types of catalysts.

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