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NOVEL MATERIALS FOR POWER SYSTEMS. PART I. SCHIZOPHRENIC CATALYSTS

R. G. Squires

Purdue University

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13. ABSTRACT

The work performed under this program can be subdivided into three areas: PART I - Schizophrenic Catalysts; PART II - Protonic Semi-Conductors; and PART III - Selective Emitters for Energy Conversion.

PART I - Schizophrenic Catalysts

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.

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PART I

Schizophrenic Catalysts

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Schizophrenic Catalysts

R. G. Squires

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 (ESCA).

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 species.

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 technqiues 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.

The dispersion of the active catalysts on an inactive support has been varied in hopes that the stable oxidation state at given ambient conditions will be influenced by the degree of dispersion of the catalysts.

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 dispersion of these samples is being measured by chemisorption of carbon monoxide gas in a recording microbalance. Kinetic studies of the oxidation of carbon monoxide lead to the following conclusions:

1. A maximum activity for the catalyst produced by CrO_3 impregnation exists at about 3% Cr, and a similar maximum is also found for the catalyst produced by oxalic acid complexing of chromium nitrate

at about 2%. This type of behavior has never been reported for chromia-silica systems or for CO oxidation.

2. The CO oxidation by NO is much faster than by O_2. This is in agreement with Shelef et al (47) in their over chromia-alumina.
3. The oxidation state of the chromium oxide surface is lower for NO passage or reaction with NO and CO, than it is for O_2 passage or the O_2 + CO reaction. This also agrees with Shelef et al (47).
4. The activity of both catalyst series for CO oxidation by O_2 goes through a broad minimum at 5.5% for chromic acid catalysts and 3% for oxalic acid complexed catalyst. The activity then increases again for both catalysts.
5. Additional pretreatment in cycling oxidizing and reducing atmospheres at 450°C reduces the absolute catalytic activity but does not alter the general shape of the rate is % Cr curves.
6. The activity at low concentrations (< 1%) of chromium (215-233°C) seems higher for the oxalic acid complexed catalyst than for the chromic acid catalyst.
7. The Union Carbide Reactor is yields gradientless kinetics when the reaction rate is no greater than about $2x10^{-5}$ moles CO_2 formed per minute per gram of catalyst.
8. The reactor and pure silica, show no significant activity for CO oxidation.
9. When NO and O_2 are used simultaneously to oxidize CO, the NO does not participate to any great extent. These results are masked somewhat by the complexity of analysis and the considerable amounts of NO_2 which are formed.

10. The total surface area, as measured by the BET N_2 adsorption technique, decreases after impregnation of the silica with chromic acid and subsequent heat treatments at 450°C.

11. An X-ray diffraction pattern of a sample impregnated with 1.35% $Cr(CrO_3)$ and subsequently reduced shows no lines associated with α-Cr_2O_3. This indicates that the chromia is either amorphous or that the crystal size is less than about 50A.

D. Implications for Further Research

In order to finish this current project and meet the objectives proposed in the first section of this report (OBJECTIVES) we propose to:

1. Produce and analyze more catalyst samples to more fully characterize the rate vs % Cr relationship. Both chromic acid impregnation (A) and chromium nitrate-oxalic acid complexed (B) catalyst will be used.
2. Check the analysis of the NO reaction so that better reproducibility and closed material balances can be obtained.
3. Complete the analysis for specific reaction rate activation energy, and selectivity as a function of % Cr and relative dispersion of chromia on silica.
4. Determine the stable surface oxidation state during reaction. This will be related to the relative dispersion and rates of the O_2 and NO oxidation of CO.
5. Determine the relative dispersion of certain catalyst of interest. This will be related to the activity and selectivity of the catalysts as well as the method of catalyst production.

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5. Determine the relative dispersion of certain catalyst of interest. This will be related to the activity and selectivity of the catalysts as well as the method of catalyst production.

E. Special Comments

At the suggestion of the ARPA review committee during their recent site visit, this research project will be expanded next year to include a study of the control of the surface site by means of an applied voltage.

In addition, a major effort will be made to correlate the catalytic and electrochemical results with the physical and chemical characteristics of the surface. The surface sensitivity and chemical specificity of the ESCA technique are well-suited to elucidating the structure and composition of the surfaces oxides formed in these catalytic systems.

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

Schizophrenic Catalysts

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Schizophrenic Catalysts

R. G. Squires

A. Objectives

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 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. For illustrative purposes the remainder of this section will emphasize the chromia on silica system.

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:

1. To determine whether the two different methods of catalyst preparation stabilize different oxidation states of chromium oxide supported on silica.
2. To determine whether the BET surface area is altered by the two differing methods.
3. 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.
4. To determine the effect of the dispersion on the activity and selectivity of the catalyst for
   a. CO oxidation by O_2.
   b. CO oxidation by NO.
   c. Competitive oxidation of CO by O_2 and NO.
5. To determine the relationship between activity and % Cr.
6. To determine whether the stable oxidation state can be controlled by the catalyst preparation method.
7. 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.

B. Background

1. Significance of the research

The catalytic selectivity of a chromia catalyst can be changed by varying the oxidation state of the surface oxide (47). If the stable surface oxidation state can be controlled by the dispersion of the chromia, a catalyst system with controllable selectivity characteristics would result.

Shelef, et.al. (47) 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:

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

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

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.

2. Physicochemical Properties of Supported Chromium Oxide Catalysts

Relatively little is known about chromia-silica catalysts compared to the wealth of information that has been gathered on chromia-alumina catalysts. Poole and MacIver (1) have written an extensive review of physical-chemical properties of alumina supported chromium oxide. Magnetic susceptability studies by Eischen and Selwood (2,3) and Selwood (4) on chromia-alumina have produced information on the effectiveness of dispersion of the paramagnetic ions.

A series of papers by Weller and Voltz (5,6,7,8,9) discussed the surface chemistry, catalytic activity, electrical conductivity, and effects of water and other chemisorbed gases on supported and unsupported chromia. They found that the activity for hydrogen-deuterium exchange and electrical conductivity were functions of chromia oxidation state (6). They reported that the effect of the support (alumina) was to more effectively distribute the oxide as well as stabilize Cr^{+3} state.

The chromium oxide surface (supported or gel) can exist in a variety of oxidation states (+2 to +6). It is an n-type semiconductor in the presence of pure hydrogen and a p-type semiconductor in oxygen. Also at temperatures over 400°C chromia and chromia-alumina behave like n-type semiconductors (10). This is also the temperature where significant changes in crystal forms have been reported (11,12). This behavior as well as their own experimental results or chromia gel caused Kuriacose and Sastri (13) to remark, "If with rise in temperature the amphoteric semiconductor, chromium oxide, undergoes a transition from predominately p-type to predominately n-type then there will be a change in the rate determining step with increasing temperature, causing a break in the Arrhenius plot." More about this "two-faced" or polyfunctional behavior will be discussed later.

A. Interactions Between Chromium Oxide and Support

It is well known that during the heat treatment of a freshly impregnated catalyst a chemical interaction occurs between the metal oxide and carrier (14,15,16,17,18,19,20,21). It is because of this interaction that many of the unique properties of supported chromia originate. This was mentioned by Deren and coworkers (15) in their study of chromia-alumina. They discovered a stabilizing influence of the carrier on the +5 oxidation state during hydrogen peroxide decomposition. They attributed this to a crystal field effect.

A similar interaction was found by Holm and Clark (17) in their studies of reduction rates of supported chromia. The shifting of the maximum reduction of chromia to different temperatures was attributed to this interaction.

A discussion of the structure of pure CrO_3 and supported hexavalent chromium can be found in an article by Cossee and VanReijen (19). They point out that pure CrO_3 is unstable at high temperatures because of the unfavorable packing conditions. The carrier (SiO_2, SiO_2-Al_2O_3, or γ-Al_2O_3) provides a stabilizing influence.

According to both Hauffe (22) and Wolkenstein (23) the type of reaction that takes place on an oxide catalyst depends on how the reacting molecule is adsorbed on the surface. This in turn depends on the structure of the impregnated oxide and the availability of free electrons.

