



Surface chemistry model of cobalt-molybdenum catalysts supported on planar γ -Al₂O₃
by Timothy Dean Kirkpatrick

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in
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Abstract:

Cobalt-molybdenum catalysts supported on γ -Al₂O₃ are well known for their success in the hydrotreating of petroleum feedstocks and coal liquifaction products. Their surface structure has been studied by several methods including recent attempts by surface science techniques. Applications of the surface science techniques are limited due to the porosity and insulating character of the γ -Al₂O₃ supports. This study presents an alternative approach by replacing the porous γ -Al₂O₃ supports with planar γ -Al₂O₃ grown on aluminum substrates. Preparation of the model catalysts was performed completely in situ. The γ -Al₂O₃ was prepared by thermally oxidizing the planar, polycrystalline aluminum substrates. The molybdenum and cobalt were vapor deposited to approximately monolayer coverage and subsequently oxidized. The planar model catalysts were characterized by ESCA, SIHS and AES and their surface structure compared to that of industrial catalysts.

The ESCA Al 2p band was used to monitor the oxidation of the aluminum. Shifts in the binding energy enabled differentiation between amorphous and crystalline Al₂O₃. Subsequent deposition and oxidation of molybdenum resulted in broadening and binding energy shifts of the Al 2p and Mo 3d bands suggesting interaction between the molybdenum and the γ -Al₂O₃.

Addition of cobalt onto the molybdenum layer appeared to result in an interactive phase between the cobalt and the molybdenum. The Co 2p band indicated the cobalt was in tetrahedral coordination. Depth profiles, obtained with SIMS, indicated the cobalt was interacting primarily with the molybdenum. When the order of metals deposition was reversed, the cobalt appeared to interact primarily with the γ -Al₂O₃ in a CoAl₂O₄ type phase. The AES line scans suggested that both the cobalt and molybdenum were well dispersed as would be characteristic of a uniform monolayer coverage.

The findings of this study indicate similarities between the surface structure of the planar model catalysts and the industrial catalysts.

SURFACE CHEMISTRY OF MODEL COBALT-MOLYBDENUM CATALYSTS

SUPPORTED ON PLANAR $\gamma\text{-Al}_2\text{O}_3$

by

Timothy Dean Kirkpatrick

A thesis submitted in partial fulfillment
of the requirements for the degree

of

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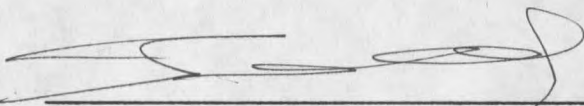
APPROVAL

of a thesis submitted by

Timothy Dean Kirkpatrick

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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ABSTRACT

Cobalt-molybdenum catalysts supported on $\gamma\text{-Al}_2\text{O}_3$ are well known for their success in the hydrotreating of petroleum feedstocks and coal liquifaction products. Their surface structure has been studied by several methods including recent attempts by surface science techniques. Applications of the surface science techniques are limited due to the porosity and insulating character of the $\gamma\text{-Al}_2\text{O}_3$ supports. This study presents an alternative approach by replacing the porous $\gamma\text{-Al}_2\text{O}_3$ supports with planar $\gamma\text{-Al}_2\text{O}_3$ grown on aluminum substrates.

Preparation of the model catalysts was performed completely in situ. The $\gamma\text{-Al}_2\text{O}_3$ was prepared by thermally oxidizing the planar, polycrystalline aluminum substrates. The molybdenum and cobalt were vapor deposited to approximately monolayer coverage and subsequently oxidized. The planar model catalysts were characterized by ESCA, SIMS and AES and their surface structure compared to that of industrial catalysts.

The ESCA Al 2p band was used to monitor the oxidation of the aluminum. Shifts in the binding energy enabled differentiation between amorphous and crystalline Al_2O_3 . Subsequent deposition and oxidation of molybdenum resulted in broadening and binding energy shifts of the Al 2p and Mo 3d bands suggesting interaction between the molybdenum and the $\gamma\text{-Al}_2\text{O}_3$.

Addition of cobalt onto the molybdenum layer appeared to result in an interactive phase between the cobalt and the molybdenum. The Co 2p band indicated the cobalt was in tetrahedral coordination. Depth profiles, obtained with SIMS, indicated the cobalt was interacting primarily with the molybdenum. When the order of metals deposition was reversed, the cobalt appeared to interact primarily with the $\gamma\text{-Al}_2\text{O}_3$ in a CoAl_2O_4 type phase. The AES line scans suggested that both the cobalt and molybdenum were well dispersed as would be characteristic of a uniform monolayer coverage.

The findings of this study indicate similarities between the surface structure of the planar model catalysts and the industrial catalysts.

INTRODUCTION

Cobalt-molybdenum on gamma alumina ($\text{Co-Mo}/\gamma\text{-Al}_2\text{O}_3$) catalysts are well known for their success in the hydrotreating of petroleum feedstocks and coal liquifaction products. These fuel sources contain elements, such as nitrogen and sulfur, which must be removed to meet environmental standards. The most common catalyst for this purpose is sulfided $\text{Co-Mo}/\gamma\text{-Al}_2\text{O}_3$.

In the past, manufacture of catalysts, such as $\text{Co-Mo}/\gamma\text{-Al}_2\text{O}_3$, has been regarded more as an art in which successful recipes were acquired by trial and error rather than scientific understanding of the processes involved [1]. However, over the past decade scientists have become more interested in the design of catalysts with well defined properties.

This interest has been spurred by the advent of the application of modern surface science and other techniques to catalysis research. These techniques provide the researcher with the ability to study the catalyst surface structure and reaction phenomena on a microscopic level. Improved understanding of the catalyst surface structure and how it relates to catalytic activity and selectivity will allow for the design of improved catalysts. This idea

is particularly enticing for the Co-Mo/ γ -Al₂O₃ catalyst since the activity and selectivity of this catalyst, and therefore the surface structure, is greatly dependent on the preparation parameters [2].

A large volume of research on Co-Mo/ γ -Al₂O₃ catalysts has been conducted with the goal of trying to characterize its surface structure. Numerous analytical techniques such as electron spectroscopy for chemical analysis (ESCA), Mossbauer emission spectroscopy (MES), Raman spectroscopy, infrared spectroscopy (IR), ion-scattering spectroscopy (ISS), and x-ray diffraction (XRD) have been employed in these studies. While the application of these techniques has been successfully demonstrated, there is still much debate as to the structure of the catalyst and how the structure relates to activity and selectivity.

Because the industrially used γ -Al₂O₃ supports are very porous insulators, some of the more powerful surface science techniques for studying the surface structure and adsorption phenomena of the catalyst have not been employed. These techniques include secondary ion mass spectrometry (SIMS), ultraviolet photoelectron spectroscopy (UPS), electron energy loss spectroscopy (EELS) and Auger electron spectroscopy (AES).

If model Co-Mo/ γ -Al₂O₃ catalysts were supported on a planar γ -Al₂O₃ surface, the surface science techniques

listed above could be used to investigate their adsorption properties and surface structure.

The objective of this study is to develop the procedures for preparing planar model Co-Mo/ γ -Al₂O₃ catalysts and to study their surface structure to determine if the planar models are representative of the industrial catalysts.

BACKGROUND

Importance of Co-Mo/ γ -Al₂O₃ Catalysts

Coal liquifaction products and petroleum feedstocks consist predominantly of various hydrocarbons, but also contain lesser amounts of sulfur, nitrogen, and oxygen in the form of a variety of organic compounds. The presence of these heteroatoms, particularly sulfur and nitrogen, pose several problems.

The levels of both sulfur and nitrogen in fuels must meet EPA emission standards. The presence of nitrogen and sulfur in refining feedstocks can also lead to problems in refining operations. The organosulfur content of the feed to a hydrocracker must be reduced to avoid poisoning of the hydrocracking catalyst. Heterocyclic nitrogen containing compounds such as quinolines, pyridines and acridines are strongly basic. These strongly basic compounds are of particular concern in acid-catalyzed reactions, such as catalytic cracking, since they poison the catalysts [3].

The removal of sulfur and nitrogen from fuels in refining is known as hydrotreating. More specifically, sulfur removal is known as hydrodesulfurization (HDS) and nitrogen removal as hydrodenitrogenation (HDN). The HDN and HDS procedures are basically catalytic hydrogenations

designed to selectively remove sulfur and nitrogen from the various organic compounds and convert them H_2S and NH_3 .

In general, a catalyst is a substance that increases the rate of a chemical reaction without being appreciably consumed in the process. The catalyst does this by providing an alternate path of lower activation energy for the reaction to proceed. In the hydrotreating of refinery feedstocks where numerous reactions are possible due to the variety of compounds present, the catalyst must selectively catalyze the desired reaction(s). For example, if HDS of a heterocyclic compound is desired, the catalyst must selectively promote replacement of the sulfur with hydrogen while allowing minimum hydrogenation of the unsaturated aromatics.

One of the more commonly used catalysts for hydrotreating is $\text{Co-Mo}/\gamma\text{-Al}_2\text{O}_3$. The catalyst is particularly effective for HDS. Industrially, the catalyst is prepared by impregnating the porous $\gamma\text{-Al}_2\text{O}_3$ supports with salt solutions of the metals. The metals are calcined to their oxides. Prior to use, the metals are sulfided to insure proper activity. The composition of these catalysts are usually in the range of 3-6 wt% Co and 12-18 wt% Mo [2]. The balance of the composition is the support. These metal composition ranges correspond to approximately those required for monolayer coverages.

Surface Structure of Co-Mo/ γ -Al₂O₃ Catalysts

Perhaps because of their success in the selective removal of sulfur from petroleum feedstocks, and the environmental importance of sulfur removal, the most studied of the hydrotreating catalysts has been Co-Mo/ γ -Al₂O₃. Much of the more recent research on this catalyst has focused on the utilization of surface science and other techniques to characterize the catalyst surface structure. Despite the number of these investigations performed, the nature of the surface species on this catalyst is still not fully understood [4, 5].

Generally, the role of Co is believed to be that of a promoter while Mo is the active component [5]. The promoting role of Co is not fully understood. As summarized by Massoth [6], the promoting role of Co has been ascribed to (1) an increase in Mo dispersion; (2) an increase in Mo reduction; (3) an increase in H₂ mobility; (4) an intercalation effect with MoS₂; (5) a synergism between MoS₂ and Co₉S₈ crystallites; (6) a specific kinetic effect; (7) a decrease in deactivation; (8) an increase in surface segregation of mixed sulfide phases; and (9) the prevention of MoS₂ crystallization. All of these factors may have some influence on the activity of Co-Mo/ γ -Al₂O₃ catalysts [7].

Studies of the surface structure of the catalyst have been conducted with the catalyst in both the oxidic and

sulfided states. While the sulfided form of the catalyst is the active form used in hydrotreating, a thorough understanding of the oxidic precursor is important [5]. Much of the concern in characterizing the surface structure of the catalyst is in understanding the interactions between the metals and the $\gamma\text{-Al}_2\text{O}_3$ support and how these interactive species affect catalyst activity and selectivity. Studies of the catalyst in the oxide form may provide insight into those interactions.

Studies on the oxide form of the catalyst to date have identified numerous species including: (1) three dimensional compounds that include aluminum, oxygen, cobalt, and/or molybdenum such as CoMoO_4 , Co_3O_4 , MoO_3 , CoAl_2O_4 and $\text{Al}_2(\text{MoO}_4)_3$ [7-12]; (2) two dimensional species that involve Mo- $\gamma\text{-Al}_2\text{O}_3$ and Co-Mo interactions [5, 13]; and (3) dispersed Co and Mo ions with coordination symmetry dependent on that available on the $\gamma\text{-Al}_2\text{O}_3$ surface [5, 11, 13].

The discrepancies in the conceptions of the structure of Co-Mo/ $\gamma\text{-Al}_2\text{O}_3$ catalysts probably result from their great intrinsic structural complexity which may be sensitive to preparation parameters, and from the difficulty of experimentally studying this catalyst system. Such studies should be carried out in situ in order to avoid exposure of the catalyst to the atmosphere [14].

Variables in catalyst preparation include calcination conditions, percent metal loading on the catalyst, and the order of metal impregnation. In addition, the condition of the $\gamma\text{-Al}_2\text{O}_3$ support prior to metals impregnation affects the surface structure. Increased calcination temperature and time enhances the interaction between Mo and $\gamma\text{-Al}_2\text{O}_3$ [11]. Percent metal loading has a marked effect on the observed species of both Co and Mo [7, 11]. The order of metal impregnation has been shown to affect the interaction of the Co and the Mo phases [8, 9]. The state of dehydration-dehydroxylation of the $\gamma\text{-Al}_2\text{O}_3$ support also affects the interactions of Co and Mo [7].

As with the oxide form of the catalyst, controversy exists as to the exact chemical makeup of the active sulfided form. It is widely accepted that the dispersion of Mo on the support is very high and that it probably involves monolayer type coverage [5]. Several models have been proposed to describe the structure of this monolayer, but its characteristics are still in question:

- (1) The monolayer model assumes that the Mo monolayer in the calcined catalyst remains essentially intact upon sulfiding, except for replacement of some terminal oxygen anions with sulfur anions [15]. The location of Co is somewhat uncertain but it has been proposed that it is located inside the $\gamma\text{-Al}_2\text{O}_3$, thereby stabilizing the monolayer.

- (2) The intercalation model assumes that Co intercalates into the bulk of MoS_2 [16].
- (3) The contact synergy model supposes that the active phases are present as separate phases of Co_9S_8 and MoS_2 and the promoting effect of Co is suggested to be the result of a contact between these phases [17].
- (4) More recently, the Co-Mo-S model has been proposed which suggests that Co exists with Mo as a Co-Mo-S surface phase. This surface phase is suspected to provide the necessary activity [14].

Since the active Co-Mo-S phase was proposed, numerous studies have been performed which support this model [18-21]. The activity for the HDS of thiophene has been shown to be directly related to the amount of Co located in the Co-Mo-S phase [21]. The presence of Co in this phase appears to be enhanced if Mo is impregnated first. The amount of Co contained in the Co-Mo-S phase and the HDS activity are both maximized when the Co/Mo atomic ratio is between 0.5 and 1.0 [21].

Limitations of the Literature and Experimental Methods

A variety of techniques have been utilized in the aforementioned studies. These include electron spectroscopy for chemical analysis (ESCA), Mossbauer

emission spectroscopy (MES), Raman spectroscopy, infrared spectroscopy (IR), ion-scattering spectroscopy (ISS), and x-ray diffraction (XRD).

While the success in the application of these techniques to the characterization of Co-Mo/ γ -Al₂O₃ catalysts can not be denied, the application of these surface science techniques to the study of this catalyst system is not free of significant problems. The γ -Al₂O₃ support is a very porous insulator. The insulating characteristics of the support cause electrostatic charging of the sample during many types of surface studies. Electrostatic charging results from charge imbalances in the sample surface due to the acceptance and emission of ions and/or electrons. This charging problem can make data analysis extremely difficult. This may explain the lack of applications of electron spectroscopic and microscopic techniques like Auger electron spectroscopy (AES), electron energy loss spectroscopy (ELS), scanning or transmission electron microscopy (SEM or TEM) and ultraviolet photoelectron spectroscopy (UPS) to this catalyst system.

Because of the porosity of these catalysts there is no well defined surface which can be precisely characterized by the existing surface science techniques [22]. Techniques which employ ion beams, such as secondary ion mass spectroscopy (SIMS), are not beneficial because

the sputter beam size of existing ion sources can not be made reasonably smaller than the particle or pore size of the catalyst.

The difficulty of applying the surface science techniques to porous catalysts may explain the lack of adsorption and kinetic studies performed on a microscopic level. The adsorption of nitrous oxide on the catalyst has been studied with IR [18, 19, 22]. However, the primary purpose of these studies was to identify the phases present on the catalyst surface. Studies using actual reactant compounds are more rare. In one such study pyridine adsorption was used in conjunction with Raman spectroscopy [23]. Again, however, the thrust of this study was the characterization of the catalyst surface.

Some of the more powerful techniques, such as SIMS, ELS, and UPS, which may be used for adsorption and kinetic studies are difficult to utilize with the porous catalysts for reasons already stated. Utilization of these techniques may provide information such as the surface atoms on which adsorption occurs and the mode of molecular adsorption. For example, nitrogen containing compounds adsorb on the same surface sites responsible for HDS activity. Yet, it is known that hydrogen saturation of the aromatic ring occurs before C-N bond scission for HDN; whereas for HDS, C-S bond scission occurs before hydrogen

saturation of the double bonds. This suggests a different adsorption phenomena for nitrogen containing compounds than for sulfur compounds.

Kinetic studies on Co-Mo/ γ -Al₂O₃ catalysts have basically involved flow systems in which the mechanisms were determined via analyzing the product streams from the reactor. It would be desirable to actually study the reactions as they occur on the catalyst surface. This might best be accomplished by the incorporation of static SIMS with temperature programmed desorption (TPD). There has been one such study which examined the desorption of hydrogen and thiophene and mixtures of the two under vacuum by TPD [24]. Incorporation of static SIMS with TPD may provide a means of observing reaction intermediates on the catalyst surface.

Planar Model Catalysts as an Alternative

An alternative approach for studying the Co-Mo/ γ -Al₂O₃ catalyst is to replace the industrially used porous γ -Al₂O₃ supports with a thin surface oxide layer grown on planar aluminum. As discussed in the previous section, the porosity and insulating characteristics of the industrial catalysts pose difficulties in the application of many of the techniques suitable for catalysis studies. Replacing the porous γ -Al₂O₃ supports with a well defined planar

surface should eliminate many of these difficulties and provide new avenues by which adsorption and kinetic studies of the catalyst may be performed. Utilizing planar aluminum substrates also offers the advantage of preparing the samples under clean, ultra high vacuum (UHV) conditions.

Growth of $\gamma\text{-Al}_2\text{O}_3$ on bulk aluminum metals has been extensively studied in recent years. A summary of different techniques is provided by Cocke, et al. [25]. Perhaps the simplest method is the direct thermal oxidation of aluminum metal. This can be accomplished by heating the aluminum to approximately 863 K in the presence of oxygen. The thickness of the oxide layer may be varied depending on the time allowed for oxidation. For the type of application performed in this study, thin oxide layers are desired to mitigate sample charging during the application of the various surface science techniques.

