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Determination of the Distribution of Species in Supported Metal Catalysts by X-Ray Photoelectron Spectroscopy

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A method is described for the use of X-ray photoelectron spectroscopy (ESCA) for quantitatively determining the distribution of species in supported metal catalysts. The method can determine the distribution of metal species for catalysts which contain both discrete metal oxide and metal surface phases with differing dispersions. The utility of the method is illustrated for a series of Co/Al_2O_3 catalysts containing Co_3O_4 and both tetrahedrally and octahedrally coordinated Co^{2+} surface phases. The determination of the distribution of Co species for a series of Co/Al_2O_3 catalysts by the present method is consistent with results from studies using other techniques.

INTRODUCTION

The nature of the species formed on the surfaces of alumina-supported metal catalysts has been the subject of numerous investigations using a variety of experimental techniques (*1–14*). With few exceptions, previous work has focused solely on identification of the various species formed as a function of metal loading and catalyst treatment. In the oxidic state, it is generally agreed that at least two phases exist on the surfaces of oxidic supported metal catalysts: discrete metal oxide particles and a "surface phase," comprised of metal ions which have diffused into the support lattice structure.

Qualitative identification of the metal species on the surfaces of supported metal catalysts is an important first step in catalyst characterization. Quantitation of the various surface species will provide an even better assessment of the effect of catalyst preparation conditions, and the effects of additives and promoters on catalyst activity. Ultimately, the use of analytical techniques to determine quantitatively the distribution of supported metal species may aid in the prediction of catalyst activity and in the tailoring of catalysts for specific chemical reactions.

The recent publication of Wivel *et al.* (*11*) represents one of the few attempts at quantitation of the species present on Co/Al_2O_3 catalysts. In that work, Co quantitation was accomplished through the use of Mössbauer spectroscopy. The present communication will outline a method for quantitatively determining the distribution of species for supported metal catalysts using ESCA and will demonstrate the utility of the method for obtaining the distribution of Co species on Co/Al_2O_3 catalysts. Also, it will be shown that the results obtained with ESCA are consistent with those obtained by Mössbauer spectroscopy and with other characterization techniques.

EXPERIMENTAL

Catalyst Preparation

A series of Co/Al_2O_3 catalysts was prepared by pore volume impregnation of γ-Al_2O_3 (Harshaw Chemical Co., AL-1401P; BET surface area; 180 m^2/g; pore volume, 0.43 ml/g) with solutions containing various amounts of cobalt nitrate. Catalysts having cobalt contents ranging from 1.5 to 10 wt%

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as Co metal were prepared. Catalyst samples were dried at 135°C for 24 h then calcined in air at 600°C for 6 h. The BET surface areas of the catalysts were unchanged (±5 m^2/g) as a result of Co impregnation.

Bulk Characterization Techniques

X-Ray diffraction (*XRD*). X-Ray diffraction patterns of catalyst samples were obtained with a Diano 700 diffractometer, which utilizes nickel-filtered Cu$K\alpha$ radiation. Diffraction patterns were obtained with the X-ray gun operated at 50 kV and 25 mA and at a scanning rate of 0.4° min^{-1} (2θ). Samples were run as powders mounted on glass slides using silicone grease as an adhesive. Compound identification was accomplished through comparison of the measured spectra with ASTM powder diffraction file data.

Microbalance. Catalyst reduction/oxidation behavior was studied using a Cahn 113 microbalance system. Prior to reduction, oxidic samples were dried at 500°C in ultrahigh purity 10% O_2/He (99.99% O_2, 99.999% He) until constant weight was achieved. Samples were then reduced with ultrahigh purity hydrogen (99.999%) at a temperature of 500°C for 12 h, followed by reoxidation at the same temperature under O_2/He. The gas flow rate in all cases was 50 cm^3/min. The percentage of Co existing as Co_3O_4 was calculated from the weight change measured during the reduction/reoxidation step relative to the weight change which would be expected assuming all Co was present as Co_3O_4.

Surface Characterization

X-Ray Photoelectron Spectroscopy (*ESCA or XPS*). X-Ray photoelectron spectra of oxidic catalysts were obtained with a Leybold–Heraeus LHS-10 surface analysis system interfaced to a Hewlett–Packard 1000 computer. In the present study, an aluminum anode (Al$K\alpha$ = 1486.6 eV) operated at 12 kV and 20 mA was employed. The residual pressure inside the spectrometer was 10^{-8} Torr or lower. ESCA measurements were performed on sample powders which had been dusted onto double-sided adhesive tape and mounted on the spectrometer probe.

It has been shown that the intensity ratio of supported phase and carrier ESCA peaks is related to the dispersion of the supported phase (*15–18*). It must be stressed that the validity of these models relies on the assumption that there is no variation in the repartition of the supported phase (i.e., relative amount of supported phase deposited on the inner parts of the support particle and that located on the external parts of the particle) (*19, 20*). In the present work, the Co/Al intensity ratios predicted for monolayer Co coverage were calculated using the model of Kerkhof and Moulijn (*15*).