Topchiev et al (14) used the thermographic method of investigation into supported chromium oxide. They state that "... it is evident that... the aluminum silicate retards the reduction of Cr^{+6} to Cr^{+3}, which may be explained by chemical interaction between the aluminum silicate and CrO_3. No interaction is observed between silicon oxide and CrO_3." This last result was explained

by Cossee and VanReijen (19) as being caused by the chromium ions remaining on the surface of the SiO_2 whereas on Al_2O_3 the ions may be build into the surface.

In a study of the structure of active centers in chromium oxide catalysts Aleksandw, et al (24) discuss stabilizing influences of the pure silica gel carrier. These researchers state that the chromium oxide is located on the surface of the support. VanReijen, et al (25) state that no solid solution of Cr^{3+} occurs in silica, but it does occur to a significant extent in alumina. From ESR work at Purdue, Santiago (16) concluded that "... an interaction exists between the chromia and silica which is dependent upon the method of preparation of the aerogel. The chromia on silica does not form a solid solution as it does in the alumina support, and therefore all the chromium ions in the silica are on the surface."

Chascosset and coworkers (18) studied propane polymerization over supported chromia catalysts. They state that they obtain significant activity only in the case where the activation treatment is carried out at a high temperature to allow any chemical interaction between the deposited oxide and the silica to occur. A similar paper published later by nearly the same group of researchers (Viullaume et al (20) concludes ..."that the base of the active centers is formed by an exothermic reaction around 300°C which fixes the Cr(III) layer by a chromosiloxane bond,"

These interactions between chromia and its support can affect catalytic activity. Habershaw and Hill (21) studying chemisorption on chromium oxide polymerization catalysts, reported enhanced activity of chromia-silica as compared to chromia-alumina. They attributed the difference in activity to reactions between hydrated chromium oxide and hydroxyl groups on the silica.

B. Dispersion

Whenever a catalyst is produced by an impregnation of the support by a metal salt or oxide (as in CrO_6), the relative dispersion, arbitrarily defined as the ratio between the area determined by oxygen chemisorption and the theoretical area for two dimensional coverage (18), can vary depending on the method of impregnation, temperature and concentration of solution, and subsequent heat treatments. It has been found that this dispersion can affect the activity and selectivity of the catalyst (26,18,15,27,28,29,30,31).

In their review of physical chemical properties of chromia on alumina, Poole and MacIver (1) stated in summarizing the works of Weller and Voltz (8,9) and Eischens and Selwood (2,3):

"... in a chromia-alumina catalyst the chromia tends to form clumps or crystallites on the alumina surface. The extent of chromia area is a function of the preparational method, as well as if the composition of the catalyst, and thus its measurement by oxygen chemisorption can be a useful guide in catalyst preparation,"

As was discussed in the last section, the carrier has a definite influence on the active site. Deren and coworkers (15) discovered in their study of chromia-alumina that the +5 oxidation state was stabilized during hydrogen peroxide decomposition. The influence of the carrier on the active site changed with chromium content, presumably because of differences in relative dispersion. Both per cent chromia and pretreatment were found to change dispersion.

Charcosset et al (18) also showed that the amount of chromia deposited on the surface altered both the relative dispersion and the average oxidation

number. They concluded that chromium oxide is stabilized by the carrier and that early thermal pretreatment plays an important part in the creation of active centers.

These researchers also reported that the specific activity is maximum for propene polymerization by chromia-alumina when the number of layers of chromium oxide was 2 or 3. They explained this phenomena as being due to the formation of clusters of bulk chromum oxide at higher concentrations which is totally inactive, and when the dispersion is maximum (1 layer), the chemical interactions between Cr atoms do not occur. This also produces low activity. Charcosset points out that the average number of layers does not define completely the dispersion state of the chromium oxide; one must also know the distribution of the number of layers. It is also very likely that several kinds of sites with different activities are contained in the catalyst.

In the third paper in a series by the French workers, Turlier et al (32) discussed the dispersion of Cr_2O_3 on alumina in terms of the magnetic properties of the chromium ions. Their results agreed with the earlier papers where selective chemisorption of O_2 was used to determine the relative dispersion.

The paper by Deren and coworkers (15) contains results similar to those of the French workers (18,32). Deren et al were studying the influence of surface structure of CrO_3-Al_2O_3 catalysts on hydrogen peroxide decomposition. They found that the specific activity passed through a minimum at about 1.5 weight per cent chromium and a maximum at about 4%. They examined the origin of the changes of the specific rate constant as caused by changes in the state of aggregation of CrO_3. At concentrations lower than about 1% chromium ions exist in the state of atomic dispersion. This is in agreement with

the magnetic susceptibility data of Eischens and Selwood (33) and the EPR studies of Kayanshii et al (34). In this region the specific activity remains constant. In the region 1-4%, the small crystal nuclei begin to grow plugging up more and more of the small capillaries. BET measurements showed that the surface area was decreaseing at higher Cr concentrations. The absolute activity remains constant while specific activity drops through a minimum. The authors had trouble explaining the increase in the rate constant per gram of chromium as it increased between 1 1/2% to 4% Cr. They assumed that the activity of the Cr^{+6} acceptor centers increases. This conclusion was supported by the decrease in activation energy at concentrations greater than 1.5%. The decrease in specific rate at Cr concentrations greater than 4% was assumed to be due to the closing of larger capillaries by growing CrO_3 crystallites.

There have been several very recent papers concerning chromium oxide dispersed in a solid solution with Al_2O_3. The first paper by Stone and Vicherman (35) discussed the physical chemical properties of the solid solution. This solid solution is homogeneous in composition whereas on an impregnated catalyst the active species is on the surface and must diffuse into the carrier at high temperatures. Chromia will diffuse readily in alumina but not in silica. They concluded that when chromium oxide is present in low concentrations there are no Cr-Cr interactions, and when the concentration increases Cr-Cr pairs are formed decreasing the effective magnetic moment.

Later papers by Egerton and the other authors (27,28) contained results on oxygen chemisorption and N_2O decomposition as functions of the % Cr in

the solid solution. The general effect of incorporating Cr the alumina as to enhance oxygen chemisorption. The catalyst behavior for oxygen chemisorption per Cr atom changes with increasing Cr content. It decreases considerably and then remains constant until at high concentrations of Cr it increases again. The results for low pressure N_2O decomposition indicate that the absolute rate constant does not increase monotonically with % Cr. Rather it increases rapidly to a maximum at low concentrations of Cr and then drops to a minimum. The rate constant then increases again to the value of pure α-Cr_2O_3. Similar results were determined at higher N_2O pressures (28). The explanation will be expanded here since similar behavior has been found in the chromia-silica system with CO oxidation.

The region of rising activity (low Cr concentration) was attributed to some specific effect of isolated Cr ions. "The presence of elections in unfilled d-orbitals may assist the formation of σ-bonds with adsorbed oxygen". It is well known that isolated transition metal ions are particularly active in catalysis (30,31). When the chromium concentration is increased pairing of the ions occurs and the activity per chromium ion decreases although the absolute reaction rate is continuing to increase. A maximum is then reached where the relatively inactive Cr-Cr pairs predominate. The charge unbalance that was available for chemisorption of O_2 or N_2O is now balanced out in the bonding of two chromium partners. The area of the minimum and subsequent rise in activity can probably be attributed to electron delocalization. That is, no longer are the single Cr^{+3} or Cr pairs isolated in an insulating matrix of alumina. Rather the efficiency of electron transfer in the bulk and surface increases. The Cr ions are no longer isolated single ions or pairs, and the activity increases again as the facility for electron movement developes.

C. Magnetic Susceptibility and Electron Paramagnetic Resonance

Magnetic susceptibility measurements have been used for many years by researchers in catalysis to elucidate information on the oxidation state of the paramagnetic ion, the evidence for interaction covalence and the effectiveness of dispersion of the paramagnetic ions (4). Selwood (4) and Eischens and Selwood (2,3) have shown that for an impregnated chromia-alumina catalyst a break in the susceptibility vs % Cr curve (at about 6% Cr) is related to the concentration at which the chromia is assembled in layers approximately three layers deep. They conclude that only a small fraction of the total BET area is covered with an average of three layers. "The chromia must be aggregated in very small, widely scattered nuclei (4)". They also concluded that the chromium oxide disperses on silica to at least the same extent as on alumina (3).