The incentive for utilizing planar supports is to provide a means of studying the adsorption and kinetics of hydrotreating reactions on Co-Mo/ $\gamma\text{-Al}_2\text{O}_3$ catalysts on a microscopic level. In order to insure the validity of adsorption and kinetic studies it is necessary to verify that the planar model catalysts are structurally representative of the surface of the actual industrial catalyst. A clearer picture of the catalyst's surface

structure should be revealed due to the elimination of ambiguities encountered when applying surface science techniques to the porous catalysts.

Application of ESCA in Catalysis Research

Electron spectroscopy for chemical analysis is a powerful technique in catalysis research for studying the catalyst's surface chemistry. The technique involves the irradiation of the material being studied with monoenergetic x-rays. Typically either Mg K α or Al K α x-rays are used. The kinetic energies of these x-rays are 1253.6 eV and 1486.6 eV respectively.

The impinging x-rays cause the emission of electrons from the sample by the photoelectric effect. These emitted electrons have kinetic energies determined by;

$$KE = h\nu - BE - \phi_s$$

where $h\nu$ is the photon energy, KE is the kinetic energy of the emitted electrons, BE is the binding energy of the electrons and ϕ_s is the spectrometer work function. The emitted electrons are analyzed by their kinetic energies. Since the spectrometer work function and the photon energy are known, this allows calculation of the electron binding energy. Since only those electrons which originate within tens of Angstroms of the sample surface escape with sufficient energy to be analyzed, the technique is surface sensitive.

The binding energy of the electrons is characteristic of the parent atom from which it originated. Thus, elemental identification is possible with ESCA. More importantly, however, the binding energy of an electron is also influenced by the chemical environment of its parent atom. Chemical environment may include the oxidation state or coordination of the parent atom. This gives rise to the phenomena in ESCA known as chemical shifts which may provide information on the catalyst surface chemistry. Further details on the theory of ESCA may be found in the literature [26-29].

Sample spectra for aluminum, both metallic and oxidized, are provided in Figure 1. These spectra display the shift in binding energy of the Al 2p electrons upon transition from metallic Al to crystalline Al_2O_3 . The full width at half maximum (FWHM) of the spectra, as displayed in Figure 1, may also provide information about the chemical environment of an element. For example, an increase in the FWHM of the spectra for a given element may be an indication of the presence of more than one phase containing that element.

The intensity of the spectra may provide information about the quantity of metal ions on the catalyst support. The intensity is typically taken as the area under the

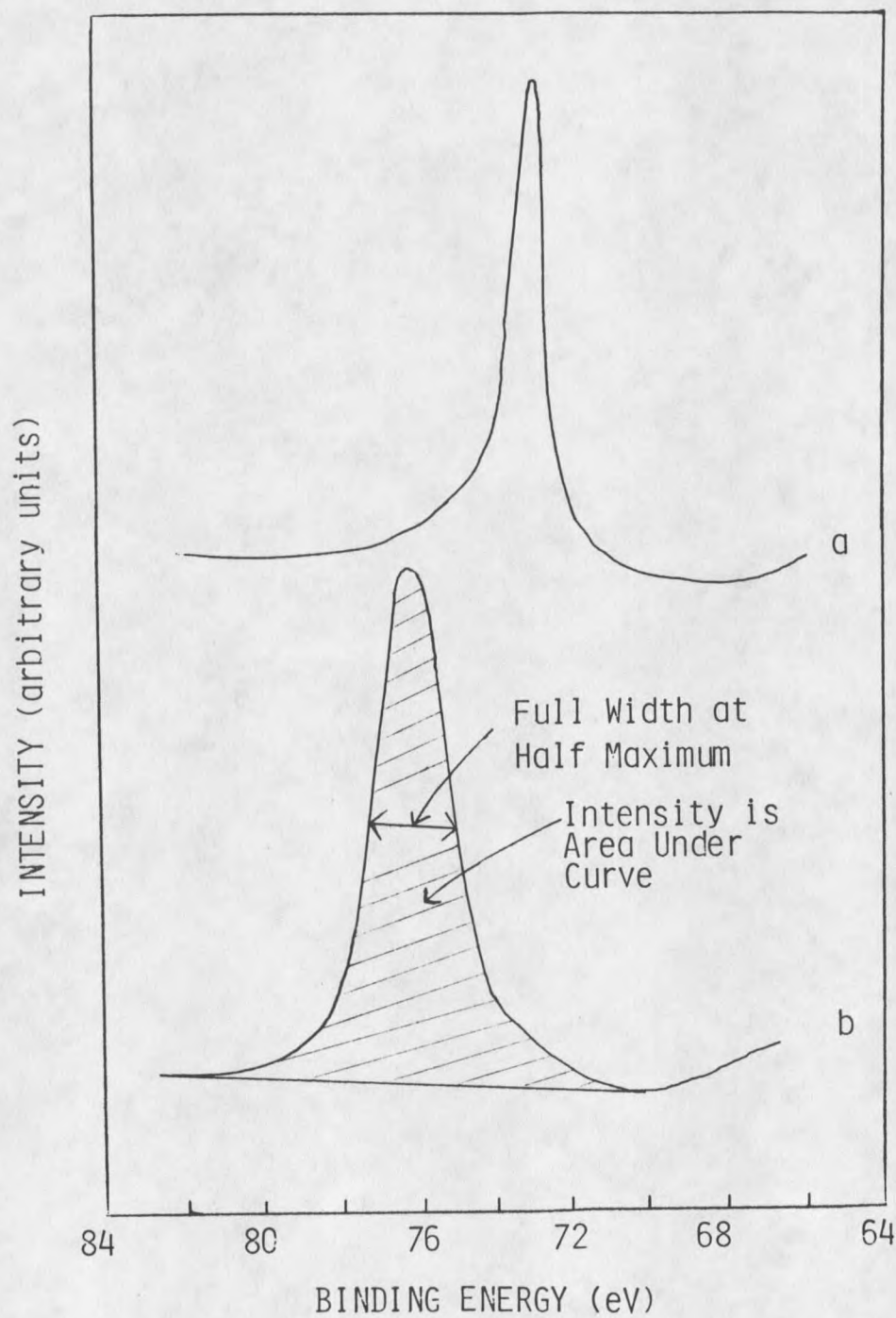


Figure 1. ESCA Al 2p Sample Spectra
(a) metallic; (b) oxidized

spectral curve. This intensity of a given spectrum may be related to the atomic concentration of that element by the following equation [30];

$$C_x = \frac{I_x/S_x}{\sum I_x/S_x}$$

where I_x is the intensity and S_x is the atomic sensitivity factor for a given element. The summation is over all elements present. Physical Electronics Inc. has compiled atomic sensitivity factors using silver as a standard [30].

The intensity ratios of the spectra for the metal atoms to spectra of the support may provide information about the distribution of the metal atoms. For example, a smaller Co/Al intensity ratio for one catalyst relative to another with the same Co loading may be indicating greater Co migration into the support lattice or the formation of Co-containing agglomerates on the support surface, resulting in less dispersed coverage of the Co.

Application of AES in Catalysis Research

When an electron vacancy is formed in one of the inner shells of an atom, such as during photoemission, it may be filled by either a radiative or nonradiative process. The nonradiative, or Auger process, occurs most frequently.

The Auger process involves the filling of an inner shell vacancy by an electron from a less tightly bound orbital. This readjustment causes the ejection of an electron from the less tightly bound orbital with an energy equal to the difference in total energies of the initial and final states. For example, consider the KLL Auger transition. The initial state has a hole in the K shell, while the final state has two vacancies in the L shell.

Similar to ESCA, the ejected Auger electrons can be analyzed by their kinetic energies. The kinetic energies of these electrons are characteristic of their parent atoms. Again, only those electrons that originate within a few Angstroms of the sample surface escape without suffering loss. A thorough review of the equipment utilized in, and the theory of, AES is provided by Carlson [26].

The Auger process may be initiated by either an impinging electron or photon beam on the material being studied. Its applicability in catalysis research stems from the fact that electron beams may be utilized. Unlike x-rays, an electron beam can be focused on a small area. By moving the finely focused electron beam about the surface of the catalyst, the spatial distribution of metal atoms on the support may be studied. In addition, the use

of an electron beam allows for high resolution photography of the sample surface.

Auger electron spectroscopy also provides for elemental identification, although in a study where both ESCA and AES are employed this would be a duplication of efforts. When a photon beam is used as the excitation source in AES, shifts in the kinetic energies of the ejected Auger electrons which depend on the chemical environment of the element may be observed. The direction of these chemical shifts parallel those observed in ESCA.

Application of SIMS in Catalysis Research

Surface analysis by SIMS is accomplished by bombarding the surface of the material being studied with high energy ions. As a result of these high energy ions striking the sample surface, particles are removed from the surface, some of which are in the form of positive and negative ions. These ions are passed through a mass spectrometer where they are separated on the basis of their mass-to-charge ratio and subsequently detected.

The technique is surface sensitive in that only those ions which originate within the first few Angstroms of the surface escape the solid for analysis. However, by

continuous bombardment of the sample with the high energy ions one digs deeper into the solid, thereby revealing the composition beneath the surface.

Secondary ion mass spectrometry analyses are commonly referred to as being either static (SSIMS) or dynamic. Operation in the static mode provides for a lesser erosion of the sample surface. The erosion rate may be controlled by varying the incident ion beam current. Further details on the theory of SIMS may be found in the literature [31, 32].

Secondary ion mass spectrometry is a valuable technique in catalysis research. Owing to its capability to probe into the bulk of the sample, the concentration of species as a function of depth into the solid are attainable. This procedure is known as depth profiling and may provide information on interactions between the metal atoms and the support. Since the coverage of metal atoms on the support is typically around a monolayer quantity, SSIMS is preferred to avoid rapid destruction of the surface. Electron spectroscopy for chemical analysis might also be employed in depth profiling studies to examine the chemical environment of the metal atoms present beneath the surface. Similar to the electron beams employed in AES, the ion beam can be focused on a given area of the sample, thus allowing examination of the lateral distribution of metal ions on the support.

Similar to ESCA, SIMS may be used to characterize the chemical structure of a catalyst surface. The secondary ions removed from the surface may be in the form of single ions or clusters of ions. By comparing the SIMS spectra of unsupported bulk compounds with SIMS spectra of the catalyst, the secondary ion clusters observed may be identified as originating from a given chemical species. A review of these and other applications of SIMS in catalysis research is provided by Brown and Vickerman [33].

RESEARCH OBJECTIVES

The objectives of this research are essentially two-fold:

1. Development of the experimental procedures for preparation of the planar model catalysts. This includes preparation of the planar $\gamma\text{-Al}_2\text{O}_3$ by following the works of other researchers and developing a suitable technique for impregnating the planar supports with the Co and Mo.
2. Characterization of the surface structure of the planar model catalysts with ESCA, SIMS and AES and comparing the findings with published observations on the industrial catalysts.

EXPERIMENTAL

Sample Handling System

The samples were prepared in the vacuum system associated with the ESCA equipment. This vacuum system consisted of a main analysis chamber and a preparation chamber. These two chambers were sealed from one another. Oxidation of the samples was performed in the preparation chamber. Vapor deposition of the Co and Mo was performed in the analysis chamber.

The sample handling rod, shown in Figure 2, allowed for transport of the samples from the preparation chamber to the analysis chamber without exposure to the atmosphere. Titanium (Ti) foil was employed as the sample holder. The 7mm X 7mm X 1mm aluminum coupons were held in place by folding the Ti foil over the edges of the aluminum. The rod contained electrical leads to the sample holder allowing for resistive heating. Thus, the sample holder served as a heater for the aluminum.

A thermocouple attached to the underside of the Ti foil was used to monitor the sample temperature. Since the thermocouple actually measured the Ti temperature and not the sample itself, an infrared pyrometer was also employed to monitor the surface temperature of the samples.

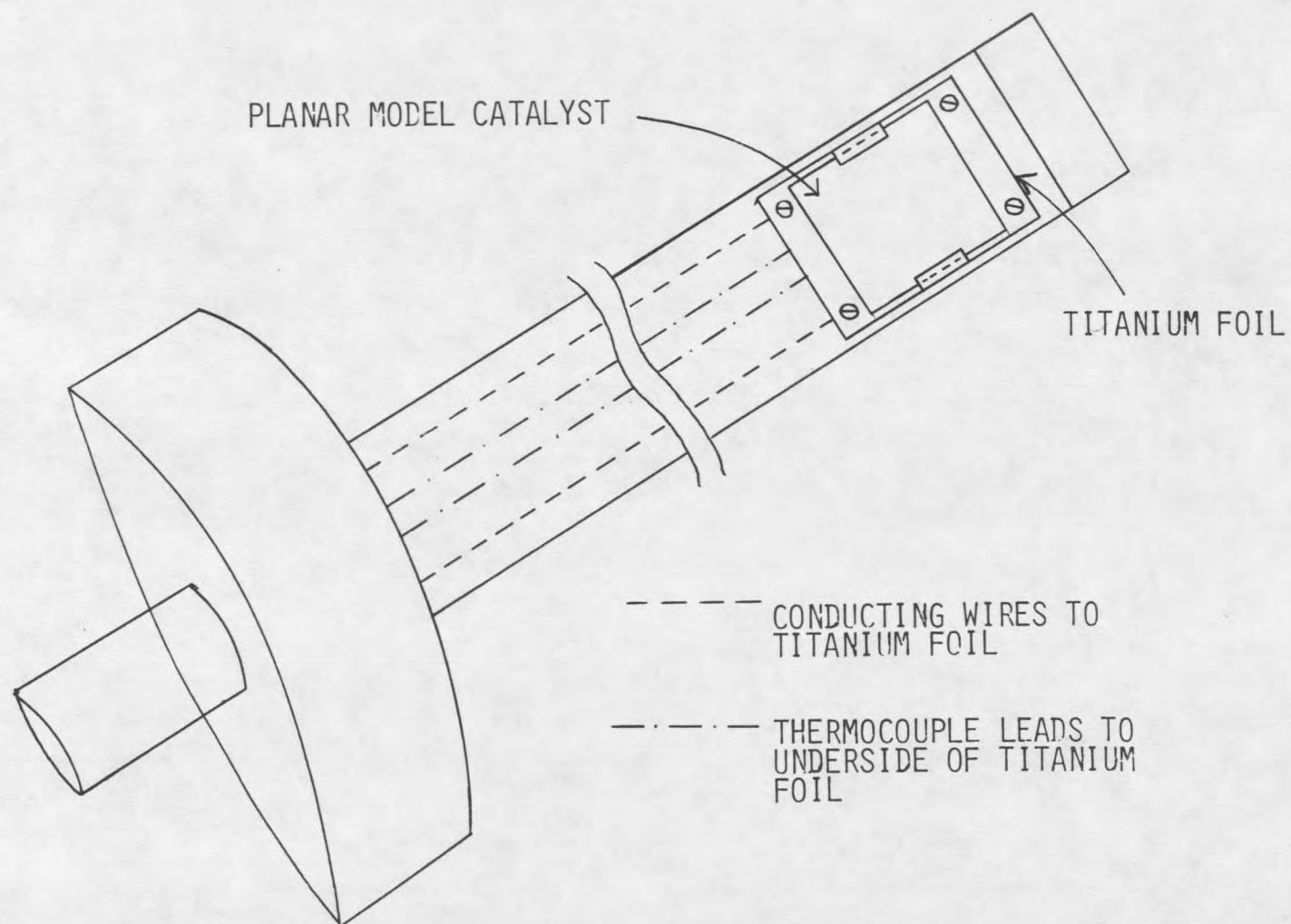


Figure 2. Sample Handling Rod

Preparation of the Planar γ -Al₂O₃

Preparation of the planar model catalysts followed the works of Merrill [34] for the development of a γ -Al₂O₃ surface layer. Prior to placing in vacuum, the 99.999%+ pure polycrystalline aluminum samples were mechanically polished to remove surface imperfections and cleaned to remove residual organics. Mechanical polishing was performed with alumina powders. Cleaning was performed ultrasonically with acetone followed by methanol.

Once placed in the vacuum, the samples were annealed and sputter cleaned with argon ions to remove any surface or subsurface adsorbed oxygen and any remaining Al₂O₃ powders on the surface. ESCA survey scans were used to verify completion of the in situ cleaning.

Oxidation of the aluminum was accomplished via exposing the samples to a mixture of O₂/H₂O at 10⁻⁴ torr for 0.5 hr at 823 K. The Al 2p peak binding energy was used to monitor the oxidation process. Since the Al 2p band displays very distinct shifts upon transition from pure aluminum to amorphous Al₂O₃ and finally to crystalline Al₂O₃, it was possible to verify the presence of crystalline Al₂O₃. This was confirmed by comparison of the various Al 2p band binding energies with values reported in the literature [25]. The experimental conditions assured that the crystalline Al₂O₃ formed was γ -Al₂O₃.

Thin oxide layers were desired to avoid sample charging problems in the ensuing studies. Since the escape depth of secondary electrons analyzed by ESCA is approximately 20Å, the presence of a small Al 2p band for pure aluminum provided a rough idea of the oxide thickness.

Deposition of Cobalt and Molybdenum

Deposition of the Co and Mo on the $\gamma\text{-Al}_2\text{O}_3$ was attempted via two techniques. The first technique was the industrially used incipient wetness technique. This technique required removal of the oxidized samples from the vacuum and immersing them in an aqueous solution of cobalt nitrate or ammonia hepta molybdate. This technique posed several drawbacks. It was difficult to determine the solution concentration required to provide the desired monolayer coverage of the metals on the sample surface. Some of the samples did not wet very well which resulted in agglomeration of the Co and/or Mo atoms on the sample surface as verified by Auger line analysis.

The other technique utilized was direct physical evaporation of the Co and Mo on the sample surface. This was accomplished by passing electrical current through a pure Co or Mo filament positioned close to the sample in the vacuum chamber. This technique proved superior to incipient wetness in that more even surface coverage of the

metals was obtained. In addition, the physical vapor deposition was done in situ, whereas incipient wetness required removal of the samples from the vacuum.

Two planar model catalysts were prepared, utilizing the physical vapor deposition technique. The difference between the two samples was the order of metals deposition.

As previously mentioned, approximately monolayer coverage of both the Co and Mo on the sample surface was desired. Two methods were employed to monitor the amount of metals deposition. The first method utilized a quartz crystal oscillator (QCO) positioned close to the sample in the vacuum chamber. As the metals evaporated onto both the sample and the QCO, the frequency of the QCO decreased. The frequency drop of the QCO was related to the thickness of the deposited layer by the following equations [35];

$$d = [A/(pnN_A)]^{1/3}, \quad \Delta F = dCp$$

where; d = thickness monolayer - cm

A = molecular weight of metal - g/mol

ρ = density of metal - g/cm³

n = number of atoms in a molecule

N_A = Avogadro's number

C = 56,497,175 cm²/gsec for 5 MHz quartz crystal

ΔF = frequency drop of QCO

A sample calculation utilizing this equation is provided in Appendix A.