Matsunaga (36) working on the same catalyst as did Selwood a decade earlier, concluded by magnetic susceptibility that although the alumina support stabilizes the plus-three state of chromium oxide it is not effective enough to prevent the oxidation of the surface. He states, ..."In the limiting case, infinite dilution of chromium, the oxidation number increases until it finally reaches six, namely chromia is completely oxidized to chromic anhydride. This chemical change is in sharp contrast to our knowledge of the thermal decomposition of chromic anlydride."

Another device that utilizes the magnetic properties of the active centers, electron paramagnetic resonance (EPR), has been used quite extensively on chromia systems. EPR measurements yield values of the relative amounts of the

odd states of chromium oxide. A large amount of work on chromia-alumina catalysts has been reported by O'Reilly and MacIver (37,38). They concluded that the chromia is clustered in patches on the support; these patches become more dispersed as the concentration of chromia is decreased. The dispersed chromia was called the δ-phase and the bulk chromia was named the β-phase. In the intermediate concentration (.5-3.6 wt. %) the δ-phase intensity did not change upon oxidation of the catalyst indicating that the alumina-chromia interaction stabilized the ion in the Cr^{3+} state. The β-phase signal changed considerably upon oxidation. They found that the δ-phase resonance was due to isolated Cr^{3+} ions widely dispersed on the alumina. The β-phase was interpreted as due to Cr^{3+} ions clustered on the surface. A third phase, γ, was also found and was interpreted as being election trapped in the oxidized chromia. "Intermediate types of Cr may involve small clusters of Cr^{3+} ions which, due to dipolar and, in particular, exchange interactions, do not contribute to either δ-or β-phase type resonance" (38).

Thus, the results of O'Reilly and MacIver differ from those of Matsunago (36) who stated that at infinite dilution all chromium in the +3 valence state would be converted to +6. As O'Reilly and MacIver point out though, Matsunago's data are for concentrations only as low as 1% Cr.

Other investigators have used EPR, to determine the nature of the active sites during reaction. Kazanshii et al (34,39,24) have reported on using EPR to investigate the stable oxidation state of chromium oxide on different supports for polymerization of ethylene, and propane. The concluded that the +5 ions are connected with the stabilizing action of the crystal lattice of the carrier (alumina) and that these ions are located on the surface as adsorption centers. Eden et al (40) used EPR measurements to determine that possibly Cr^{+4} not Cr^{+5} was the active site for polymerization. They assert

that it is quite reasonable that Cr^{+4} is stabilized by the support. In yet another paper concerning supported chromium oxide polymerization catalysts, Turlier et al (32) used EPR to define more precisely the dispersion state of chromium oxide.

Cossee and Van Reijen (19) studied the valence state of chromium with magnetic methods. They conclude that the yield of Cr^{+5} on silica was very poor, and Cr^{+3} is not present in considerable amounts on SiO_2. Van Reijen et al (25) in their study of supported chromia catalysts for dehydrogenation were able to distinguish the surface state of the chromia as being considerably different from the bulk.

The view held by Ellison and Sing is "that the γ-phase signal must be associated with the surface of a thin layer, or clump, of chromium oxide rather than with Cr^{+5} dispersed in the oxide matrix".

In a letter to the editor of the Journal of Chemical Physics, Howard and Lindquist (42) reported a fourth EPR phase, the ϕ phase. They used low concentrations of chromia on alumina, and attributed the ϕ line to electrons trapped on the semiconductor chromia. They also found that the δ-phase (dispersed phase) was dependent upon the alumina support since it does not appear in samples of bulk chromia or chromia on silica. These Cr^{3} ions are isolated either on the surface or in the interior of the alumina.

In a review of magnetic methods in catalysis, Kokes (43) explained the absence of the δ-phase on silica, "In a silica lattice the environment is tetrahedral. This virtually eliminates the δ-phase since Cr^{3+} is unstable in a tetrahedral environment."

Recent evidence, however, points to the contrary. Not only did Santiago (16-44) find a δ-phase in his EPR studies on chromia-silica he also found that contrary to the work of O'Reilly and MacIver (38) performed on an alumina support, the δ-phase on silica was easily oxidized even at room temperature. Since the chromia on silica does not form a solid solution as it does in the alumina support all of the chromium ions in the silica aerogel are on the surface. O'Reilly, Salamony, and Squires (46) reported recently that the dispersed δ-phase could be enhanced by oxalic acid complexing.

D. Oxidation States

Chromium oxide is generally found to exist in any of the oxidation states between +2 and +6. The bulk of evidence presented in the previous sections seems to indicate that by controlling the dispersion of the chromia on the carrier, different surface oxidation states might be stabilized. Since different oxidation states seem responsible for the different reactions (hydrogenation, dehydrogenation, polymerization, hydrogen peroxide decomposition, CO oxidation by O_2, and CO oxidation by NO), then the activity or the selectivity may likewise be controlled.

Many transition metal oxides exhibit dual function behavior; they have the ability to promote two different types of reactions (13). This polyfunctional behavior is dependent on the position of the Fermi level which in turn is a function of the adsorbate/adsorbent interaction. "The ability to promote the different kinds of reactions is latent in the chromia catalyst depending on its method of preparation, the relative activities being determined by the nature of the reactants adsorbed on the surface and their interaction with the catalyst..." (13).

Shelef et al (47) in their work on catalysts for automobile exhaust emission control found that for a chromia-alumina catalyst the surface oxidation state during reaction varied with the different reactants. They were able to measure the average surface oxidation state during the carbon monoxide oxidation by O_2, NO, and both O_2 and NO. To keep the bulk oxidation state at the +3 valency they kept the oxygen partial pressure below .03 atm. In this way the average oxidation state was determined without bulk contributions.

3. Kinetics of the CO Oxidation over Supported Chromium Oxide

a. Adsorption and Kinetics

The chromium oxide catalyst is used industrially in the dehydrogenation of paraffinic hydrocarbons and the polymerization of ethylene and propene (18,48,49,39,50,51,25). It was also under consideration as a catalyst for removal of CO from automobile exhausts (73,47,67). Chromia has been the subject of extensive work in both the gel and supported forms (10,19,52,45,53, 54,55,74,56,57).

Studies have also been reported on the chemisorption of CO, O_2 and NO on supported and unsupported chromium oxides (50,59,60,16,61). Santiago (16) studied the infrared spectra of the chemisorption of NO as well as CO, CO_2, O_2, NO_2, and NH_3 at Purdue. The CO oxidation by oxygen over chromia-silica has also been investigated at Purdue and a considerable amount of literature concerning adsorption and kinetics of CO and O_2 was cited by Kuchanski (62) and Battaglia (63).

The poisoning effect of water vapor and oxygen have also been examined by other researchers (64,56,7,65). Both tend to change the chromium oxide valence state readily (47,25). It was also pointed out by Shelef and Otto (47) that the oxygen competes strongly with carbon monoxide for chemisorption on chromia-alumina during the oxidation reaction. Burwell, et al. (65) demonstrated that carbon monoxide was not as strongly chemisorbed as oxygen on chromia gel. Also carbon dioxide was mentioned briefly as being more strongly adsorbed than CO but less so than oxygen. Santiago (16) found the same general results on chromia-silica aerogel.

It is generally assumed that oxygen adsorption is near equilibrium with the surface while CO and CO_2 molecules complete for the open sites (66). NO

does not adsorb as readily as O_2, and therefore there are more cites for chemisorption of CO. However, when both oxidizing gases (O_2 and NO) are present simultaneously, the O_2 chemisorbs strongly increasing the average surface oxidation state and lowering the reaction rate to that comparable to when no nitric oxide is present (47).

Burwell and Haller (65) viewed the adsorption of oxygen as a charge transfer complex. Although the exact state of adsorbed oxygen was not established they suggested (75)

$$Cr^{3+} + O_2 = Cr^{4+} O_2^-$$

The chemisorption of oxygen entails a change in the oxidation state of the chromia. Carbon monoxide is generally thought to react with the oxidized chromia reducing it to a lower oxidation state with the production of CO_2.