The close proximity of the hot Co and Mo filaments to the QCO tended to increase its frequency due to heating. Therefore, ESCA peak areas (see Application of ESCA in Catalysis Research) were also determined after each evaporation to provide an approximation of the Co and Mo surface concentrations. In order to implement this method, the planar model catalysts were assumed to have a layered type structure as shown below:

1	-----	Mo
2	-----	O ²⁻
3	-----	Al ³⁺
4	-----	O ²⁻
5	-----	Al ³⁺
6	-----	O ²⁻
7	-----	Al ³⁺
8	-----	O ²⁻
9	-----	Al ³⁺
10	-----	Al

This is an example of Mo deposited directly onto the γ -Al₂O₃. Since the Al-O bond distance is approximately 1.91Å, the average thickness of each layer was assumed to be 2.0Å. Considering the escape depth of the secondary electrons to be 20Å, approximately 10 layers of the structure are 'seen' by the spectrometer. For the above example, the ratio of the Mo 3d peak area to the sum of the areas of the Al 2p, O 1s and Mo 3d peaks (corrected with sensitivity factors) should equal 0.1 for a monolayer of Mo atoms. A sample calculation is provided in Appendix A.

This calculation typically showed that more than one monolayer of Co or Mo had been deposited while being monitored by the QCO. For those cases, the samples were lightly sputtered with Ar^+ until the ESCA area ratios indicated monolayer coverage of the metals.

Oxidation of Cobalt and Molybdenum

Following deposition of each of the metals, the metals were oxidized. For example, on the Co-Mo/ $\gamma\text{-Al}_2\text{O}_3$ (Mo deposited first) planar model, the Mo was deposited and oxidized followed by deposition and oxidation of the Co layer. The oxidizing conditions for oxidation of the metals are shown in Table 1. These conditions were determined by trial and error. The samples were oxidized and the Co 2p or Mo 3d ESCA spectra was obtained. If the spectra indicated incomplete oxidation of the Co or Mo, this process was repeated with increased temperature and/or oxygen pressure.

Table 1. Oxidizing Conditions for the Cobalt and Molybdenum

<u>Planar Model</u>	<u>Metal</u>	<u>Temperature (K)</u>	<u>$\text{O}_2/\text{H}_2\text{O}$ Pressure (Torr) 10^3</u>	<u>Time (hr)</u>
Co-Mo/ $\gamma\text{-Al}_2\text{O}_3$	Mo	773-853	0.5	0.25
			130.0	0.25
			150.0	0.25
			500.0	0.25
	Co	773-833	160.0	0.17
Mo-Co/ $\gamma\text{-Al}_2\text{O}_3$	Co	843-863	20.0	0.25
	Mo	853	400.0	0.50

ESCA Analysis

The ESCA analyses of the planar model catalysts were performed by a Leybold-Heraeus x-ray photoelectron spectrometer (L-H EA11). Non-monochromatized Mg K α (KE=1253.6 eV) x-rays were used as the radiation source. All ESCA data was obtained with the pressure in the vacuum chamber at 10^{-8} torr or lower.

As described in the discussion on sample preparation, ESCA data was collected at each step in preparation of the planar models. The Al 2p, Al 2s, O 1s, Mo 3d and Co 2p spectra were all recorded as applicable. The O KLL, Mo MNN and Co LMM x-ray induced Auger spectra were also recorded as applicable. In addition, Mo 3d and Co 2p spectra of pure Mo and Co foils, both metallic and oxidized, were obtained for reference. The ESCA data was recorded both with an analog and digital recorder. The latter was performed by a Tektronix computer, and stored on a magnetic disc.

The ESCA data was analyzed with the aid of a special computer program developed by XEROX and modified by the Montana State University Physics Department. This program provided the capability to smooth the data and obtain the kinetic energy locations of the peaks. In addition, the peak areas and FWHM of the spectra were obtained with the

program. The program was also used to deconvolute the shake up satellites from the parent peaks in the Co 2p spectra.

Auger Analysis

The Auger line analyses were done by a Physical Electronics (PHI 595) scanning Auger microprobe. Analysis with the PHI 595 was only performed on the Co-Mo/ γ -Al₂O₃ model. Since the PHI 595 was associated with a different vacuum system, the sample was briefly exposed to atmosphere for transport to the PHI 595.

The line analyses were obtained at a resolution of 1000 X. The pressure in the vacuum chamber was 10^{-9} torr or lower. The electron beam voltage was 5.0 KeV and the beam current was 0.2 μ A. This beam current provided for a beam diameter of approximately 7000Å.

The Auger data was recorded digitally on a magnetic disc with the use of a DEC PDP 11/04 computer. Special computer programs, developed by Physical Electronics Inc., were used to smooth the data and account for topographical effects on the sample surface.

SIMS Analysis

The SIMS analyses were performed by a Leybold-Heraeus secondary ion mass spectrometer (L-H SSB/10)

employing a quadrapole mass filter. The SIMS analysis was only performed on the Co-Mo/ γ -Al₂O₃ model catalyst. The analysis was done in the PHI 595 vacuum system. Argon ions (Ar⁺) were used for the primary ion beam.

The depth profiles of the elements (Al, O, Co, Mo) were obtained at four different locations on the sample surface. The primary ion energy was 2.8 kV. The base pressure in the chamber was 3.0×10^{-9} torr before backfilling with argon gas. The depth profiles were obtained with a noble gas pressure of 2.0×10^{-8} torr. The ion beam was rastered over an area of 0.25 mm². The ion beam current was approximately 20 μ A/cm².

Survey scans were also obtained with SIMS at the bottom of the craters left from the depth profiling. The primary ion energy and chamber pressures were the same as those employed for the depth profiles. The ion beam was rastered over a smaller area to minimize effects from the crater edges. The survey scans covered 0-150 amu.

RESULTS AND DISCUSSION

Growth of γ -Al₂O₃

The Al 2p bands in Figure 3 display the binding energy shifts observed during oxidation of the Al. After exposure to 10^{-6} torr O₂ and 673 K for 0.33 hr, an additional band appeared at 2.9 eV higher binding energy indicating the formation of an amorphous oxide layer. After additional exposure to 10^{-6} torr O₂ and 823 K for 0.33 hr, the oxide band shifted 3.8 eV higher than that for metallic Al, indicating the formation of crystalline Al₂O₃. These values are consistent with Al 2p binding energy ranges reported in the literature [25].

Co-Mo/ γ -Al₂O₃ Model Catalyst ESCA Analysis

Deposition and Oxidation of Molybdenum: The Al 2p and Mo 3d spectra of the Co-Mo/ γ -Al₂O₃ planar model are provided in Figures 4-6. Numerical values of the peak binding energies are tabulated in Appendix B. The binding energy of the Al 2p line decreased 0.6 eV following deposition of the Mo. The Mo 3d band is also at a slightly higher binding energy compared to the pure metallic Mo band.

The FWHM of the spectra are provided in Table 2. For the Mo spectra, the FWHM is taken over the entire Mo 3d

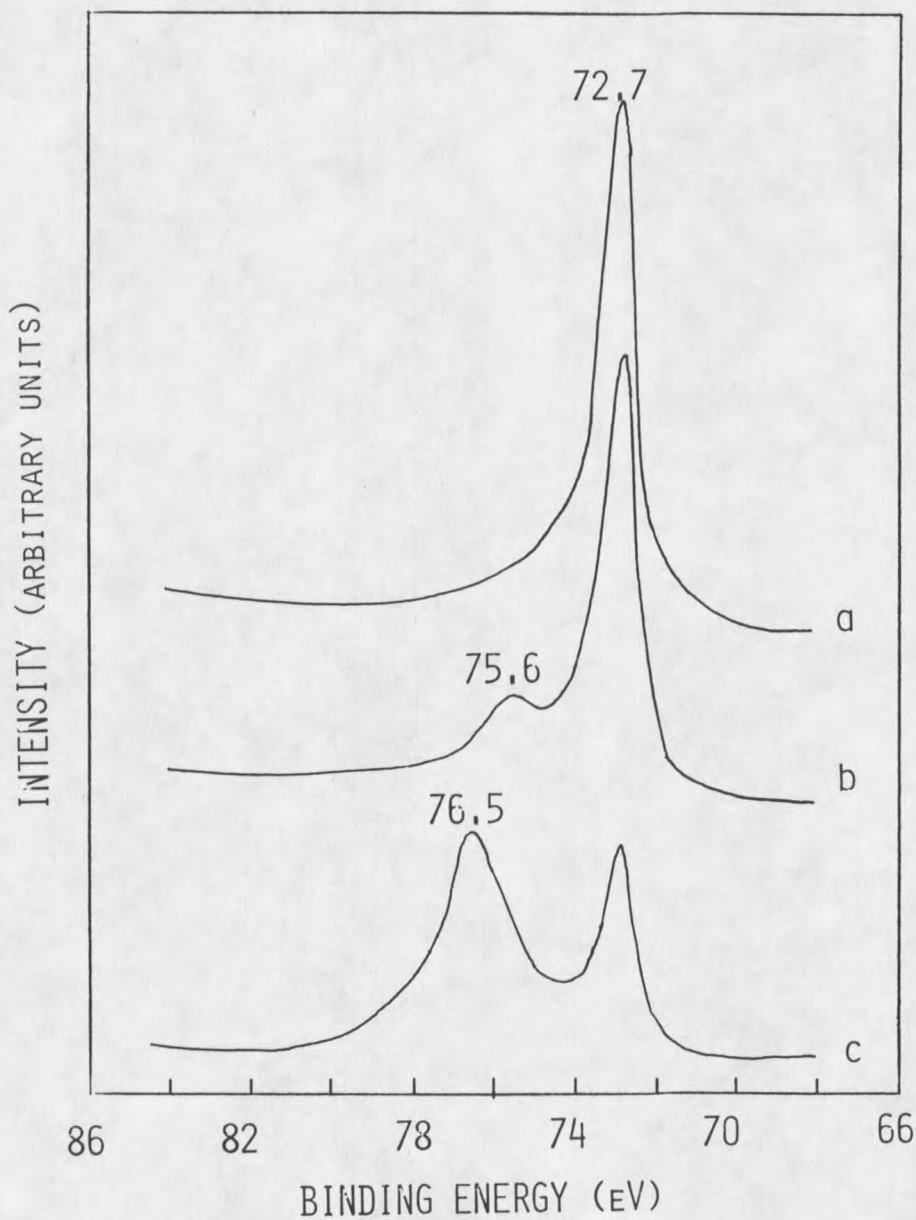


Figure 3. Al 2p ESCA Spectra Displaying Oxidation of Aluminum Foil
(a) cleaned aluminum foil; (b) after exposure to 10^{-6} torr O_2 , 673 K, 0.33 hr;
(c) after additional exposure to 10^{-6} torr O_2 , 873 K, 0.33 hr

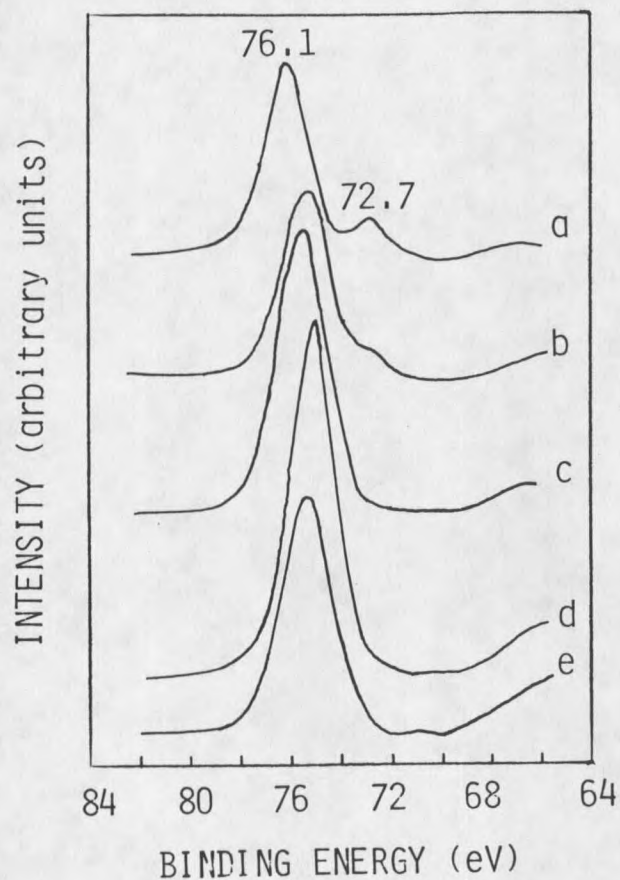


Figure 4. Al 2p ESCA Spectra for the Co-Mo/ γ -Al₂O₃ Model Catalyst
 (a) aluminum foil oxidized 10^{-4} torr O₂/H₂O, 823 K, 0.5 hr; (b) after Mo deposition; (c) after Mo oxidation; (d) after Co deposition; (e) after Co oxidation

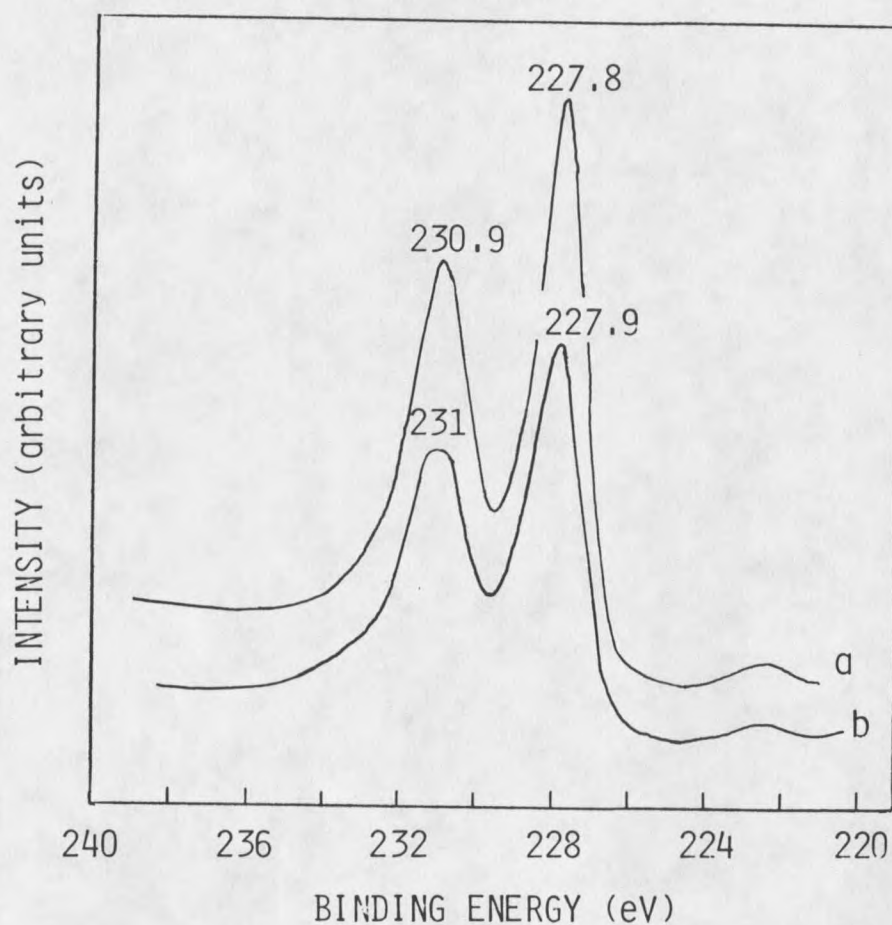


Figure 5. Mo 3d ESCA Spectra for the Co-Mo/ γ -Al₂O₃ Model Catalyst After Molybdenum Deposition and for Molybdenum Foil
(a) pure cleaned Mo foil;
(b) deposited Mo layer

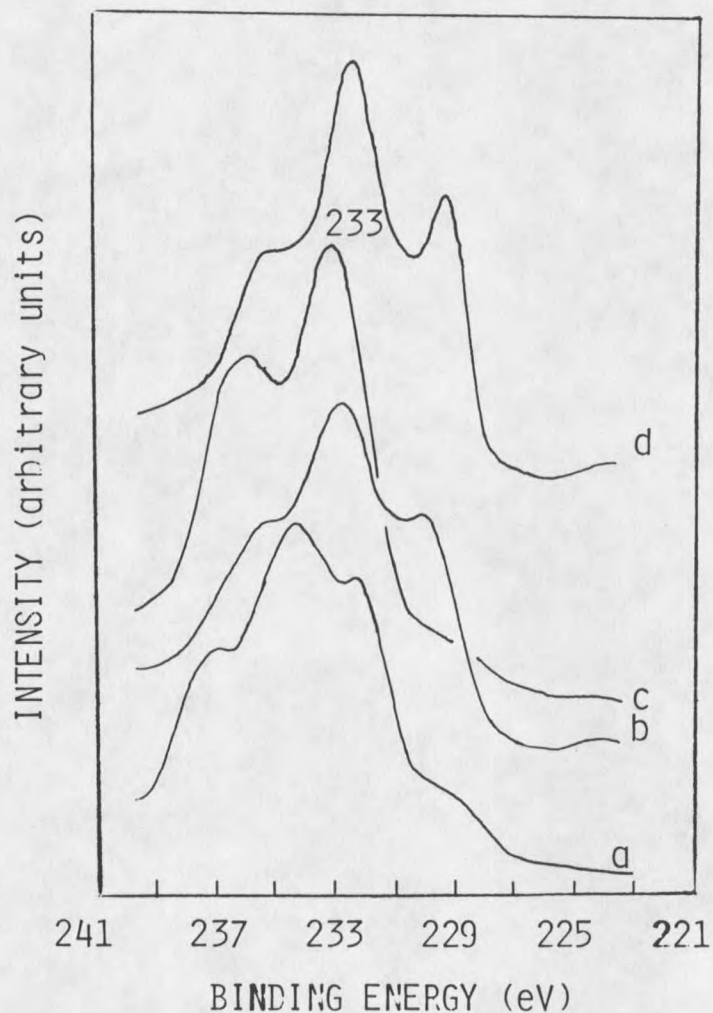


Figure 6. Mo 3d ESCA Spectra for the Co-Mo/ γ -Al₂O₃ Model Catalyst After Molybdenum Oxidation and for Oxidized Molybdenum Foil
 (a) oxidized Mo layer; (b) oxidized Mo layer after Co deposition; (c) oxidized Mo layer after Co oxidation; (d) oxidized pure Mo foil

band. Initially, the amount of Mo deposited was greater than a monolayer. The FWHM of the Mo 3d band was 4.75 eV. After sputtering to remove the excess Mo, the FWHM of the Mo 3d band increased to 5.00 eV.

Table 2. Peak Widths^{*} (eV) for the Co-Mo/ γ -Al₂O₃ Model Catalyst

	Al 2p	O 1s	Mo 3d ¹	Co 2p _{3/2}
Al Oxidized	2.19	3.08	---	---
Mo Deposited	2.21	2.65	5.00	---
Mo Oxidized	2.40	3.06	6.50	---
Co Deposited	2.10	2.47	7.00	4.38
Co Oxidized	2.42	2.94	5.63	4.81
Mo Metal	---	---	4.75	---
Co Metal	---	---	---	2.50
Co Metal Oxidized	---	---	---	3.75

^{*} Full Widths at Half Maximum

¹ Taken Over Entire Mo 3d Band

These observations indicate interaction between the Mo and γ -Al₂O₃. The Mo may be partially oxidized by sharing the terminal oxygens of the γ -Al₂O₃. This would have the net effect of decreasing the oxidation state of the Al, resulting in a shift to lower binding energy of the Al 2p band. The O 1s spectra shown in Figure 7 are supportive of an oxygen-sharing interaction. The decreased binding energy of the O 1s band following deposition of the Mo indicates an increase in the valency of the oxygen environment [36].

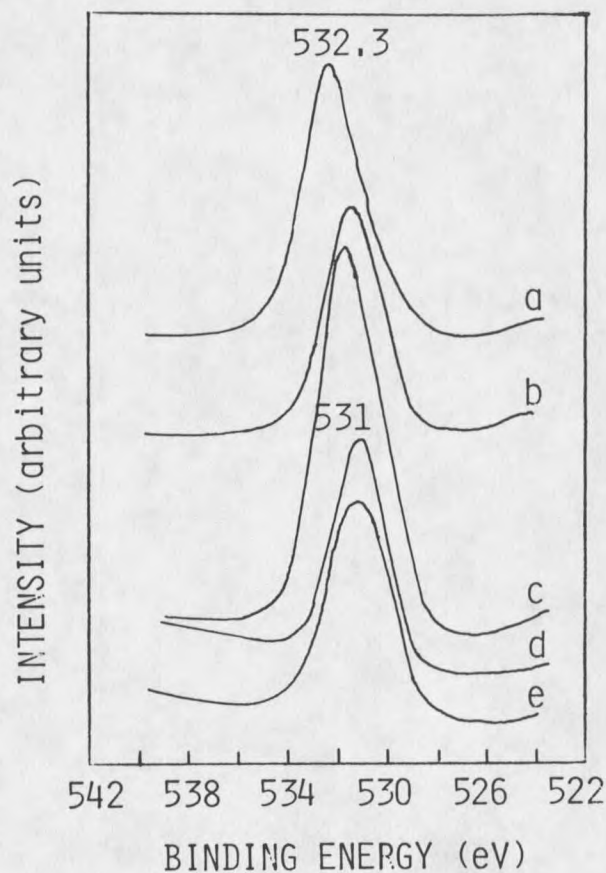


Figure 7. O 1s ESCA Spectra for the Co-Mo/ γ -Al₂O₃ Model Catalyst
(a) oxidized Al foil; (b) after Mo deposition; (c) after Mo oxidation; (d) after Co deposition (e) after Co oxidation

Oxidation of the Mo did not result in an additional shift of the Al 2p band binding energy (see Fig. 4, curves b&c). However, the FWHM of the band increased suggesting enhanced interaction between the Mo and $\gamma\text{-Al}_2\text{O}_3$. The intensity ratios of the ESCA spectra are provided in Table 3. The Mo/Al intensity ratio decreased following oxidation of the Mo. Assuming the additional oxygen affects both spectra equally, this observation may be attributed to movement of Mo into the subsurface sites of the $\gamma\text{-Al}_2\text{O}_3$ lattice due to counter diffusion of the Mo^{+n} and Al^{+3} ions. This also suggests increased interaction between the Mo and $\gamma\text{-Al}_2\text{O}_3$, although, the possibility of some MoO_3 evaporation can not be excluded since MoO_3 evaporates at 973 K and one atmosphere pressure.

Table 3. Peak Areas and Area Ratios for the Co-Mo/ $\gamma\text{-Al}_2\text{O}_3$ Model Catalyst

	Normalized Peak Areas [*] (10^3)				Peak Area Ratios	
	Al 2p	O 1s	Mo 3d	Co 2p	Mo/Al	Co/Al
Al Oxidized	34.7	42.2	----	----	----	----
Mo Deposited	16.5	20.2	5.53	----	0.336	----
Mo Oxidized	20.0	30.6	3.99	----	0.200	----
Co Deposited	16.4	21.9	2.98	6.24	0.182	0.382
Co Oxidized	13.4	24.9	3.60	3.24	0.259	0.243

* Area under the peak is divided by the sensitivity factors (S_x) obtained from reference 30.

$S_{\text{Al 2p}} = 0.11$, $S_{\text{O 1s}} = 0.63$, $S_{\text{Mo 3d}} = 1.2$, $S_{\text{Co 2p}} = 4.5$

These sensitivity factors were determined using a double pass, cylindrical mirror analyzer. It was assumed they are accurate for the hemispherical analyzer used in this study.

The Mo 3d band became quite broad with three distinct peaks as shown in Figure 6. Compared to the Mo 3d band prior to oxidation, the entire envelope is shifted to higher binding energy. This is expected due to the increased oxidation state of the Mo. The shape of the band indicates the presence of more than one oxidation state of the Mo. The Mo⁶⁺, Mo⁵⁺ and Mo⁴⁺ oxidation states of Mo may all be present.

It is not clear whether the incomplete oxidation of the Mo is due to interaction with the γ -Al₂O₃. As evidenced by the changes in the Al 2p bands and the Mo/Al intensity ratios, there is strong interaction between the Mo and γ -Al₂O₃. Furthermore, it is obvious from the Mo 3d band that a bulk phase of MoO₃ is not forming on the γ -Al₂O₃ surface, as this would result in a resolved doublet of the Mo 3d band [37]. Preliminary experiments indicated difficulty in oxidizing Mo to Mo⁶⁺ under vacuum conditions. This is evidenced by the multi-peak characteristic of the Mo 3d spectra of oxidized Mo foil shown in Figure 6. Preliminary experiments also indicated that oxidation of Mo containing samples under atmospheric pressure was more complete.

Deposition and Oxidation of Cobalt: Following deposition of the Co, the Mo 3d band maintained the same shape but the entire band shifted to a lower binding

energy. This might be attributed to an oxygen-sharing interaction between the Co and Mo, resulting in a decreased oxidation of the Mo.

The Co 2p spectra of the Co layer deposited on the Co-Mo/ γ -Al₂O₃ model catalyst and pure Co foil are shown in Figure 8. The binding energy of the Co 2p_{3/2} band is higher and the FWHM is greater (see Table 2) compared to the Co foil. The O 1s band also shifted to a lower binding energy (see Fig. 7, curves c&d). These observations support an oxygen-sharing interaction between the Co and Mo.

The Al 2p band shifted to a lower binding energy and narrowed upon Co deposition. It is suspected that this is due to a shielding effect by the Co layer. A greater fraction of the detected Al 2p electrons are from the Al-Mo interactive species. Since the sample was at room temperature during the evaporation, interaction of the Co and Al as a result of Co migration into the Al lattice is expected to be minimal at this point. However, as previously stated, it appeared that following oxidation of the Mo layer, some of the Mo migrated into the γ -Al₂O₃ lattice which may have left some exposed γ -Al₂O₃ for interaction with the Co.

After oxidation of the Co layer, the Mo 3d band returned to its more characteristic doublet form with the

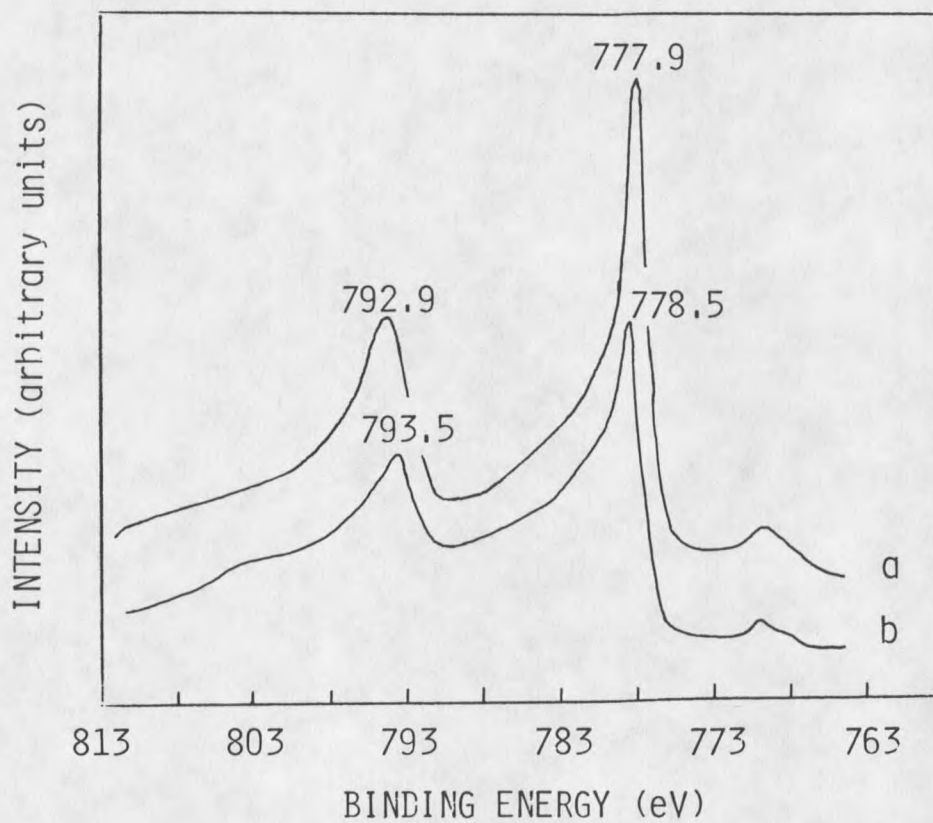


Figure 8. Co 2p ESCA Spectra for the Co-Mo/ γ -Al₂O₃ Model Catalyst After Cobalt³ Deposition and for Cobalt Foil

- (a) pure cleaned Co foil;
- (b) deposited Co layer

Mo $3d_{5/2}$ binding energy equal to 233.0 eV. This is the expected Mo $3d_{5/2}$ binding energy for Mo^{6+} [37]. The Mo 3d doublet is fairly broad and not well resolved, which is attributed to the presence of more than one Mo^{6+} -containing phase [38].

It is difficult with ESCA to distinguish between different Mo^{6+} compounds, such as MoO_3 and $CoMoO_4$, because their Mo 3d band binding energies are approximately the same [5]. Considering the difficulty in oxidizing the Mo layer prior to Co deposition (see Table 1), it is suspected that the more complete oxidation of the Mo after oxidation of the Co layer is due to interaction of the Co with the Mo. An increase in the Mo/Al intensity and a decrease in the Co/Al intensity ratio was observed (see Table 3), which indicates migration of some Co into or through the Mo layer. This may also indicate interaction of the Co with the Mo.

The Co 2p spectra of oxidized pure Co foil and the oxidized Co layer are shown in Figure 9. The Co 2p spectra of oxidized Co contain several features useful in analysis. The spin orbit splitting of the Co $2p_{3/2}$ and $2p_{1/2}$ levels (ΔE) and the difference between the $2p_{3/2}$ level and its shake up satellite at higher binding energy (ΔS) can provide information on the oxidation state and coordination of the Co [39].

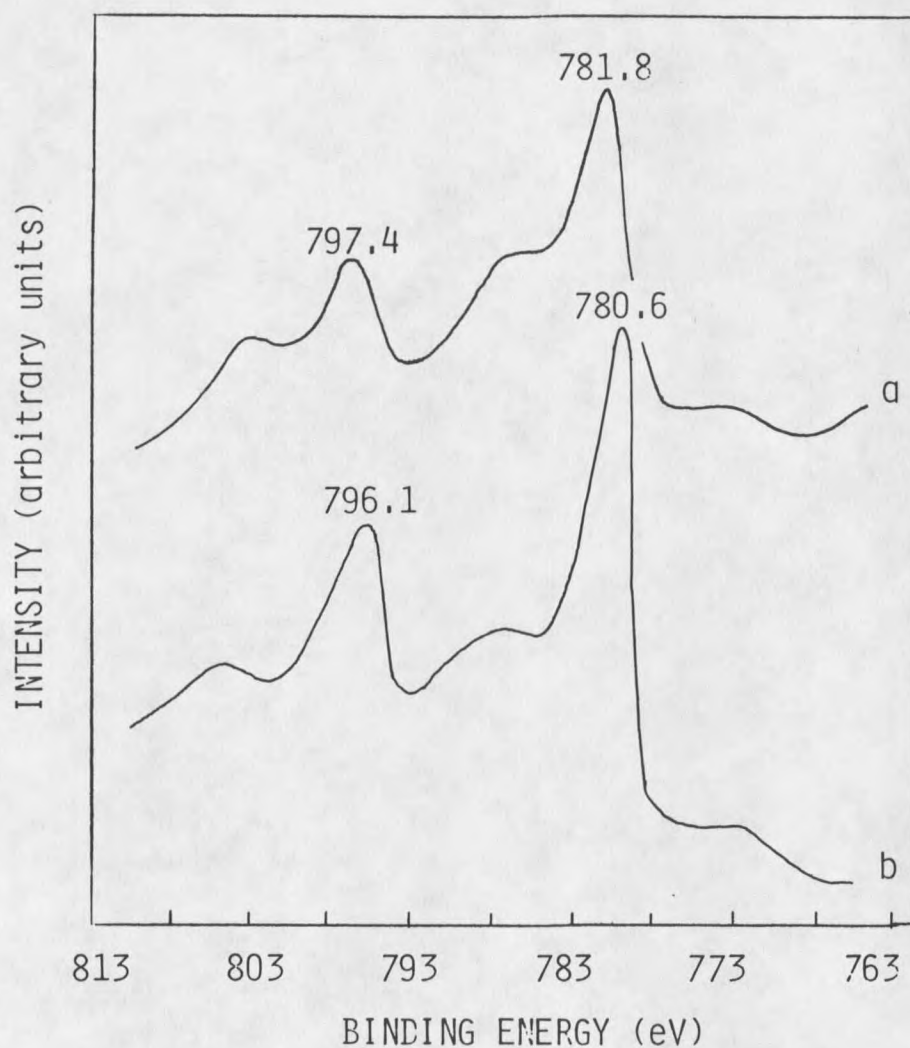


Figure 9. Co 2p ESCA Spectra for the Co-Mo/ γ -Al₂O₃ Model Catalyst After Cobalt³ Oxidation and for Oxidized Cobalt Foil

(a) oxidized Co layer;
(b) oxidized pure Co foil

For paramagnetic cobaltous (Co^{2+}) compounds ΔE has been found to be approximately 16 eV, whereas for diamagnetic cobaltic (Co^{3+}) compounds and Co metal ΔE is approximately 15 eV [39]. The ΔS of the Co $2p_{3/2}$ level has been found to be 6.2 eV for CoMoO_4 (Co octahedral) and 5.1 eV for CoAl_2O_4 (Co tetrahedral) [5]. It is also known that Co^{3+} displays a much weaker satellite intensity relative to Co^{2+} [39]. Therefore, the intensity of the satellite relative to the intensity of the entire Co $2p_{3/2}$ band may provide an indication of the Co oxidation state.

Analysis of the Co 2p band for the oxidized Co foil reveals ΔE to be 15.4 eV (see Fig. 9, curve b). Based on this, the presence of both CoO (Co^{2+}) and Co_3O_4 (Co^{2+} , Co^{3+}) is possible. However, comparing the satellite intensity of the oxidized Co foil to those in Co 2p spectra of CoO and Co_3O_4 obtained by Stoch and Ungier [36] suggests the presence of Co_3O_4 . In addition, the oxidized Co foil appeared black in color which suggests Co_3O_4 .

The ΔS of the Co $2p_{3/2}$ band of the Co-Mo/ γ - Al_2O_3 model catalyst is 5.2 eV and ΔE is 15.7 (see Fig. 9, curve a). These values indicate predominantly Co^{2+} ions in tetrahedral coordination, although the presence of some Co^{3+} can not be discounted.

The absolute binding energies of the Co $2p_{3/2}$ band for Co compounds decrease in the order $\text{CoAl}_2\text{O}_4 > \text{CoMoO}_4 > \text{Co}_3\text{O}_4$ [2, 5]. The Co $2p_{3/2}$ band binding energy of the Co-Mo/ $\gamma\text{-Al}_2\text{O}_3$ model catalyst is greater than that of the oxidized Co foil. This could be an indication of the presence of either CoAl_2O_4 or CoMoO_4 type phases. Considering the ΔS , it might be surmised that the Co is predominantly present as tetrahedrally coordinated Co^{2+} in a CoAl_2O_4 type phase. However, as the Mo 3d spectra and the SIMS depth profiles (see later discussion) indicated there was interaction of the Co with the Mo.

Further substantiating speculation of interaction between the Co and Mo are the atomic surface concentrations of the elements shown in Table 4. These values may be interpreted as the amount of each element 'seen' by the spectrometer. Of particular importance is the increase in the Mo concentration coupled with a decrease in the Co concentration following oxidation of the Co layer. Assuming the additional oxygen affected both equally, this can only be explained by movement of Co into or through the Mo layer.

The Al 2p band binding energy and its FWHM increased to approximately the same values as following oxidation of the Mo layer. These observations may be an indication of interaction between the Co and $\gamma\text{-Al}_2\text{O}_3$. While species

identification based on the Al 2p band is not possible, these data may be indicating a reduction of the shielding effect caused by the deposited Co layer due to migration of Co into the $\gamma\text{-Al}_2\text{O}_3$. Considering the decrease in the Co/Al intensity ratio, some of the Co may have migrated completely through the Mo layer, allowing for direct interaction with the $\gamma\text{-Al}_2\text{O}_3$.