Shelef et al (47) have made a study of the oxidation of CO by O_2 and NO over chromia-alumina. They report that different oxidation states are stabilized during the different reactions and that the NO reaction is much faster than the oxidation by O_2. A considerable amount of N_2O was found in the outlet during oxidation by NO. This was determined as being a true gas phase intermediate and the following stoichiometric reactions were written (67):

$$2NO + CO \rightarrow CO_2 + N_2O$$

$$N_2O + CO \rightarrow CO_2 + N_2$$

The evidence (47,67) is that N_2 does not form until most of the NO has been reduced to N_2O. Chromia catalysts do not have strong activity for N_2O decomposition (68,69,70,71,66) or reduction by CO (47,68,67). Shelef et al (47) point out that when NO is used in excess over CO then the threshold temperature for N_2 formation is increased. This indicates that it is easier for CO to reduce NO to N_2O than it is to complete the reduction of N_2O to N_2.

b. Activity and Selectivity vs % Cr

Stone (72) reported recently that the activity and selectivity of a catalyst are functions of the concentration of the metal oxide, ie. degree of dispersion. Recent papers by Egerton, Stone, and Vickerman (27,28) described the behavior of chromia-alumina as a function of the % Cr in solid solution. The N_2O decomposition was used as the test reaction. Their results indicate that the activity at low concentrations of chromium (well dispersed in the alumina phase) uses very rapidly as additional chromium is added to the catalyst. A maximum in the absolute rate is reached, and there after the activity decreases. A minimum is attained at about 5% Cr, and the activity rises again nearly monotonically to the value at pure α-Cr_2O_3.

Other authors have reported similar behavior over chromia-alumina, eg. hydrogen peroxide decomposition (15) and polymerization (18). On those studies where it was measured, the average oxidation state of the chromium oxide was found to vary as the dispersion was changed.

The maximum and minimum in absolute activity has not been previously reported for either chromia-silica catalyst or the CO oxidation reaction.

C. Technical Results

The bulk of the experimental work over the past year has centered on the following:

1) Characterization of the Union Carbide Gradientless Reactor.

2) Catalyst activity and selectivity for CO oxidation by O_2 + NO.

3) Catalyst activity as a function of % Cr.

4) Catalyst surface characterization.

1. Union Carbide Reactor

Interphase and intraparticle mass and heat transfer processes accompany the heterogeneous catalytic reaction, and normally only bulk phase measurements of concentration and temperature are available. External heat and mass transfer gradients occurring between the bulk phase and catalyst surface and internal gradients produced within the catalyst pellet can be minimized but never removed entirely.

The temperature and composition on the catalyst pellet may be determined by designing a reactor in which external heat and mass transfer gradients are minimized so that gas phase values closely approximate the surface conditions. In addition the reactor must be run in such a way that differential conversions are obtained over the catalyst thus minimizing concentration gradients through the reactor. This method of differential kinetics results in composition changes of small magnitude which are difficult to accurately analyze. Therefore, a reactor is needed which produces a relatively larger percent conversion overall but retains the advantages of differential kinetics over the catalyst.

The vapor phase gradientless reactor developed by Bertz et al (76,77) at Union Carbide meets all of the criteria. This reactor, shown in Figure 1,

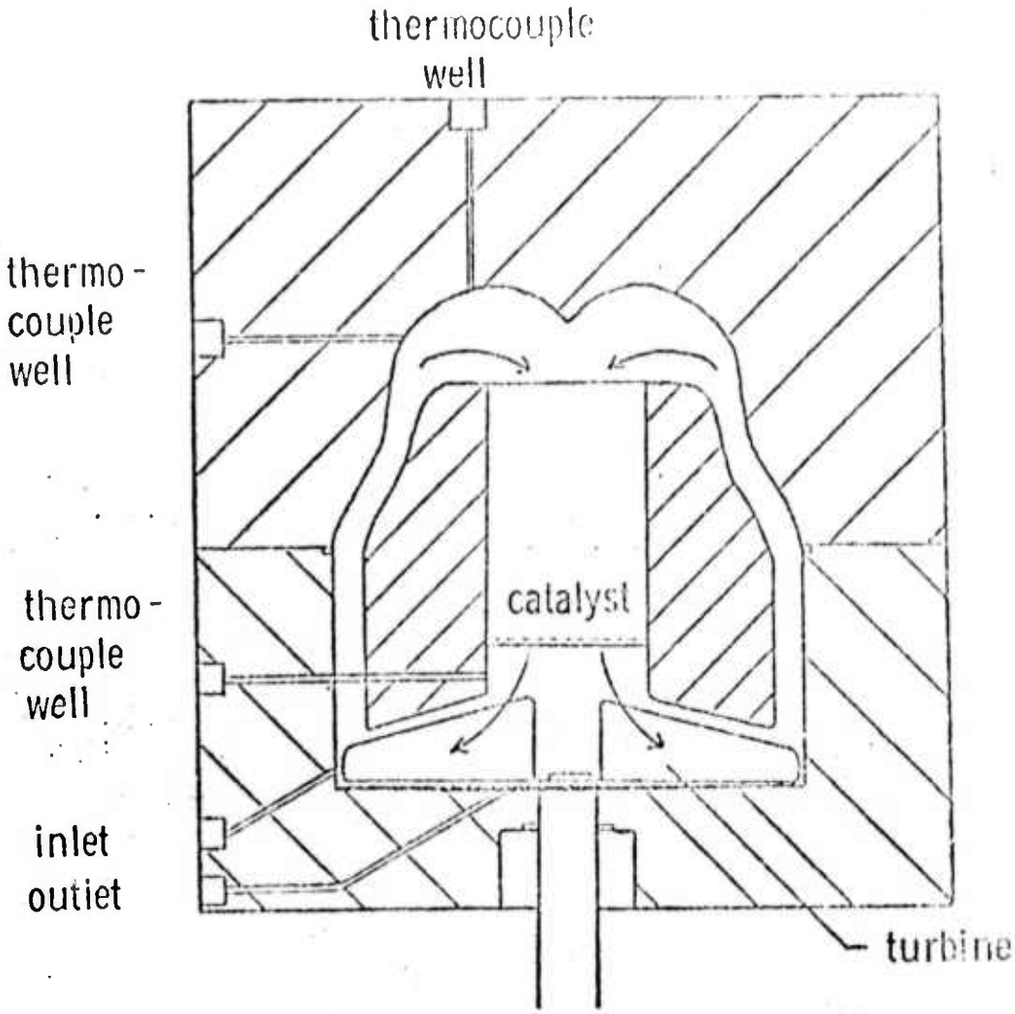

FIGURE 1.
Union Carbide Reactor

is made of all 316-stainless steel material, and it is designed to achieve temperatures to about 550°C and pressures exceeding 1000 psi. A large internal recycle rate allows higher overall conversions to be achieved while maintaining differential conversions per pass. The large mass flux minimizes film effects at the pellet surface. The reactor has a well-defined internal gas flow, hence the recycle rate and consequently heat and mass transfer rates can be estimated (76,77,78).

The catalyst pellets are placed in the center tube. The turbine at the reactor bottom is driven by a magnetically coupled stirring assembly. This turbine forces the gas up along the annulus on the outside of the draft tube and then down through the catalyst bed. Thermocouples are used to measure the temperature within the catalyst bed as well as the temperature rise of the gas across the bed.

Before meaningful kinetic data can be obtained the entire reactor system must be "characterized". Blank reactor runs must be made in order to determine whether the empty reactor and for pure silica support have any activity for CO oxidation. The reactor must be tested for bulk mixing characteristics and accurate temperature measurement free from radiation influences. The catalyst system must also be checked to determine catalyst stability and reproducibility of results as well as gradientless operation and effects of pure diffusion (effectiveness of catalyst surface).

The following conclusions were drawn as a result of the reactor "characterization":

1) The reactor showed negligible activity after the interior had been well oxidized at moderate temperatures.

2) Pure silica has negligible activity.