Table 4. Atomic Surface Concentrations for the Co-Mo/ $\gamma\text{-Al}_2\text{O}_3$ Model Catalyst*

	Al	O	Mo	Co
Al Oxidized	0.45	0.55	---	---
Mo Deposited	0.39	0.48	0.13	---
Mo Oxidized	0.37	0.56	0.07	---
Co Deposited	0.34	0.46	0.06	0.13
Co Oxidized	0.30	0.55	0.08	0.07

$$* \text{ Calculated by } C_x = \frac{I_x/S_x}{\sum I_x/S_x}$$

Mo-Co/ $\gamma\text{-Al}_2\text{O}_3$ Model Catalyst ESCA Analysis

The ESCA intensity data for this sample following deposition of the Mo was hampered due to difficulties with the signal pre-amplifier. This explains the substantially smaller peak areas following deposition of the Mo shown in Table 5. Because of the noise in the spectra, which was caused by this equipment malfunction, the accuracy of the peak areas following deposition of the Mo is questionable. This difficulty did not hinder determination of the peak binding energies of the FWHM.

Deposition and Oxidation of Cobalt: The Al 2p spectra of the Mo-Co/ γ -Al₂O₃ catalyst are shown in Figure 10. Numerical values of the peak binding energies are tabulated in Appendix B. The Al 2p band shifted to a lower binding energy following deposition of the Co. This, again, is probably due to the Co interacting with the surface oxygens of the γ -Al₂O₃. The higher Co 2p_{3/2} band binding energy relative to Co foil and the decreased binding energy of the O 1s band, shown in Figures 11 and 12, support an oxygen-sharing interaction of the Co with the γ -Al₂O₃.

Oxidation of the Co resulted in a decrease of the Co/Al intensity ratio as shown in Table 5. This decrease could be attributable to two factors; (1) migration of Co into the Al₂O₃ lattice, or (2) the formation of Co₃O₄ crystallites on the Al₂O₃ surface. The Co 2p_{3/2} band binding energy is greater than that for the oxidized Co foil as shown in Figure 13. In fact, it is higher than the binding energy of the Co-Mo/ γ -Al₂O₃ model catalyst (see Fig. 9, curve a). This suggests the presence of CoAl₂O₄. The ΔS is 4.9 eV which also supports the presence of CoAl₂O₄. Based on these observations, there was probably migration of Co into the tetrahedral sites of the γ -Al₂O₃ lattice. However, the ΔE is only 15.5 eV suggesting the

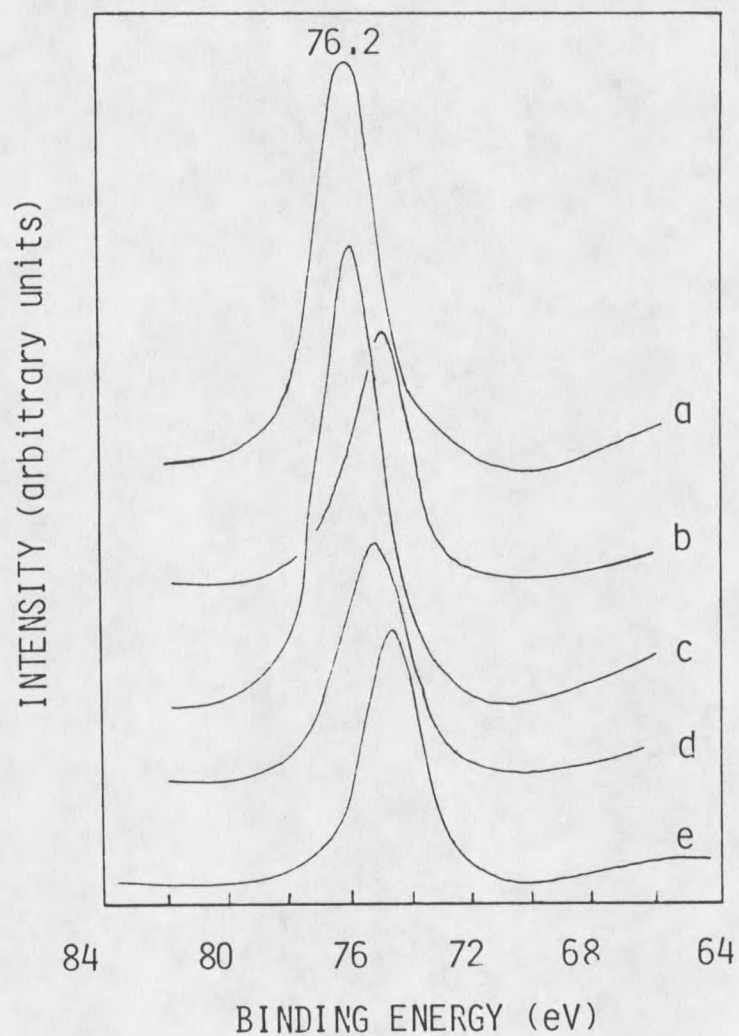


Figure 10. Al 2p ESCA Spectra for the Mo-Co/ γ -Al₂O₃ Model Catalyst
 (a) aluminum foil oxidized 10^{-6} torr O₂/H₂O, 823 K, 0.5 hr;
 (b) after ²Co deposition;
 (c) after Co oxidation;
 (d) after Mo deposition;
 (e) after Mo oxidation

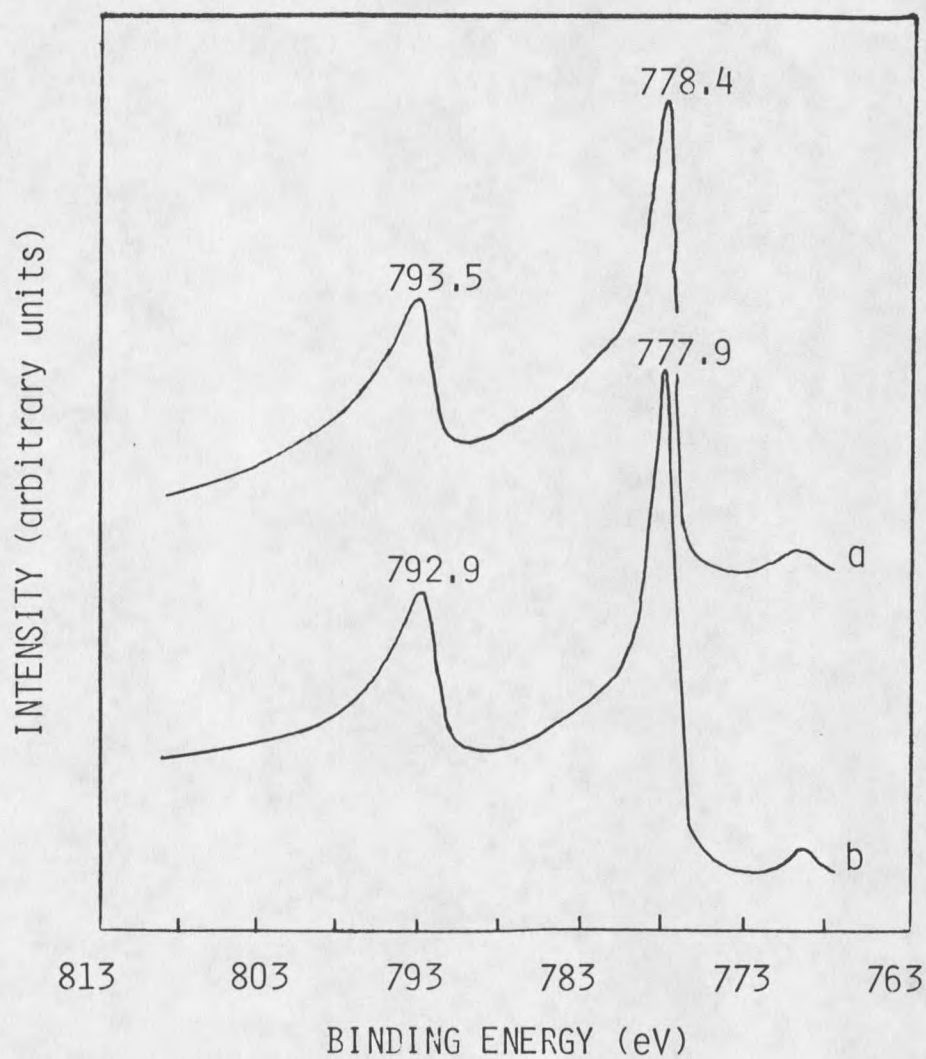


Figure 11. Co 2p ESCA Spectra for the Mo-Co/ γ -Al₂O₃ Model Catalyst After Cobalt³ Deposition and for Cobalt Foil

(a) deposited Co layer;
(b) cleaned pure Co foil

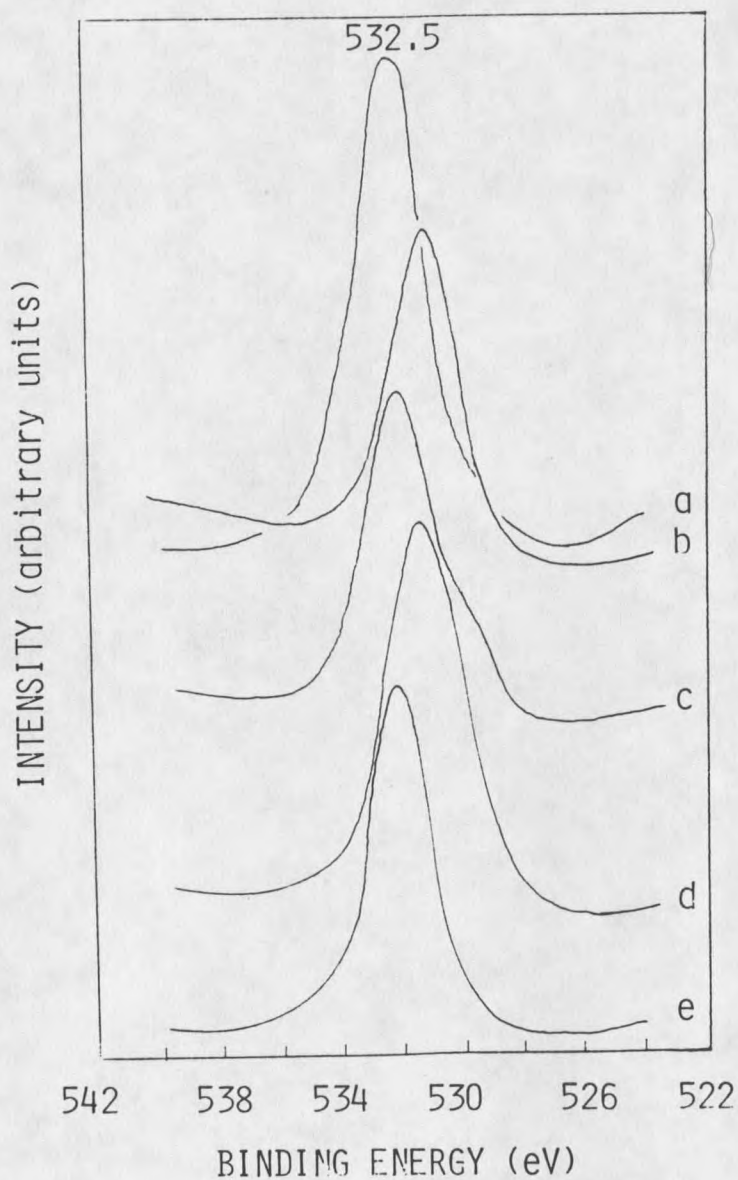


Figure 12. O 1s ESCA Spectra for the Mo-Co/ γ -Al₂O₃ Model Catalyst
(a) oxidized Al foil; (b) after Co deposition; (c) after Co oxidation; (d) after Mo deposition; (e) after Mo oxidation

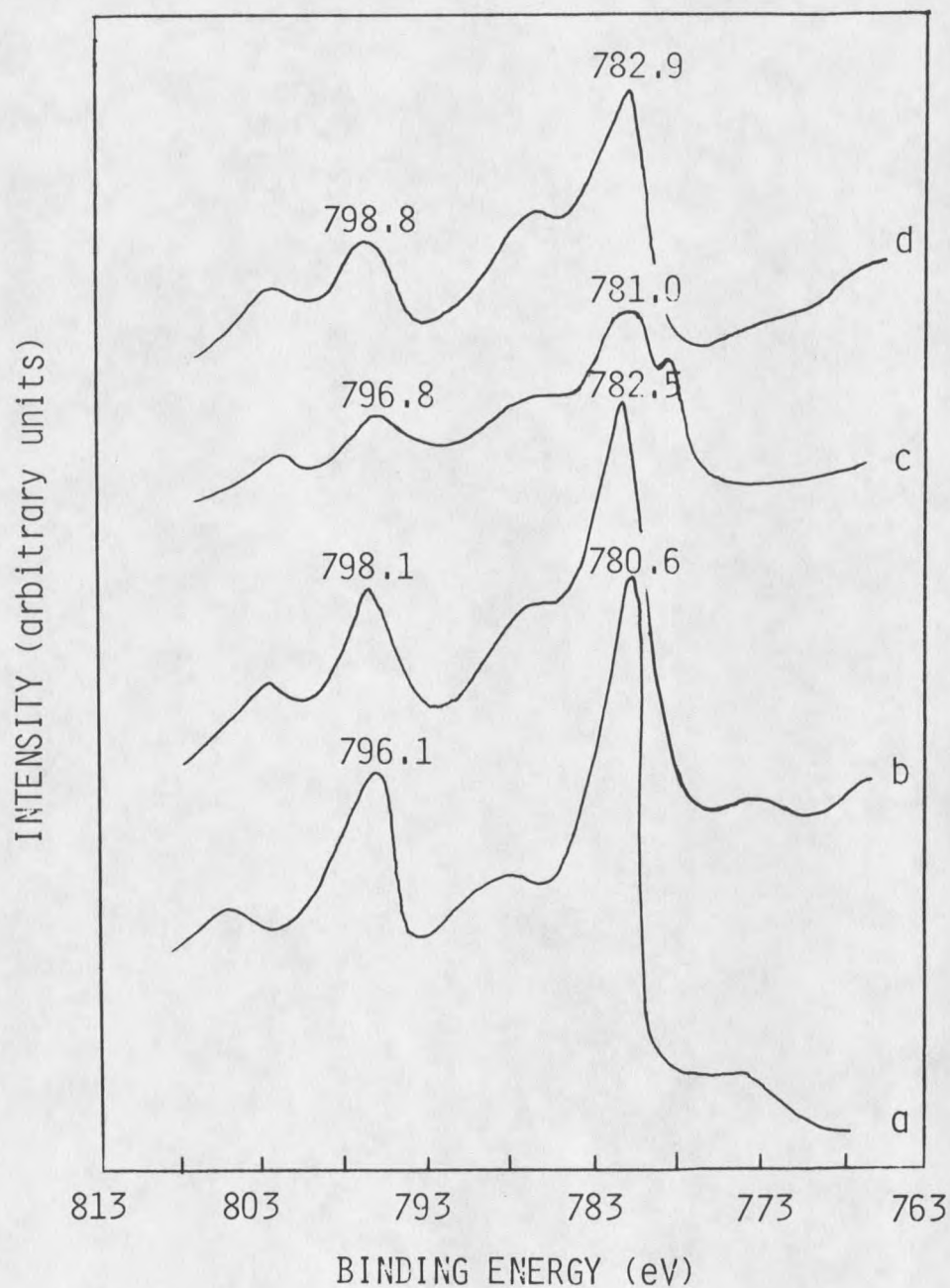


Figure 13. Co 2p ESCA Spectra for the Mo-Co/ γ -Al₂O₃ Model Catalyst After Cobalt Oxidation²³ and for Oxidized Cobalt Foil

(a) oxidized pure Co foil; (b) oxidized Co layer; (c) oxidized Co layer after Mo deposition; (d) oxidized Co layer after Mo oxidation

presence of some Co^{3+} . It appears that oxidation of the Co resulted in the formation of both CoAl_2O_4 and Co_3O_4 .

The Al 2p band binding energy increased to just below that for $\gamma\text{-Al}_2\text{O}_3$. A slight broadening of the band also occurred as shown in Table 6. The increased FWHM suggests enhanced interaction between the Co and $\gamma\text{-Al}_2\text{O}_3$. The increased binding energy of the Al 2p band may be explained by migration of Co ions into the tetrahedral sites of the $\gamma\text{-Al}_2\text{O}_3$ lattice, thus forcing more of the Al ions into the octahedral sites. The binding energy of Al 2p electrons is greater when the Al ions are in octahedral coordination [40].

Table 5. Peak Areas and Area Ratios for the Mo-Co/ $\gamma\text{-Al}_2\text{O}_3$ Model Catalyst

	Normalized Peak Areas [*] (10^3)				Peak Area Ratios	
	Al 2p	O 1s	Mo 3d	Co 2p	Mo/Al	Co/Al
Al Oxidized	30.5	39.4	----	----	----	----
Co Deposited	16.1	19.4	----	5.87	----	0.365
Co Oxidized	35.6	51.1	----	7.13	----	0.200
Mo Deposited	2.8	4.6	0.69	0.49	0.246	0.175
Mo Oxidized	88.3	132.0	9.50	8.13	0.108	0.092

* Area under the peak is divided by the sensitivity factors (S_x) obtained from reference 30.

$$S_{\text{Al 2p}}^x = 0.11, S_{\text{O 1s}} = 0.63, S_{\text{Mo 3d}} = 1.2, S_{\text{Co 2p}} = 4.5$$

These sensitivity factors were determined using a double pass, cylindrical mirror analyzer. It was assumed they are accurate for the hemispherical analyzer used in this study.

Deposition and Oxidation of Molybdenum: The Mo 3d spectrum, recorded following deposition of the Mo, is shown in Figure 14. The higher Mo 3d band binding energy and the greater FWHM, relative to pure Mo foil, indicate partial oxidation of the deposited Mo layer. The binding energies of the Al 2p and Co 2p_{3/2} bands decreased, suggesting oxygen-sharing interactions between both elements and the Mo.