3) The reactor gas phase is perfectly mixed under reaction conditions, even without mechanical agitation.

4) Radiation effects are negligible.

5) The catalyst is relatively stable after a pretreatment of two hours in cycling oxygen and carbon monoxide at 450°C. An activation of 2 hours at 400°C in flowing Ar is used before activity is measured.

6) Reaction rates above $2x10^{-5}$ moles of CO_2 formed per min. per g of catalyst are not necessarily gradientless.

7) No intrapellet heat or mass transfer limitations exist when the reaction rate is below about 10^{-4} moles/min g.

2. Activity and Selectivity for CO Oxidation by O_2 and NO.

Two series of catalysts were prepared by different methods to obtain varied dispersion of the transition metal oxide on a silica carrier. A summary of the catalysts, A and B, is shown in Table 1.

Table 1
Catalyst Preparation

CATALYST SERIES	NUMBER	MATERIALS	% C_r Range
A	12	CrO_3	.28 - 20%
B	12	$Cr(NO_3)_3 + H_2C_2O_4$	.04 - 4.71%

The procedures for preparing the two catalyst series were identical except for the starting materials. The chemicals were dissolved in distilled water. Silica gel granules were added, and the system was allowed to stand overnight. The excess solution was then drained off, the pellets were placed on absorbent paper to dry for 2 hours, and then they were placed in an oven for 15-20 hours at 120°C. The A series catalysts were orange, and the B series were blue

indictative of the nitrate compound. Pretreatment consisted of two cycles of alternating oxygen and carbon monoxide for a total of two hours at 450°C. The catalyst were cooled and placed in sealed containers. All catalysts were shades of brown to dark green depending on Cr concentration. The nitrogen compounds and oxalic acid were expelled from the B catalyst during pretreatment.

One of the research objectives was to find a difference in catalytic activity and for selectivity between the two catalyst series in the region were the Cr concentration overlaps. This might then be correlated with the oxidation state of the chromium oxide stabilized during reaction.

Preliminary work with only the $CO + O_2$ reaction indicated that at 233°C and at low concentrations, about 1% Cr, a significant difference in activity might exist. It seemed likely that this was due to a real difference in dispersion since at below .5% Cr, where atomic dispersion predominates, no activity difference could be perceived.

Additional data have now been obtained over a larger number of catalysts with a larger range of % Cr (see Table 1). Temperatures were varied to allow for the determination of activation energies. The following reactions were analyzed at 160-260°C:

$$CO + 1/2\ O_2 \rightarrow CO_2$$

$$CO + NO \rightarrow 1/2\ N_2 + CO_2$$

$$CO + (NO + O_2) \rightarrow N_2 + CO_2$$

Results of the $CO + O_2$ activity for the preliminary work as well as for the more recent analysis is shown in Figures 2 and 3. It must be pointed out that for preliminary work only a 1 hour pretreatment was used whereas for all later analysis the catalysts were pretreated for two hours. This obviously

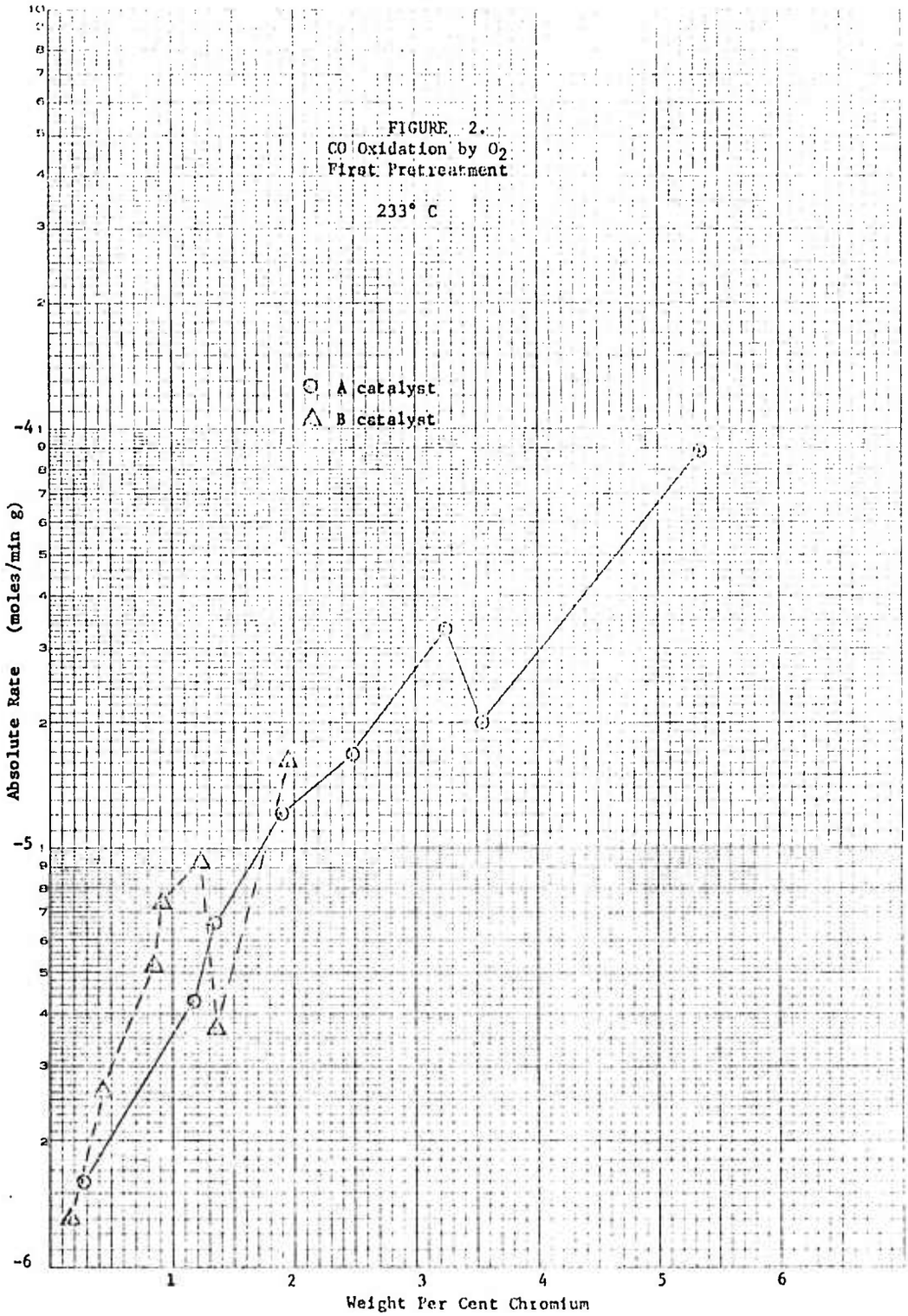
FIGURE 2.
CO Oxidation by O_2
First Pretreatment
233° C
A catalyst
B catalyst
Absolute Rate (moles/min g)
-4
-5
-6
1
2
3
4
5
6
Weight Per Cent Chromium

has an effect since the longer pretreatment results in a catalyst of lower activity for oxidation of carbon monoxide by oxygen. The shapes of the curves, however, are identical. This observation will be expanded upon later.

Figure 3 portrays the relationship between the absolute rate of CO oxidation by O_2 and the weight per cent chromium. Both catalyst series A, chromic acid impregnation, and B, chromium nitrate - oxalic acid complexing, are shown at two different temperatures.

The data for the NO reaction have not been shown since the analysis was not as accurate as for the simpler O_2 system. The quadrapole mass spectrometer was not able to distinguish between the relative yileds of N_2O and CO_2, and the reaction rate analysis is based on the amount of CO_2 produced since this is always the same as the amount of CO consumed due to stoichiometry. This problem may now be solved since there is evidence (47) that very little nitrogen is formed and that the reaction stoichiometry may be written as

$$CO + 2NO \rightarrow N_2O + CO_2$$

Since the relative sensitivity of the mass spectrometer for the gases is known the peaks can now be resolved assuming equal amounts of CO_2 and N_2O are formed.

A second problem is also apparent; the two different reaction rates differ by about one order of magnitude. It is therefore extremely difficult to achieve an overlapping temperature region where conversions remain relatively low and diffusion limitations are absent.