Table 6. Peak Widths* (eV) for the Mo-Co/ γ -Al₂O₃ Model Catalyst

	Al 2p	O 1s	Mo 3d ¹	Co 2p _{3/2}
Al Oxidized	2.36	2.69	---	---
Co Deposited	2.33	2.58	---	3.13
Co Oxidized	2.49	2.69	---	4.04
Mo Deposited	2.63	3.25	5.50	7.50
Mo Oxidized	2.39	2.61	5.00	3.27
Mo Metal	---	---	4.75	---
Co Metal	---	---	---	2.50
Co Metal Oxidized	---	---	---	3.75

* Full Widths at Half Maximum

¹ Taken Over Entire Mo 3d Band

The Co 2p spectrum (see Fig. 13, curve c), in particular, indicates a strong interaction between the Co and Mo. This is evidenced by the appearance of a new peak on the low binding energy side of the Co 2p_{3/2} band. This new peak suggests substantial reduction of some of the Co. Since the Co in CoAl₂O₄ is nonreducible, this is probably due to interaction between the Mo and the Co that was retained on the surface as Co₃O₄ following oxidation of the

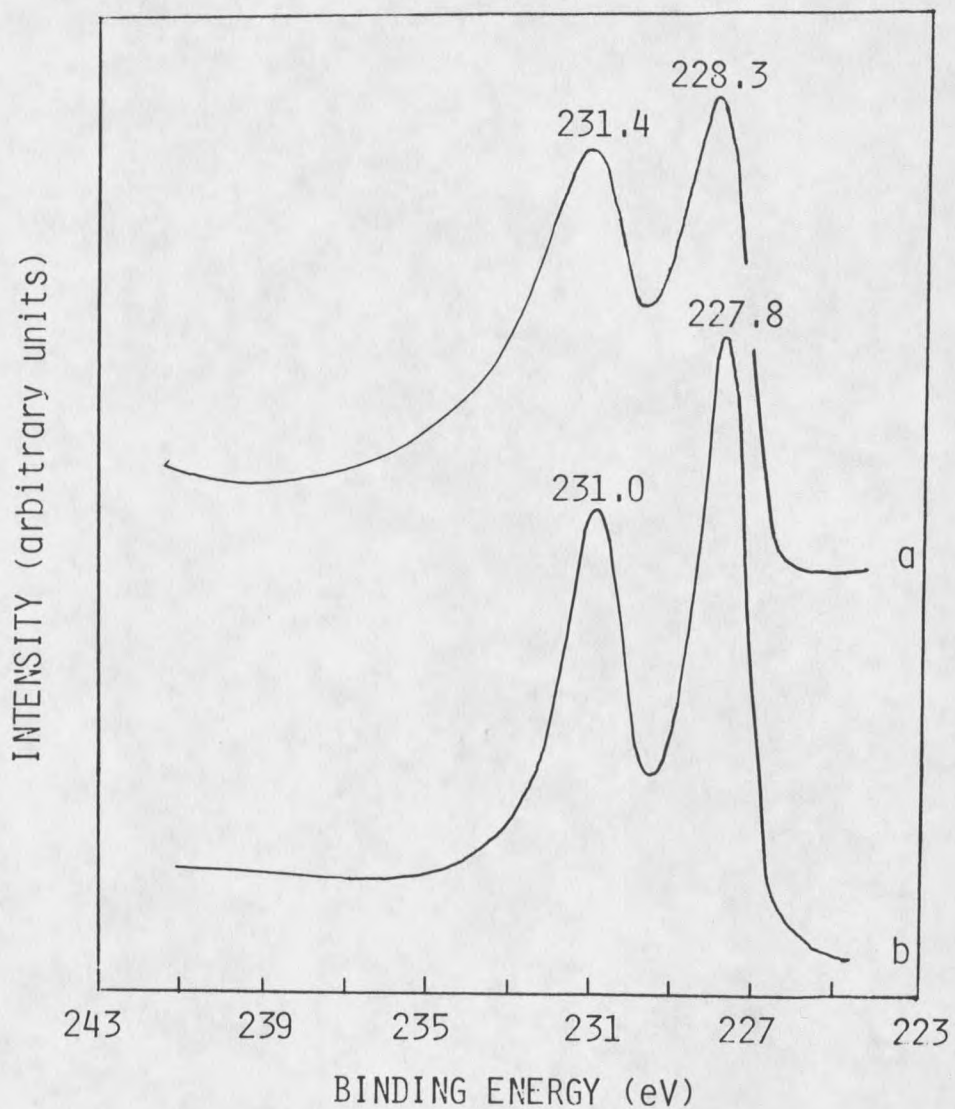


Figure 14. Mo 3d Spectra for the Mo-Co/ γ -Al₂O₃ Model Catalyst After Molybdenum Deposition and for Molybdenum Foil
(a) deposited Mo layer; (b) pure cleaned Mo foil

Co layer. The suggested interaction between the Mo and Al is plausible, provided that oxidation of the Co layer resulted in penetration of some of the Co into subsurface sites in the $\gamma\text{-Al}_2\text{O}_3$ lattice, thus leaving surface sites available for interaction with the Mo.

Following oxidation of the Mo layer, the Co $2p_{3/2}$ band binding energy increased to slightly above that after Co oxidation and the FWHM decreased (see Fig. 13, curves b&d). The ΔE increased to 15.9 eV while the ΔS remained at 4.9 eV. There was also a decrease in the Co/Al intensity ratio and an increase in the satellite intensity ratio. These observations indicate an increase in the CoAl_2O_4 type phase. The Co that had previously situated in the $\gamma\text{-Al}_2\text{O}_3$ lattice may have diffused deeper into the lattice, thus leaving surface sites available for any Co^{3+} that was retained on the surface prior to Mo oxidation [8].

Considering the Co $2p$ data, it appears that the interaction of the Co with the Mo was reduced at the expense of an increase in the CoAl_2O_4 type phase. However, as shown in Figure 15, the Mo did oxidize more readily compared to the Co-Mo/ $\gamma\text{-Al}_2\text{O}_3$ model catalyst (see Fig. 6, curve a) prior to Co deposition which may be attributable to some interaction with the Co.

The direction of shifts in the x-ray induced O KLL, Mo MNN and Co LMM Auger spectra paralleled the related ESCA

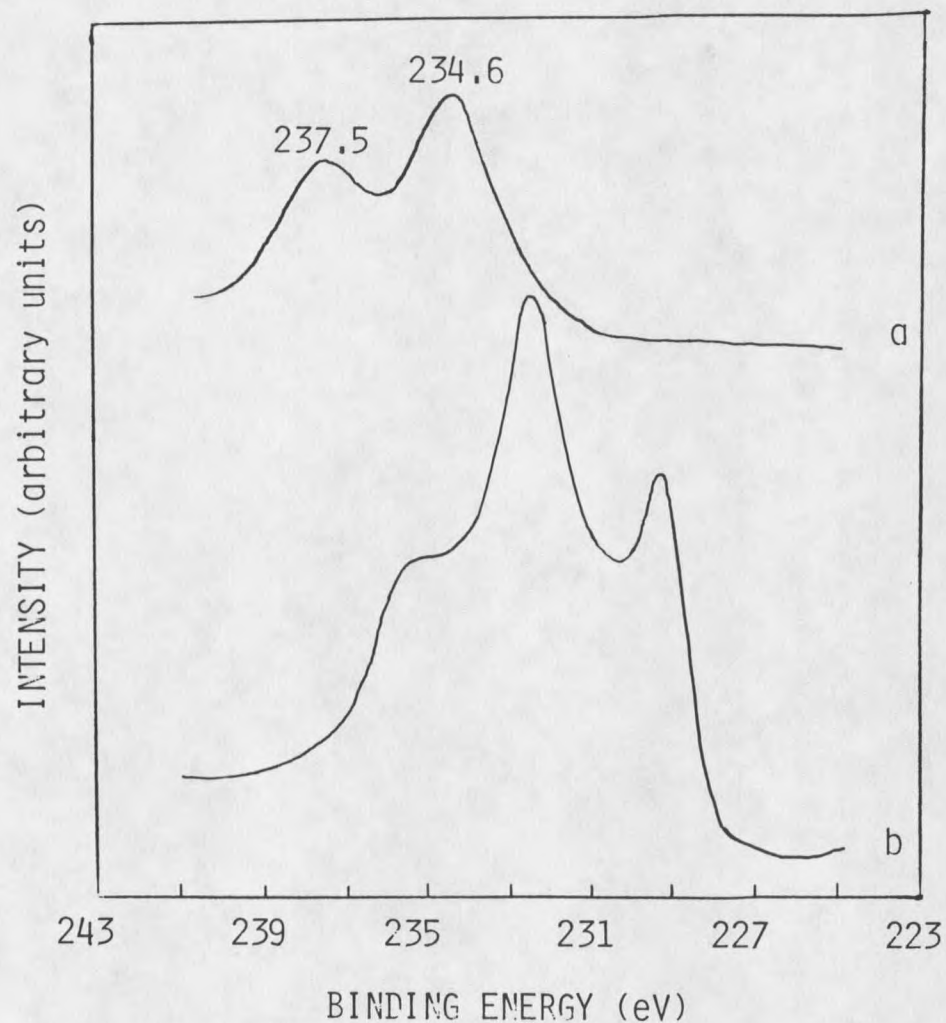


Figure 15. Mo 3d ESCA Spectra for the Mo-Co/ γ -Al₂O₃ Model Catalyst After Molybdenum Oxidation and for Oxidized Molybdenum Foil

- (a) oxidized Mo layer;
- (b) oxidized pure Mo foil

binding energy shifts. While these spectra were omitted from the discussion of the ESCA analysis, they are provided in Appendix C.

Co-Mo/ γ -Al₂O₃ Model Catalyst SIMS Analysis

Depth profiles of the Al, O, Co and Mo, obtained with SIMS are shown in Figure 16. The Mo⁺ ion intensity increased at the onset of the analysis, while the Co⁺ ion intensity steadily decreased from the beginning. Coupled together, these two observations suggest that some of the Co was maintained on top of, or together with, the Mo layer. It is not believed that this was due to surface contamination, otherwise an increase, similar to that observed in the Mo⁺ ion intensity, would have been observed in the Co⁺ ion intensity.

The Co⁺ ion intensity decreased more rapidly than the Mo⁺ ion intensity. This indicates that, in addition to some Co remaining on top of the Mo layer, some Co was dispersed in the Mo layer. The retention of Co, either on top of, or together with the Mo layer strengthens the speculation of a Co-Mo interactive species.

A SIMS survey scan taken at the bottom of one of the depth profiling craters is shown in Figure 17. The data indicates the presence of both Co and Mo, which supports the Co-Al₂O₃ and Mo-Al₂O₃ interactions suggested by the

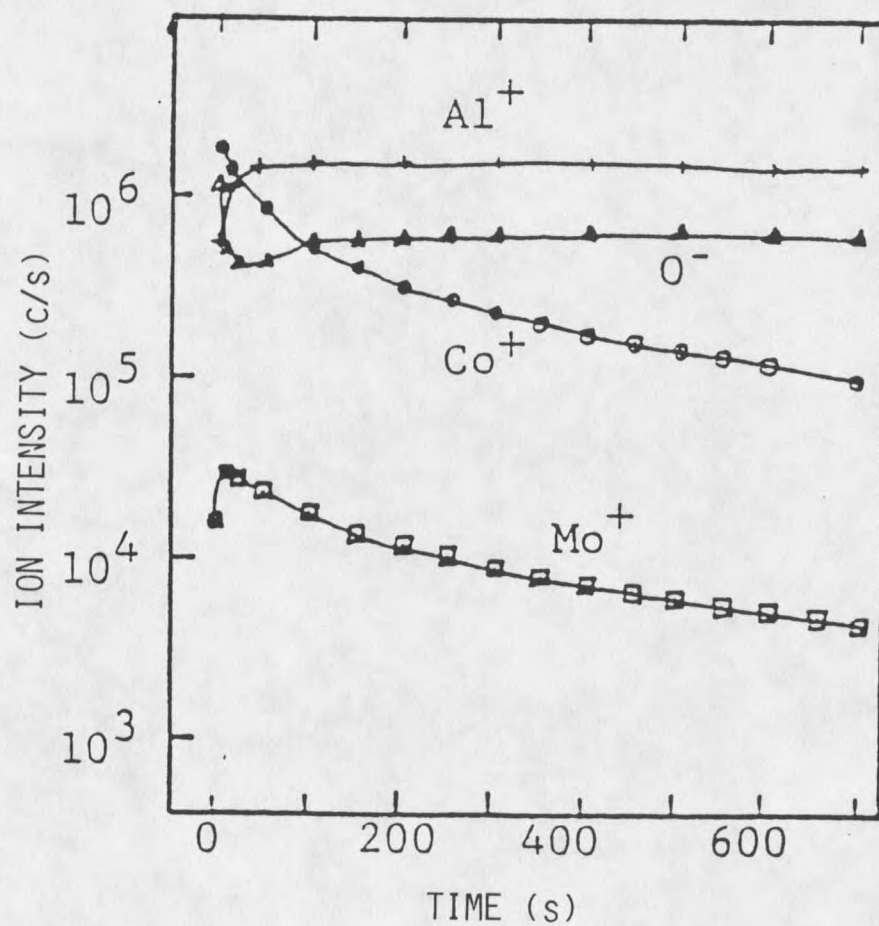


Figure 16. SIMS Depth Profiles of the Co-Mo/ $\gamma\text{-Al}_2\text{O}_3$ Model Catalyst

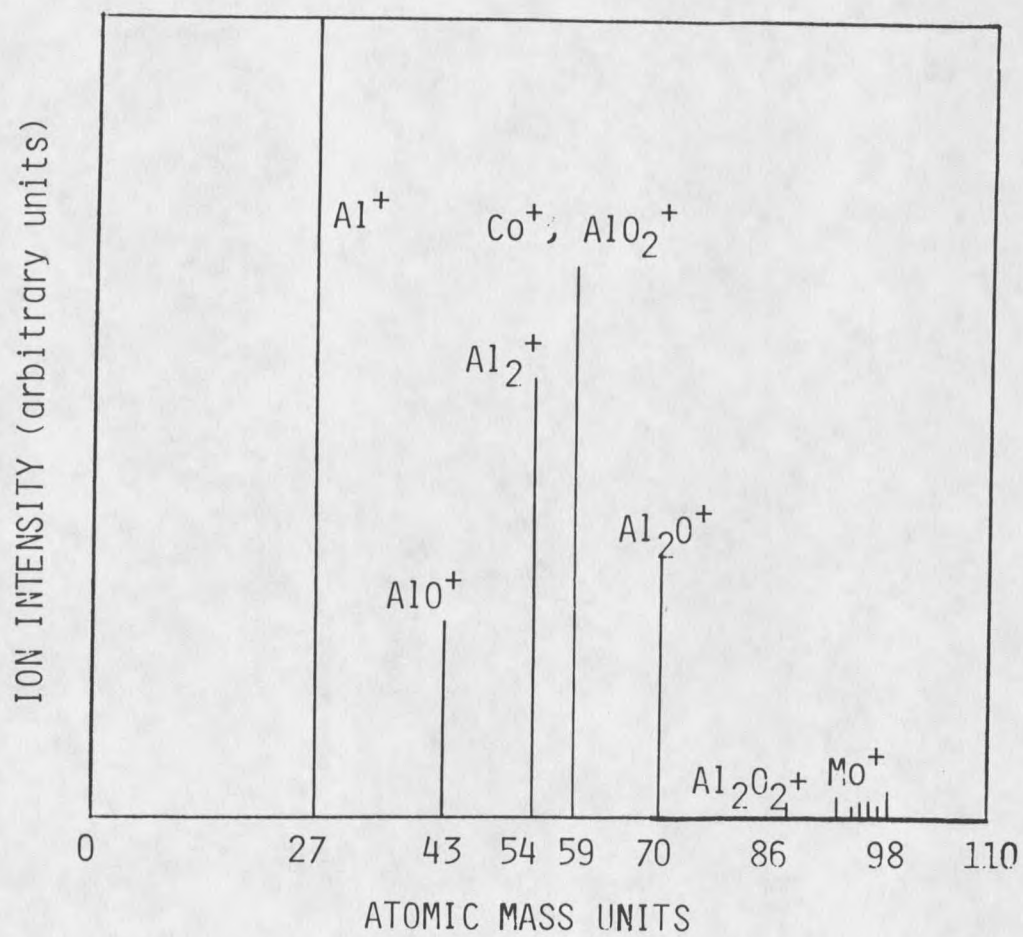


Figure 17. SIMS Survey of the Co-Mo/ γ - Al_2O_3 Model Catalyst

ESCA results. However, the contribution of matrix ionization effects to this observation can not be ruled out.

Co-Mo/ γ -Al₂O₃ Model Catalyst AES Analysis

The AES line scans for the Al, O, Co, and Mo are provided in Figure 18. The purpose of the line scans was to determine whether or not there was formation of bulk phases, such as MoO₃ or Co₃O₄, on the surface.

The line scans indicate fairly homogeneous surface coverage of both the Co and Mo. The decrease in Co intensity, and the corresponding increase in Mo intensity at 40 microns was due to agglomeration of Mo around an imbedded Al₂O₃ particle from sample polishing. The Al and O line scans also display an increase in intensity at this same location.

The presence of small microcrystallites can not be ruled out based on these data. Recalling the Co 2p spectra of this sample, the presence of some Co³⁺, possibly as Co₃O₄, was indicated. Since the line analysis traversed 100 microns across the sample, small crystallites may not have been detectable.

An electron micrograph of the sample surface is shown in Figure 19. This micrograph, obtained at a magnification of 1000X, is the same area from which the line scans were obtained. The surface of the sample appears fairly smooth.

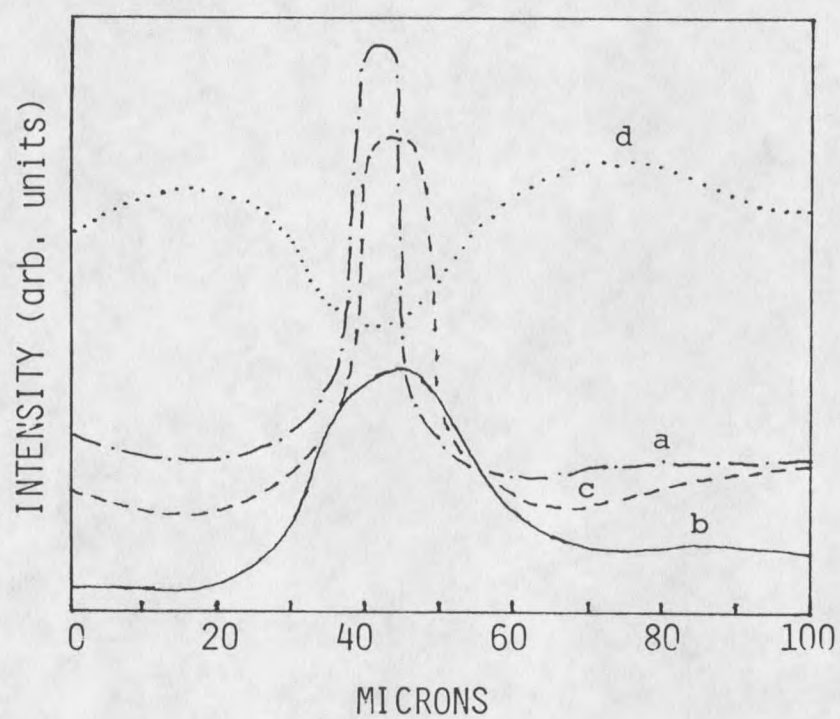


Figure 18. AES Line Scans of the
Co-Mo/ γ -Al₂O₃ Model Catalyst.
(a) aluminum; (b) molybdenum;
(c) oxygen; (d) cobalt

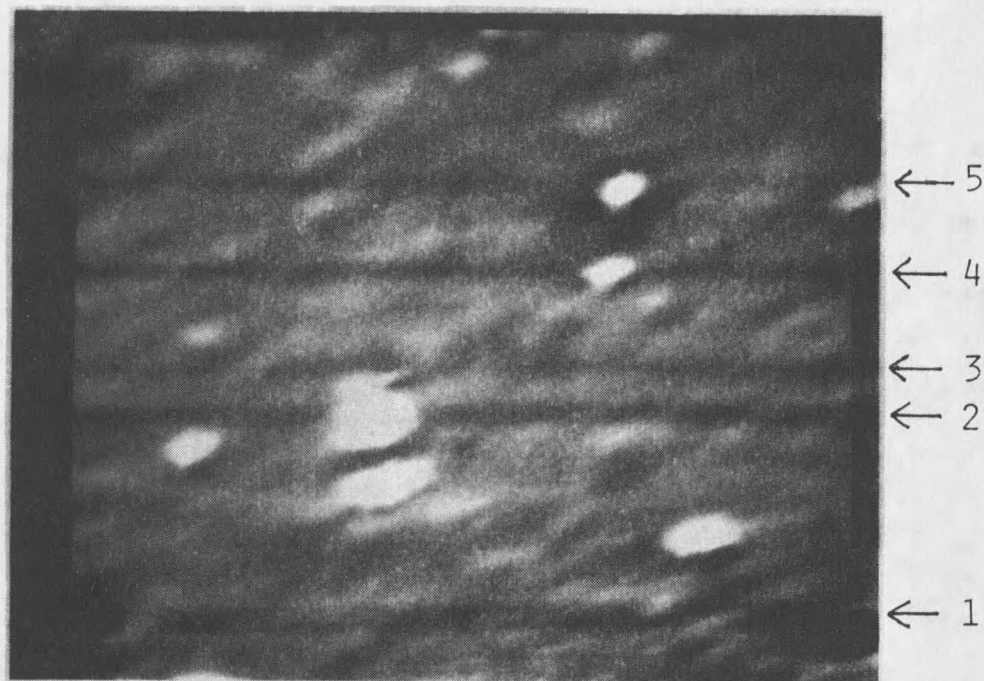


Figure 19. SEM Micrograph of the Co-Mo/ γ -Al₂O₃ Model Catalyst Surface

Note: This micrograph is from the same area in which the AES line scans were performed. The 5 dark lines are carbon burns from the electron beam. Line #2 is where the data in Figure 18 was obtained. The white patches are imbedded alumina polishing powders.

The white patches in the micrograph are the Al_2O_3 polishing powders imbedded in the surface. The dark lines running horizontally through the micrograph are carbon burns resulting from the AES line scans. The line labeled number 2 is where the data in Figure 18 was obtained.

Comparison of Planar Models to Industrial Catalysts

The literature on studies of the surface structure of the calcined industrial Co-Mo/ $\gamma\text{-Al}_2\text{O}_3$ catalysts is vast. Depending on the preparation parameters and the analytical techniques employed in the studies, a variety of surface species have been identified. Since the purpose of this study is to determine if the planar model catalysts are structurally similar to the industrial catalysts, a comparison of the findings of this study with the literature is appropriate. Since a more complete analyses was performed on the Co-Mo/ $\gamma\text{-Al}_2\text{O}_3$ model catalyst, the discussion is directed towards that sample. However, where applicable, the ESCA results for the Mo-Co/ $\gamma\text{-Al}_2\text{O}_3$ model catalyst are utilized.

Recalling the ESCA results of the Co-Mo/ $\gamma\text{-Al}_2\text{O}_3$ model catalyst after oxidation of the Mo layer, it appears that there is strong interaction between the Mo ions and the $\gamma\text{-Al}_2\text{O}_3$. This interaction is suspected to be the result of the Mo ions interacting with the terminal oxygens of the $\gamma\text{-Al}_2\text{O}_3$. It is widely believed on the industrial catalysts

that the Mo is highly dispersed over the $\gamma\text{-Al}_2\text{O}_3$ support in essentially a monolayer [6]. This monolayer is believed to differ from bulk MoO_3 . Rather, the Mo is thought to interact with the support forming a surface molybdate with the Mo in tetrahedral or octahedral surroundings [11]. While determination of the Mo coordination was not possible with the techniques employed in this study, the AES line scans indicated the Mo was well dispersed on the surface as in monolayer type coverage.

The Co in the Co-Mo/ $\gamma\text{-Al}_2\text{O}_3$ planar model appeared to be distributed throughout the Mo layer. Based on the SIMS depth profiling, the majority of the Co was retained on top of, or together with the Mo layer suggesting interaction between the Co and Mo. The enhanced oxidation of the Mo in the presence of Co and the ESCA intensity ratios further indicated interaction between the Co and Mo, although the SIMS surveys and ESCA results indicated some interaction of the Co with the $\gamma\text{-Al}_2\text{O}_3$.

The Co $2p_{3/2}$ band binding energy of the Co-Mo/ $\gamma\text{-Al}_2\text{O}_3$ model catalyst is between that of the oxidized Co foil and the Mo-Co/ $\gamma\text{-Al}_2\text{O}_3$ model catalyst. Assigning Co_3O_4 as the predominant Co species for the oxidized Co foil and tetrahedrally coordinated Co^{2+} , in a CoAl_2O_4 type phase, as the predominant Co species in the Mo-Co/ $\gamma\text{-Al}_2\text{O}_3$ model

catalyst, it might be assumed that the Co $2p_{3/2}$ band binding energy of the Co-Mo/ γ - Al_2O_3 model catalyst is the result of a Co-Mo interactive species.

The assignment of the Co as $CoAl_2O_4$ in the Mo-Co/ γ - Al_2O_3 model catalyst would seem valid since, in the absence of an underlying Mo layer the Co might more freely diffuse into the γ - Al_2O_3 lattice [8]. Contrary to this speculation, studies on the industrial catalysts indicate a greater tendency for Co_3O_4 formation when Co is added directly to the γ - Al_2O_3 supports [8, 12]. This Co_3O_4 formation has been observed with Co concentrations as low as 2 wt%. However, the extent of Co_3O_4 formation is dependent on the mode of Co addition and the calcination temperature. The fact that the Mo-Co/ γ - Al_2O_3 model catalyst indicates most of the Co is $CoAl_2O_4$ may be attributed to the differences in preparation between the planar models and the industrial catalysts. The Co $2p$ spectra of the Mo-Co/ γ - Al_2O_3 model catalyst did indicate the presence of some Co^{3+} prior to oxidation of the Mo layer.

The suggestion of a Co-Mo interactive phase on the Co-Mo/ γ - Al_2O_3 model catalyst is not meant to imply that $CoMoO_4$ is actually forming on the model catalyst. The ΔS indicated tetrahedral coordination of the Co^{2+} ions (Co^{2+} in $CoMoO_4$ is octahedral). The majority of the Co^{2+} ions in

the Co-Mo/ γ -Al₂O₃ model catalyst may be tetrahedrally coordinated in a Co-Mo interactive phase. The SIMS and ESCA data also indicated some interaction between the Co and the γ -Al₂O₃. This interaction might be in the form of tetrahedrally coordinated Co²⁺ situated in the γ -Al₂O₃ lattice in a CoAl₂O₄ type phase. In addition, the presence of some Co³⁺ in the Co-Mo/ γ -Al₂O₃ planar model is not discounted based on the ESCA data. This may be due to small crystallites of Co₃O₄ on the surface, or from the presence of Co³⁺ in the Co-Mo interactive phase.

Numerous investigators have suggested the presence of Co-Mo interactive species on the calcined industrial catalysts [5, 8, 13, 20, 41]. Gajardo et. al. [13] reports the presence of a Co-Mo bilayer in which some of the Co is retained on top of the Mo layer. They suggest the Co in the bilayer is present as Co³⁺ in octahedral surroundings, although the presence of octahedrally coordinated Co²⁺ is not excluded. The remaining Co is dispersed in the γ -Al₂O₃ as CoAl₂O₄. Okamoto et. al. [41] propose a similar bilayer structure with some Co situated on top of the Mo layer.

The Co-Mo interactive species proposed by Chin and Hercules [5] is somewhat different than the bilayer models. They propose the existence of a Co-Mo interaction species with the Co predominantly present as tetrahedrally

coordinated Co^{2+} . The key difference in their structure is the tetrahedrally coordinated Co^{2+} is primarily contained in the Co-Mo interaction phase, not as CoAl_2O_4 .

It is not helpful to speculate further, based on the data of this study, on the nature of the Co species in the Co-Mo/ $\gamma\text{-Al}_2\text{O}_3$ model catalyst. For example, determination of whether the tetrahedrally coordinated Co^{2+} is present as CoAl_2O_4 or as a Co-Mo interactive species might be accomplished by reducing the model catalyst under hydrogen and examining the Co 2p ESCA spectra. Since CoAl_2O_4 is not reducible, this may reveal the extent of CoAl_2O_4 formation. This is, in fact, how Chin and Hercules determined the Co^{2+} in their catalyst was tetrahedrally coordinated in the Co-Mo interactive phase. The presence of Co^{3+} as Co_3O_4 could be verified by x-ray diffraction [8].

SUMMARY AND CONCLUSIONS

The objective of this study was to establish the techniques for preparing planar model cobalt-molybdenum on $\gamma\text{-Al}_2\text{O}_3$ catalysts and compare their surface structure to the industrially used catalysts. The salient findings of this study are as follows:

1. Growth of $\gamma\text{-Al}_2\text{O}_3$ on planar aluminum was successfully demonstrated via direct thermal oxidation.
2. Physical vapor deposition of the cobalt and molybdenum on the planar $\gamma\text{-Al}_2\text{O}_3$ was superior to the industrially used incipient wetness technique for these samples. Physical vapor deposition provided for more even surface coverage of the metals and enabled complete in situ preparation of the planar model catalysts.
3. Similar to the calcined industrial catalysts, the molybdenum deposited directly onto the planar $\gamma\text{-Al}_2\text{O}_3$ appeared to be well dispersed, as in monolayer coverage, and interacting with the $\gamma\text{-Al}_2\text{O}_3$.
4. When cobalt was deposited on top of the molybdenum layer, the cobalt appeared to be in tetrahedral coordination and to interact primarily with the molybdenum. While more data is needed to

characterize the nature of the Co species, this observation is similar to those made on the calcined, industrial catalysts.

5. While based on more limited data, there appeared to be less interaction between the cobalt and molybdenum when cobalt deposition preceded molybdenum. In this case, the Co appeared to exist primarily as CoAl_2O_4 .

RECOMMENDATIONS

Based on the experience gained from this experimental work and the literature review, the following recommendations are provided for future work:

1. The SIMS and AES analysis of the Co-Mo/ γ -Al₂O₃ model catalyst provided valuable information about the metal dispersion and interaction between the metals. These same analyses should be performed on the Mo-Co/ γ -Al₂O₃ model catalyst to provide information about the effect of metals impregnation order on the surface structure of the model catalysts.
2. While ESCA is a powerful technique for providing information about the chemical environment of atoms on the surface, future studies should incorporate a wider variety of instruments and experimental techniques in order to strengthen the findings. Examining changes in the Co 2p ESCA spectra under a reducing environment would be of great value in cobalt species identification, since CoAl₂O₄ is non reducible. X-ray diffraction, Raman spectroscopy and Mossbauer spectroscopy are among the proven techniques for elucidating information

about the chemical environment of atoms on the surface in studies on the industrial catalysts.

3. In conjunction with the above recommendation, pure reference compounds should also be analyzed by the same instruments to assist in identifying the chemical species present on the surface.

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APPENDICES

APPENDIX A

Sample Calculations

This is an example calculation for determining the surface coverage of the cobalt and molybdenum via the quartz crystal oscillator (QCO).

The equation relating the thickness of a monolayer of the metals to the frequency drop of the QCO are;

$$d = [A/(pnN_A)]^{1/3}, \quad \Delta F = dCp$$

where; d = thickness of monolayer - cm

A = molecular weight of metal - g/mol

ρ = density of metal - g/cm³

n = number of atoms in a molecule

N_A = Avogadro's number

C = 56,497,175 cm²/gsec for 5 MHz quartz crystal

ΔF = frequency drop of QCO - Hz

For this example calculation molybdenum will be used.

$$A = 95.94 \text{ g/mol}; \quad \rho = 10.2 \text{ g/cm}^3; \quad n = 1$$

$$N_A = 6.023 \times 10^{23}$$

$$d = [95.94/(10.2 \times 1 \times 6.023 \times 10^{23})]^{1/3} = 2.5 \times 10^{-8} \text{ cm}$$

$$\Delta F = 2.5 \times 10^{-8} \times 56,497,175 \times 10.2 = 14.4 \text{ Hz}$$

Therefore, when one monolayer of molybdenum atoms has been deposited on the planar model catalyst, the frequency of the QCO should have decreased 14.40 Hz.

This is an example calculation for determining the surface coverage of the cobalt and molybdenum via the ESCA peak areas. This example is for molybdenum deposited onto the $\gamma\text{-Al}_2\text{O}_3$.

The equation relating atomic concentration to the ESCA peak area is;

$$C_x = \frac{I_x/S_x}{\sum I_x/S_x}, \text{ where; } I_x = \text{peak area} \\ S_x = \text{sensitivity factor}$$

The planar model catalysts were assumed to have a layered structure as shown below;

1	-----	Mo
2	-----	O ²⁻
3	-----	Al ³⁺
4	-----	O ²⁻
5	-----	Al ³⁺
6	-----	O ²⁻
7	-----	Al ³⁺
8	-----	O ²⁻
9	-----	Al ³⁺
10	-----	Al

The following assumptions were made:

1. Average thickness of each layer equalled 2.0 Å.
2. Escape depth of secondary electrons equalled 20 Å and therefore, 10 layers are 'seen' by the spectrometer.

Considering these assumptions, C_{Mo} should equal 0.10 for a monolayer of Mo atoms on the $\gamma\text{-Al}_2\text{O}_3$ surface.

After deposition of the Mo on the Co-Mo/ γ -Al₂O₃ model catalyst, the ESCA peak areas for each of the elements present were;

$$\begin{aligned}\text{Mo } 3d &= 6.64 \times 10^3; & \text{Al } 2p &= 2.20 \times 10^3 \\ \text{O } 1s &= 1.93 \times 10^4\end{aligned}$$

The atomic sensitivity factors for these elements, as provided by the Handbook of X-ray Photoelectron Spectroscopy [30], are;

$$\text{Mo } 3d = 1.2; \text{Al } 2p = 0.11; \text{O } 1s = 0.63$$

$$C_{\text{Mo}} = \frac{6.64 \times 10^3 / 1.2}{6.64 \times 10^3 / 1.2 + 2.20 \times 10^3 / 0.11 + 1.93 \times 10^4 / 0.63} = 0.13$$

APPENDIX B

ESCA Peak Binding Energies

TABLE 7. ESCA Peak Binding Energies (eV) for the Co-Mo/ γ -Al₂O₃ Model Catalyst

	<u>Al 2p</u>	<u>O 1s</u>	<u>Mo 3d_{3/2}</u>	<u>Mo 3d_{5/2}</u>	<u>Co 2p_{1/2}</u>	<u>SS¹</u>	<u>Co 2p_{3/2}</u>	<u>SS²</u>
Al Oxidized	76.07	532.28	----	----	---	---	---	---
Mo Deposited	75.56	531.65	231.07	227.92	---	---	---	---
Mo Oxidized	75.56	531.62	*	*	---	---	---	---
Co Deposited	75.11	531.06	*	*	793.50	---	778.50	---
Co Oxidized	75.40	531.23	236.17	233.00	797.41	803.00	781.79	786.98
Mo Metal	---	---	230.97	227.84	---	---	---	---
Mo Metal Oxidized	---	---	*	*	---	---	---	---
Co Metal	---	---	---	---	792.95	---	777.90	---
Co Metal Oxidized	---	---	---	---	796.05	804.75	780.65	787.00

84

¹ Shake up satellite on high binding energy side of Co 2p_{1/2} band

² Shake up satellite on high binding energy side of Co 2p_{3/2} band

* The Mo 3d bands displayed more than two peaks

TABLE 8. ESCA Peak Binding Energies (eV) for the Mo-Co/ γ -Al₂O₃ Model Catalyst

	Al 2p	O 1s	Mo 3d _{3/2}	Mo 3d _{5/2}	Co 2p _{1/2}	SS ¹	Co 2p _{3/2}	SS ²
Al Oxidized	76.19	532.48	---	---	---	---	---	---
Co Deposited	75.12	531.25	---	---	793.50	---	778.40	---
Co Oxidized	76.02	532.15	---	---	798.08	803.75	782.54	787.45
Mo Deposited	75.20	531.40	231.40	228.30	796.75	802.50	781.00	786.50
Mo Oxidized	74.70	532.18	237.50	234.60	798.75	804.25	782.86	787.80
Mo Metal	---	---	230.97	227.84	---	---	---	---
Mo Metal Oxidized	---	---	*	*	---	---	---	---
Co Metal	---	---	---	---	792.95	---	777.90	---
Co Metal Oxidized	---	---	---	---	796.05	804.75	780.65	787.00

85

- ¹ Shake up satellite on high binding energy side of Co 2p_{1/2} band
² Shake up satellite on high binding energy side of Co 2p_{3/2} band
 * The Mo 3d bands displayed more than two peaks