When O_2 is added to the NO reaction system another problem arises, NO_2 is formed wheich further confuses the analysis. It is evident, however, that the reaction rate is about the same as when oxygen is the only oxidizing agent; the NO does not take part in the CO conversion.

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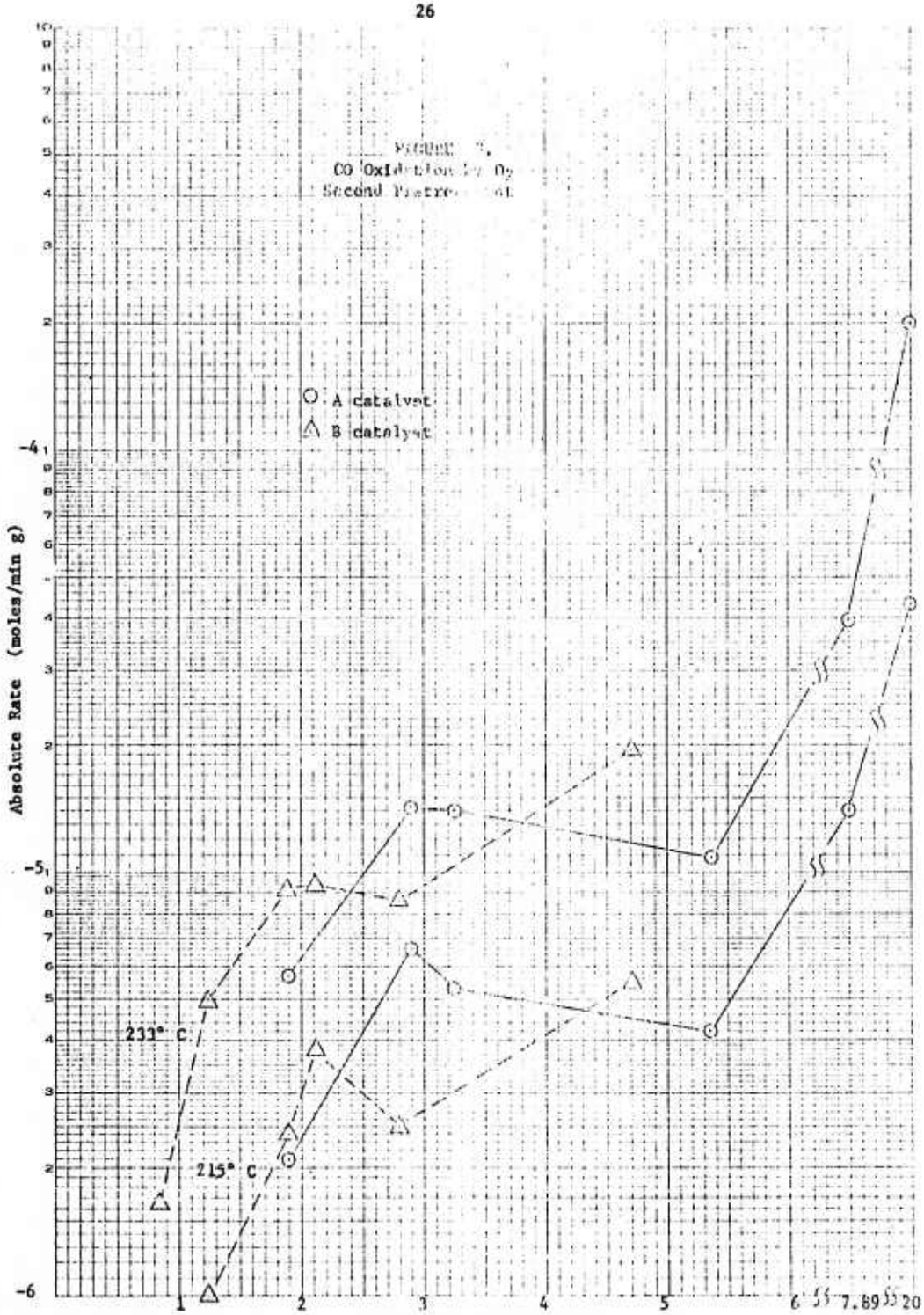


It was originally believed that only about 4 or 5 catalysts of each type, A and B, would be necessary to distinguish a difference in activity and selectivity in an overlapping % Cr region. However, due to the relative maxima and minima which have become apparent this "simple" region does not exist. Already 24 catalyst samples have been analyzed.

When the analysis is capable of showing that there is a region of significant activity and/or selectivity difference, these data will be correlated with an analysis of the relative dispersion and valency of the chromium oxide. No data have yet been determined for either of the correlations.

The following conclusions have been drawn concerning activity and selectivity.

1) Both the A and B chromia-silica catalysts are more active for CO oxidation by NO than by O_2.
2) The NO does not seem to participate in the reaction when significant amounts of O_2 are present.
3) There is a significant reactivity difference between the A and B catalysts series which varies with Cr concentration.

3. Catalyst Activity vs % Cr

Probably the most interesting result of this research is the relationship between the absolute reaction rate and the amount of chromium on the silica. As was apparent from Figures 2 and 3, the rate passes through at least one maximum and minimum. This effect, however, is very sharp, and any data that are too far apart can easily miss an inflection in the curve. At this time one cannot definitely characterize the entire relationship between activity and % Cr.

The specific activity, defined as absolute activity divided by the weight fraction of chromium in the catalyst, is plotted as a function of the % Cr in Figure 4. The relative effectiveness of the chromium atoms can now be determined. It is readily apparent that the reaction rate per chromium atom is not constant and that there is some effect caused by the addition of more chromia to the catalyst.

This effect of % Cr on the activity of CO oxidation over a chromia silica catalyst has never been reported although other researchers have found similar behavior on different catalysts and reactions (see BACKGROUND section). More data are necessary to better characterize the curve and to prove reproducibility of the catalysts impregnation procedure and subsequent reaction rate analysis.

A plot of the apparent activation energy vs % Cr is shown in Figure 5. The minimum in B at about 2% and A at about 3% correspond to the areas of maximum activity. The total range in activation energy is from about 10 to 22 kcal.

The effect of pretreatment duration is evident from Figures 2 and 3. The activity decreases after further heating at 450°C, but the relative shapes of the curves remain constant.

The effect of using the more dispersed catalyst, oxalic acid complexed (B), is to shift the maximum to lower concentrations. This is evident from Figures 2, 3 and 4. A reasonable explanation for this pehnomenon cannot be ascertained without additional information, i.e. dispersion, oxidation state, etc.