APPENDIX C

X-ray Induced Auger Spectra

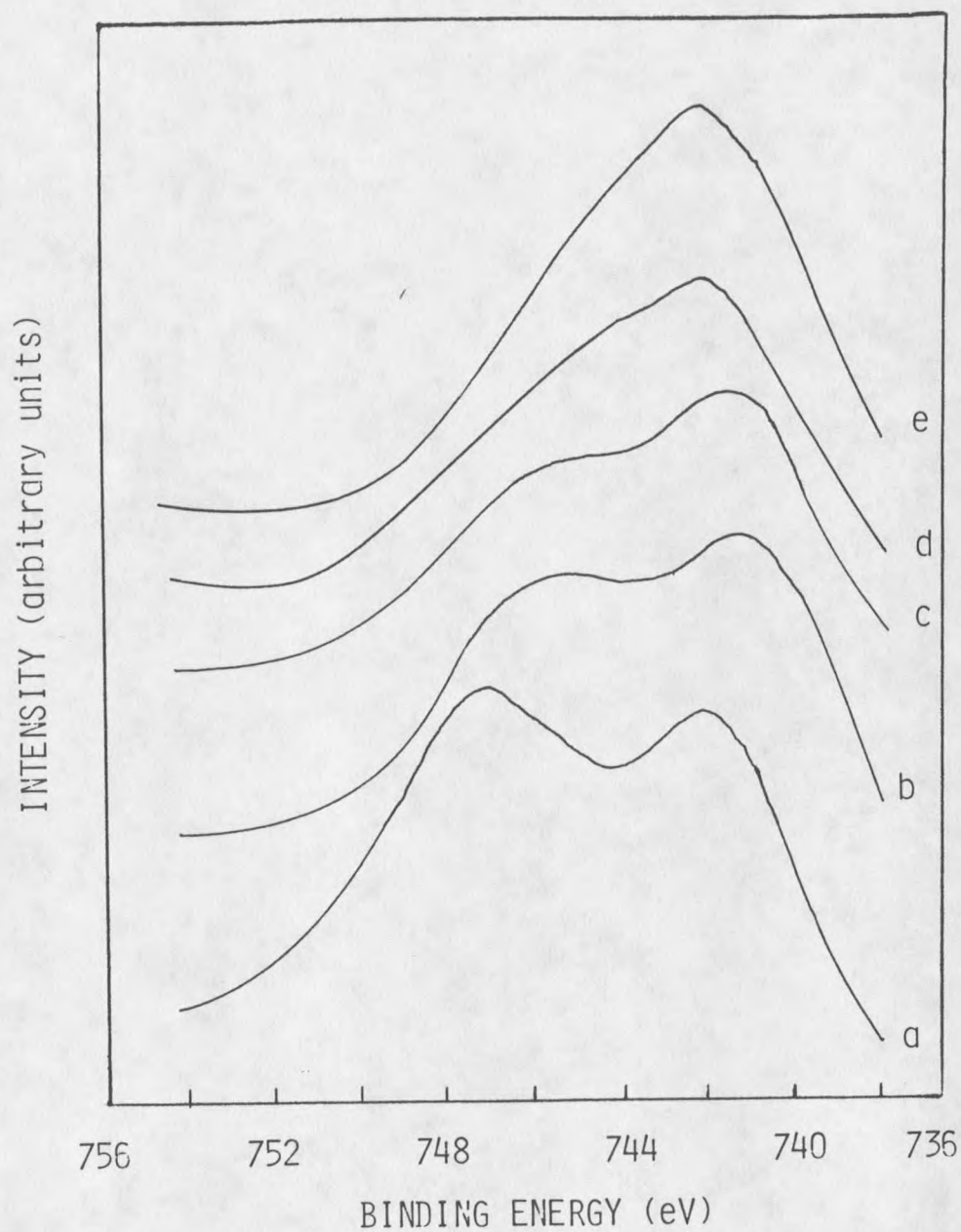


Figure 20. O KLL Auger Spectra for the Co-Mo/ γ -Al₂O₃ Model Catalyst
(a) oxidized Al foil; (b) after Mo deposition; (c) after Mo oxidation; (d) after Co deposition; (e) after Co oxidation

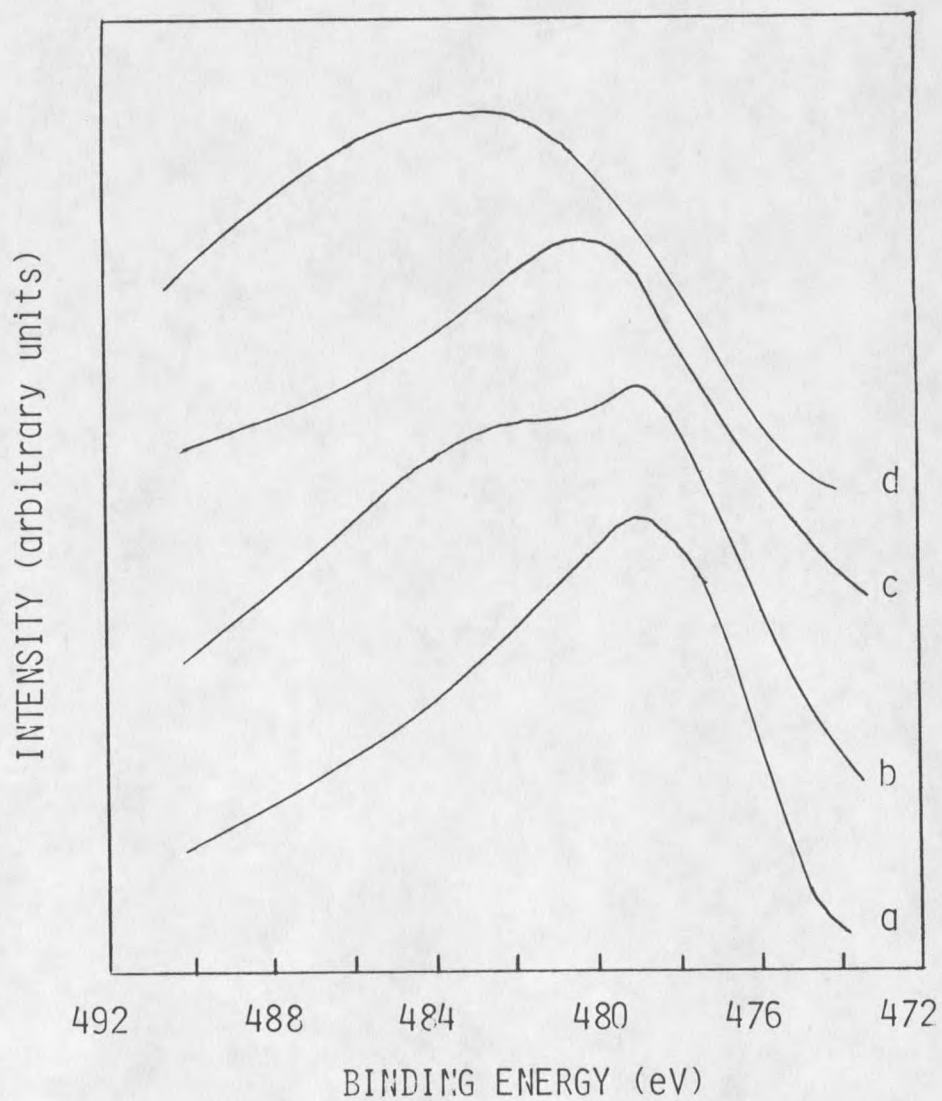


Figure 21. Co LMM Auger Spectra for the Co-Mo/ γ -Al₂O₃ Model Catalyst and Cobalt²Foil
(a) pure cleaned Co foil; (b) Co foil oxidized; (c) deposited Co layer; (d) oxidized Co layer

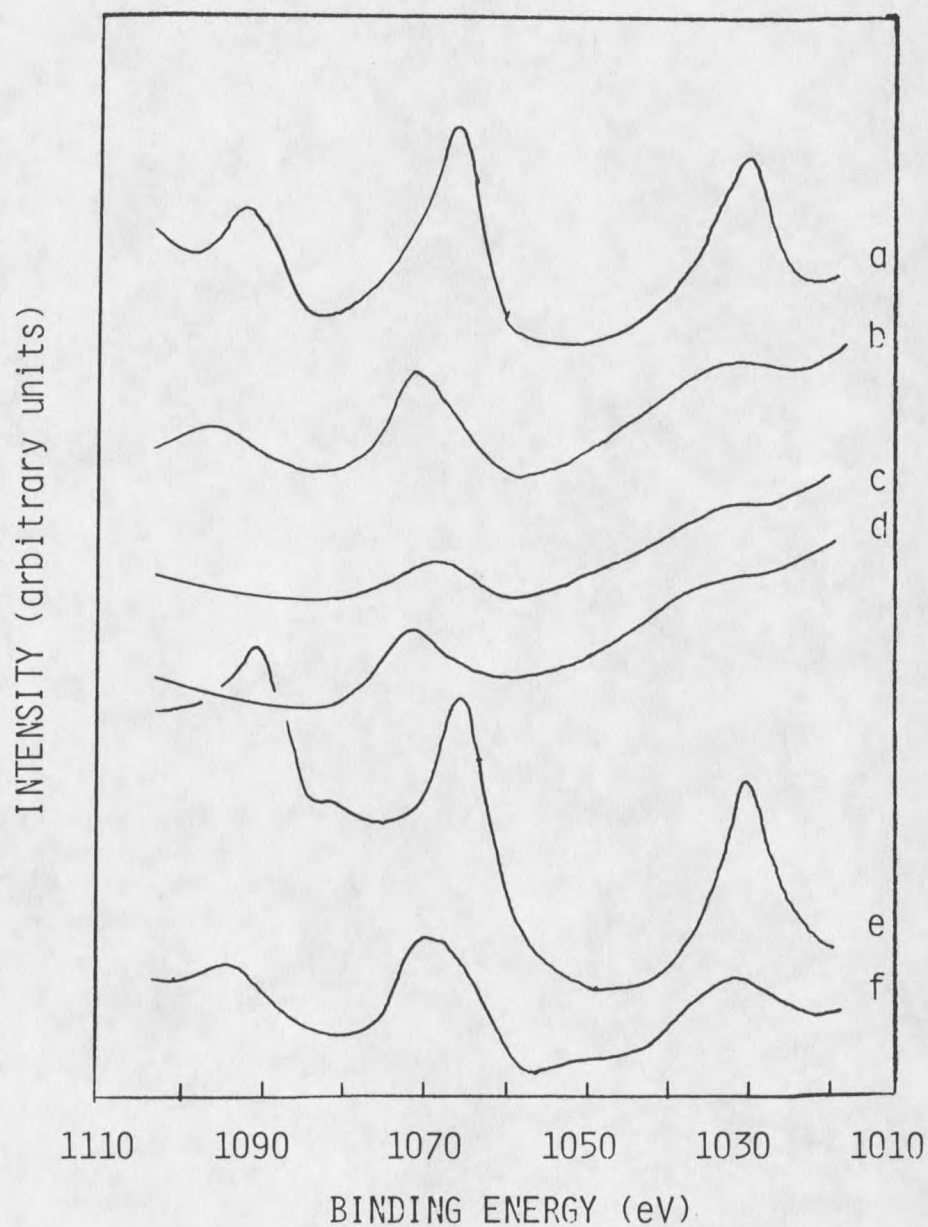


Figure 22. Mo MNN Auger Spectra for the Co-Mo/ γ -Al₂O₃ Model Catalyst and Molybdenum Foil

(a) deposited Mo layer; (b) oxidized Mo layer; (c) oxidized Mo layer after Co deposition; (d) oxidized Mo layer after Co oxidation; (e) pure cleaned Mo foil; (f) oxidized Mo foil

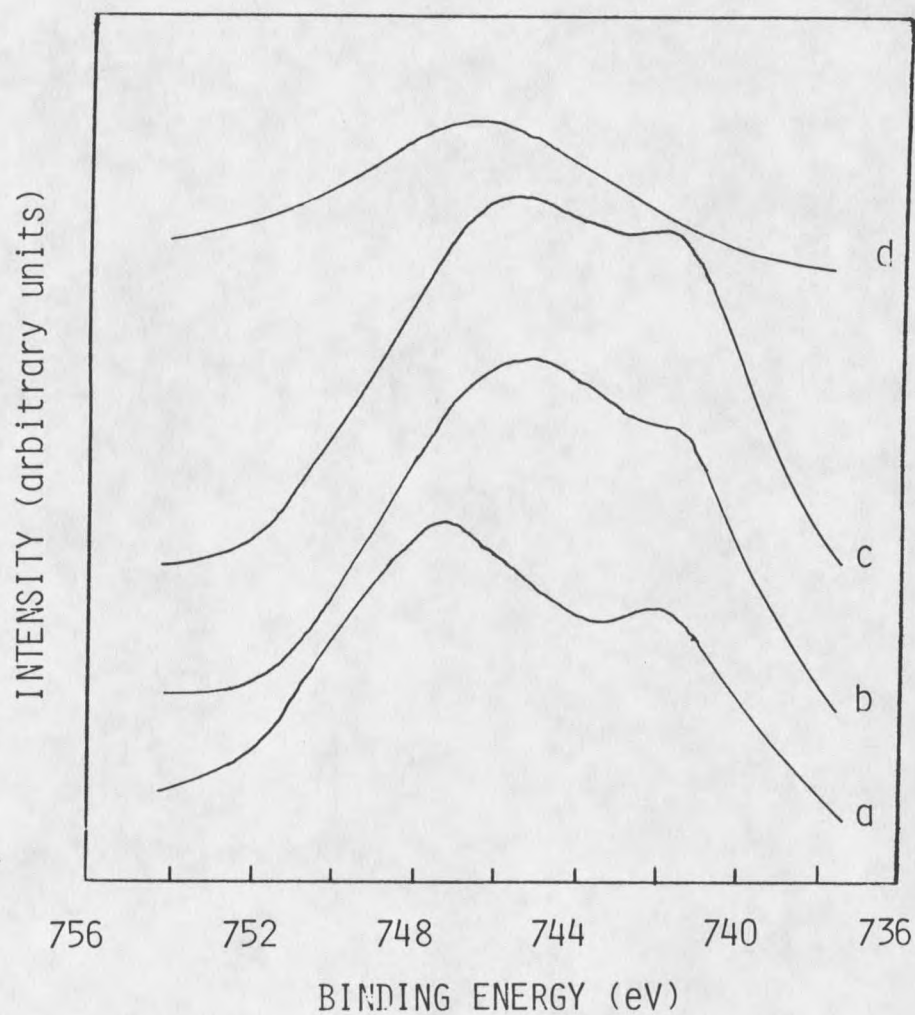


Figure 23. O KLL Auger Spectra for the Mo-Co/ γ -Al₂O₃ Model Catalyst
(a) oxidized Al foil; (b) after Co deposition; (c) after Co oxidation; (d) after Mo oxidation

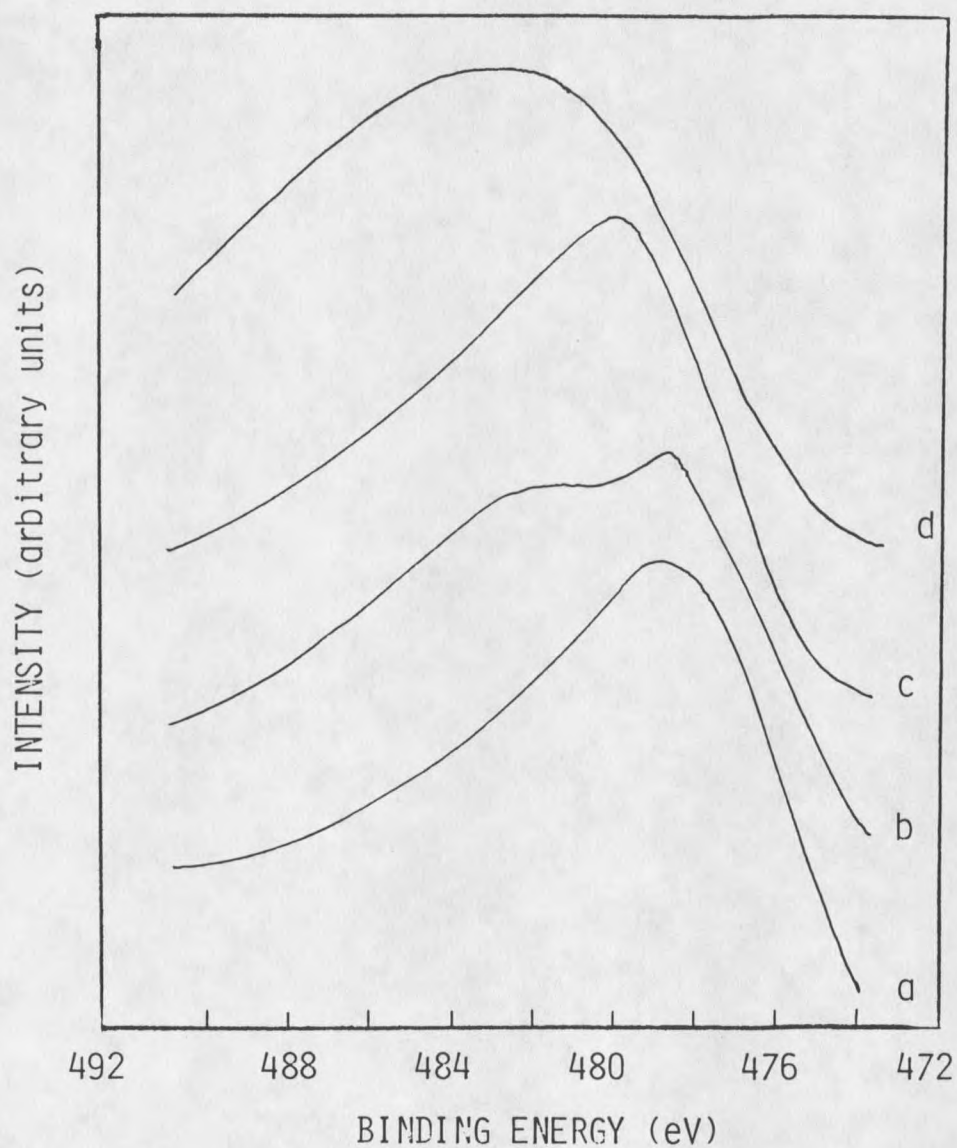


Figure 24. Co LMM Auger Spectra for the Mo-Co/ γ -Al₂O₃ Model Catalyst and Cobalt Foil
(a) pure cleaned Co foil; (b) Co foil oxidized; (c) deposited Co layer; (d) oxidized Co layer



Main
N378
K637
cop.2