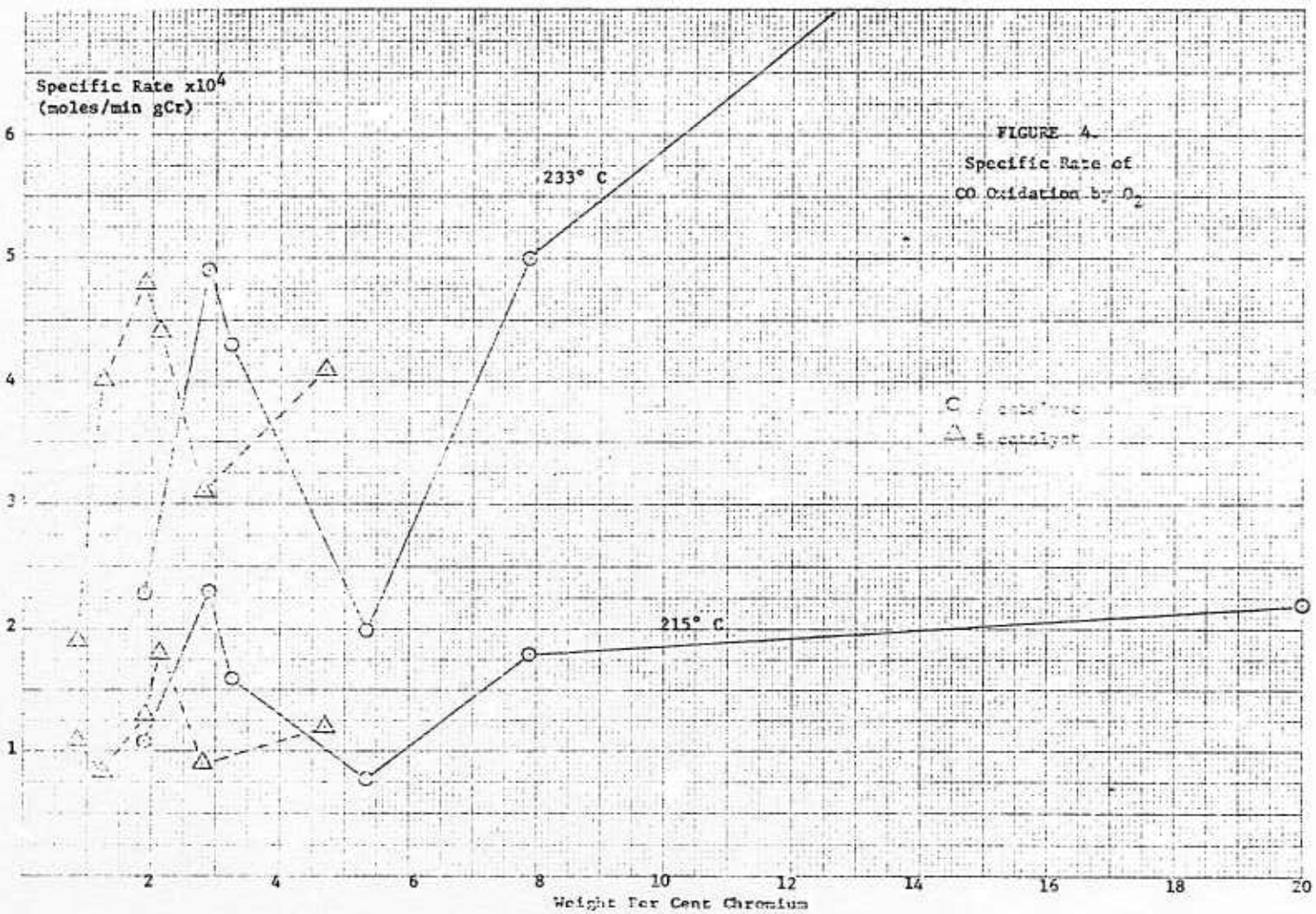
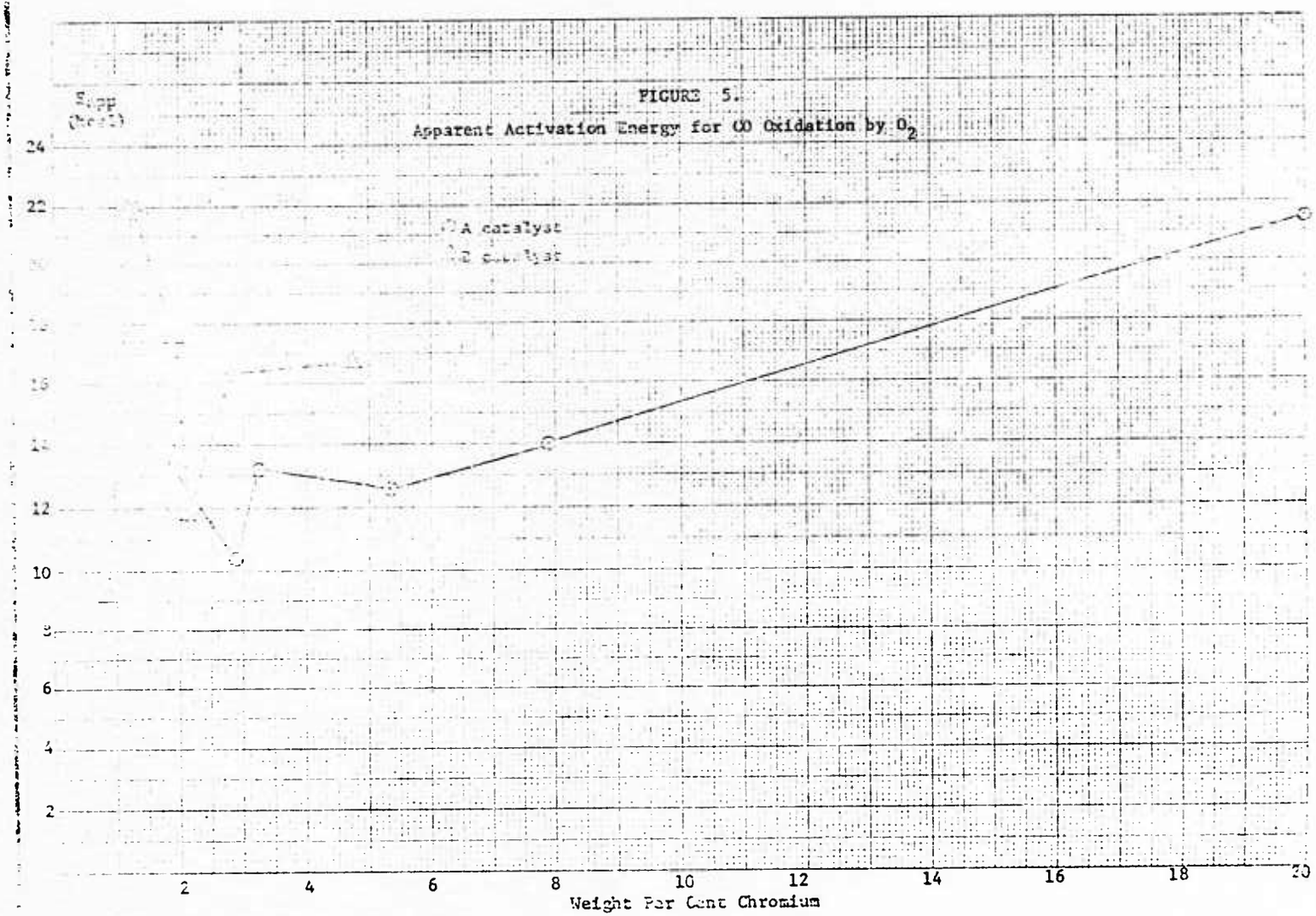


FIGURE 4.
Specific Rate of
CO Oxidation by O_2

46 1323

FIGURE 5.

Apparent Activation Energy for CO Oxidation by O_2



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ESR measurement (46) of Cr^{+3} on SiO_2 have shown that there is a definite change in the δ-phase (dispersed phase) peak at around .1% Cr. Very little kinetic data are in this region. No data have been obtained for the catalyst produced by oxalic acid complexing at concentrations greater than 5% primarily because the oxalic acid crystallizes in the chromium nitrate solution at room temperature. Heating will dissolve the acid again; however, it has been reported (3) that the heating of the impregnation solution may also alter the dispersion.

4. Catalyst Surface

It is well known that impregnation of a support by an active species alters the physio-chemical properties of the material as well as certain mechanical properties. Total surface area of the catalyst is certainly a function of the amount of chromium oxide deposited on the carrier (18). This effect was examined for sample A-3 (1.35% Cr).

The BET surface area by N_2 adsorption was calculated to be about 300 m^2/g which was somewhat less than the 340 m^2/g supplied by Davison Chemicals for the pure silica. This result indicates that the impregnation procedure causes some loss in total surface area even at such low concentrations. No further data investigating temperature effects of the silica or determining surface areas of the other catalysts have yet been obtained.

Catalyst A-3 was also analyzed for crystal structure by X-ray diffraction. No chromia lines were found indicating either an amorphous chromium oxide or crystal size of less than about 50 A.

D. Proposed Work

To finish meeting the objectives that have been presented, several experimental procedures are proposed. They are discussed in the following subsections.

1. Activity vs % Cr.

Some rather interesting results have already been found for the relationship between reactivity of the catalyst and the concentration of chromium oxide. Since the curve changes rather sharply, more data are necessary to characterize the regions of maximum and minimum as well as the region of low % Cr (see Figures 2, 3 and 4).

It is proposed that the following catalysts be prepared, analyzed for Cr concentration, and their activity for the NO and O_2 oxidation of CO be determined.

Table 2

Catalyst	% Cr	
A-10	.2%	CrO_3
A-15	1.0%	CrO_3
A-16	2.4%	CrO_3
B-10	.2%	$Cr(NO_3)_3 + C_2H_2O_4$
B-14	4.0%	$Cr(NO_3)_3 + C_2H_2O_4$

It is also proposed that replicate reaction rate runs be made on several catalysts. Another load of catalysts from the original batch should be run to determine reproducibility of catalyst activity. Previous results have shown that there is a maximum difference of out 10% for replicate runs of the same catalyst.

2. Oxidation State of Chromium Oxide During Reaction

The proposed method of determining the surface oxidation state of the catalyst in situ is a modification of the technique described by Shelef (47). After the reaction has been reached a steady state the reactor is purged with A_r. The temperature is increased to 400°C at which time a known flow of CO and A_r are metered through the reactor. The exit composition is examined continuiously by the mass spectrometer. A curve of exit CO_2 composition vs. time is constructed as in Figure 6. From the area under this curve and the known flow rates and Cr concentration, the moles surface O_2 per atom of chromium can be calculated.

The obvious drawback of this method is that the final oxidation state of the surface (after reduction) is not known precisely, and, therefore, this procedure is probably rather qualitative. Preliminary results have indicated that the procedure reproduces well, the CO_2 formed is dependent strongly on oxidation and reduction temperatures, and, in agreement with Shelef (47), the oxidation state after oxidation by NO is lower than when O_2 is used. This final result was also valid during reactions using O_2 or NO.

The maximum amount of CO_2 that can be produced per grain of catalyst is given by:

$$3 \times \frac{\% \, Cr/100}{52} \text{ moles/g catalyst}$$

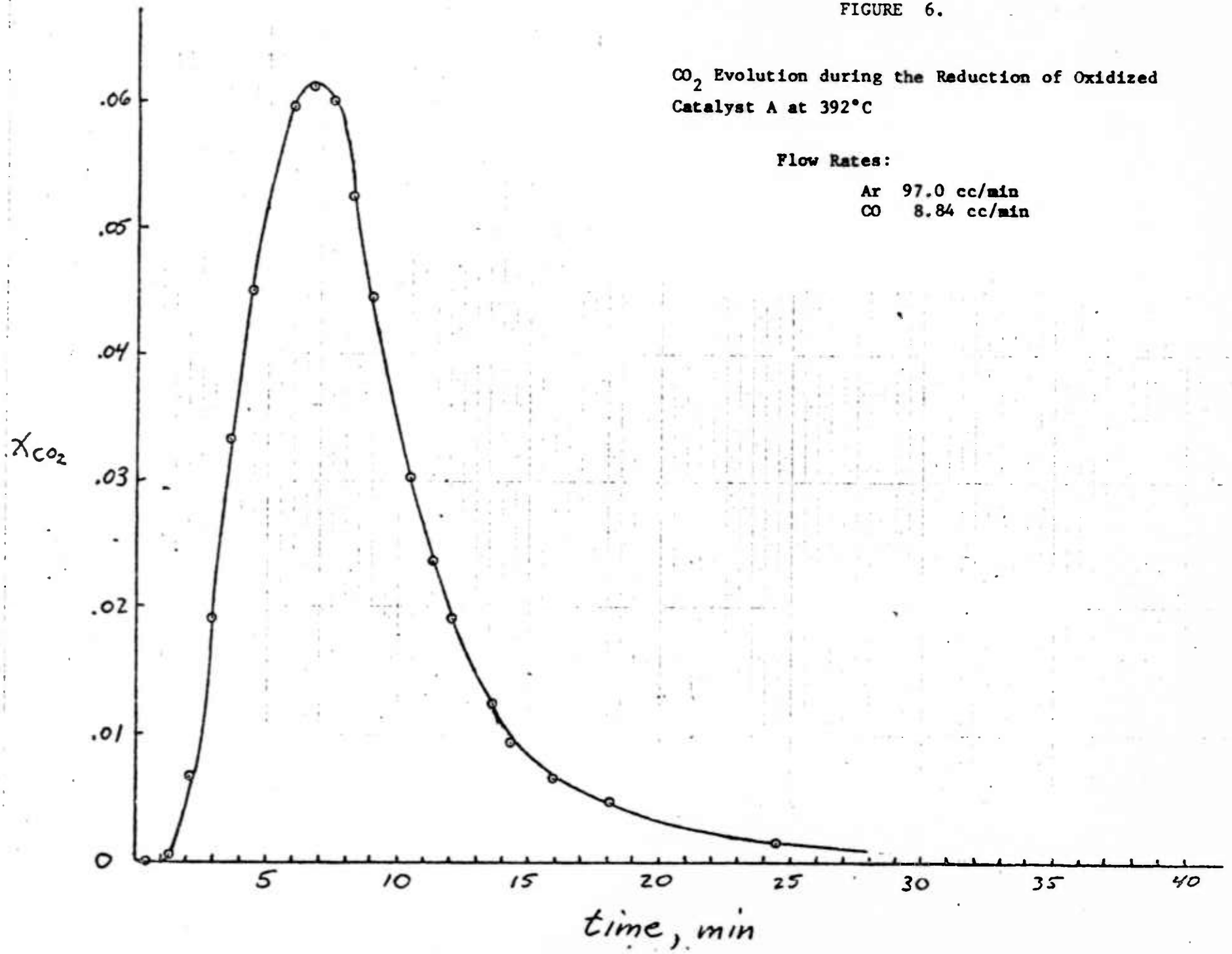
where there are 3 oxygen atoms (CO_2 molecules) transfered per Cr atom (+6 to +3) and 52 is the molecular weight of chromium. The maximum mean oxidation state of all the chromium oxide after O_2 treatment at 233°C was about 4. This is lower than was reported by Shelej (47), but this is to be expected since not all of the chromium oxide of the catalyst (A-7, 1.9%) would be surface oxide.

FIGURE 6.

CO_2 Evolution during the Reduction of Oxidized Catalyst A at 392°C

Flow Rates:

Ar 97.0 cc/min
CO 8.84 cc/min



The total amount of oxygen transferred by this oxidation reduction cycle will be correlated with the reactivity of the A and B catalysts for the NO and O_2 oxidation of CO as well as the dispersion measurements to be discussed in the next section.

A second method for determining oxidation states is also under consideration, namely the use of Electron Spectroscopy for Chemical Analysis (ESCA). This technique is capable, in theory at least, of determining the relative amounts of all the oxidation states of surface chromia. This work is being done in conjunction with the Chemistry department at Purdue.

3. Dispersion

The relative dispersion of chromia on silica is being currently determined for several of the catalyst samples. The samples that have been pretreated and used in reactions will be used in this study. The two series of samples will be analyzed, the A catalyst produced by impregnation with CrO_3 and the B catalyst impregnated with chromium nitrate complexed with oxalic acid. An oxygen chemisorption method will be employed to determine the chromia dispersion (18). These dispersion results will be related to the catalyst preparation method, the catalyst activity and selectivity for CO oxidation, and the stable surface oxidation states referred to in the previous section.

The dispersion data may also be related to the activation energy. A significant change in E with dispersion might indicate that the site which is active for CO oxidation changes in character.

4. Simultaneous reduction and oxidation catalyst

If it is possible to effect a significant difference between the roles of the two different catalysts for the CO oxidation by NO and O_2, then it

might be possible to construct a catalyst with active sites that both reduce NO and oxidize CO in excess O_2. The method for accomplishing this feat will come from the results of work that has been discussed in this section. Some ideas for the preparation method are:

1. Mix two batches with different dispersions. This gives two catalysts -- one reducing and one oxidizing in the same atmosphere.
2. Same as #1 using Cab-O-Sil. Mix two batches as a fine powder and press into pellets.
3. Consecutive preparations might be a possibility.
   a. Prepare catalyst with $Cr(NO_3)_3$ and oxalic acid.
   b. Dry and oxidize the oxalic acid and nitrate until only Cr ions are left.
   c. Impregnate again using chromic acid.
   d. Dry and pretreat.

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