To obtain ESCA spectra of reduced or sulfided catalysts, an AEI ES200 spectrometer was utilized. This permitted transfer of the treated catalysts from an external reaction chamber to the spectrometer without exposure to air, via a sealable probe. The reaction chamber and sealable probe have been described in detail elsewhere (*21, 22*). Samples were mounted on the sealable probe as pellets pressed at 2000 kg/cm^2. The ESCA Co/Al intensity ratios of catalyst pellets were identical to those of the corresponding powdered samples indicating that pressing pellets had no effect on the catalysts. Samples were reduced in a flow of ultrahigh purity hydrogen for 12 h at 500°C or sulfided in a flow of 15% H_2S/H_2 for 12 h at 400°C. The AEI instrument was interfaced to an Apple IIe microcomputer and was equipped with an aluminum anode operated at 12 kV and 20 mA. The residual pressure inside the spectrometer was 5×10^{-8} Torr.

GENERAL THEORY: METHOD FOR DETERMINING THE DISTRIBUTION OF SPECIES IN SUPPORTED METAL CATALYSTS BY ESCA

It has been well established that two loading-dependent phases can exist on the surfaces of oxidic, alumina-supported, metal catalysts: a highly dispersed surface phase comprised of metal ions which have diffused into octahedral and tetrahedral sites of the support lattice structure, and a metal oxide phase. The metal oxide phase may be well dispersed or present as large crystallites depending on the specific metal and the method used for catalyst preparation and/or treatment.

Quantitation of species on the surfaces of supported metal catalysts by ESCA is possible through the combined use of the Kerkhof–Moulijn monolayer model (*15*) and the ESCA spectra of chemically reduced catalysts. The method requires that the reduced and unreduced metal species exhibit distinct, resolvable ESCA peaks. To determine the species distribution from ESCA measurements, it is assumed that treatment of catalyst samples in hydrogen at temperatures in the 400–600°C range reduces only the metal oxide phase leaving the surface phase unreacted. This assumption is supported by gravimetric results for catalysts having low metal loadings, where metal oxide formation does not occur and catalyst reduction is not observed (*4*). The assumption that only the metal oxide phase can be reduced is consistent with previously published ESCA data from this laboratory for alumina-supported metal catalysts (*8*, *14*).

The ESCA spectrum of a supported metal catalyst in which reduction of the metal oxide phase has occurred exhibits a metal peak and an oxidic surface phase peak. The oxidic surface phase peak is a composite of spectra from atomically dispersed metal ions. This is exemplified by the ESCA Co $2p_{3/2}$ spectrum of a reduced 6% Co/Al_2O_3 catalyst, shown in Fig. 1a. The peak at 777.6 eV corresponds to metallic Co which forms as a result of reduction of Co_3O_4. The peak at 781.5 eV and its associated shake-up satellite at 785.9 eV are due to the unreduced Co surface phase.

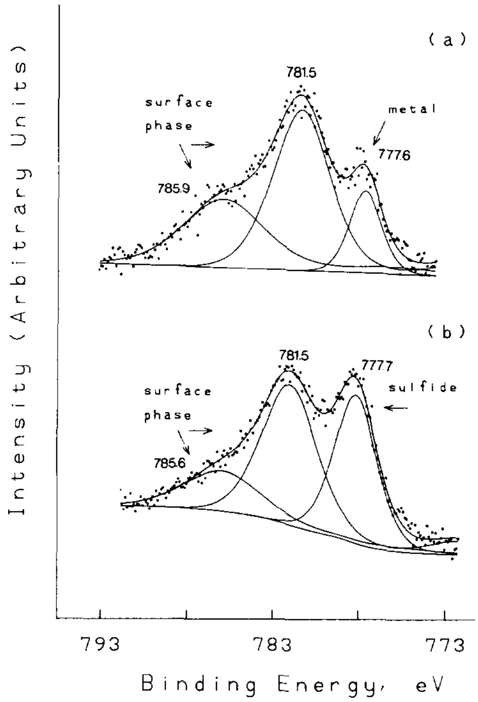

FIG. 1. ESCA Co $2p_{3/2}$ spectra of (a) reduced 6% Co/Al_2O_3 catalyst and (b) sulfided 3% Co/Al_2O_3 catalyst.

The fraction of supported metal which exists as the oxidic surface phase, $[M_{sp}]$, can be determined from the ESCA spectrum of a reduced catalyst according to

$$[M_{sp}] = (I_M \text{ unred})/(I_M \text{ tot}), \qquad (1)$$

where (I_M unred) is the metal-to-carrier ESCA intensity ratio of the oxidic part of the supported metal ESCA spectrum and (I_M tot) is the metal-to-carrier intensity ratio derived from the total metal peak intensity, prior to reduction. Thus, the fraction of metal oxide, $[M_{ox}]$, on the catalyst surface becomes

$$[M_{ox}] = 1 - [M_{sp}]. \qquad (2)$$

Assuming that the metal oxide phase is the only reducible phase, the percentage of metal oxide phase is equivalent to the percentage reduction of the catalyst.

The fractions of metal oxide and surface phase determined directly from the ESCA spectra of reduced catalysts will provide an accurate species distribution *only when all supported metal phases on the catalyst are highly dispersed*. That is, obtaining the distribution of species directly from ESCA measurements will yield inaccurate results when metal oxide crystallites having a particle size that is significantly greater than the photoelectron escape depth of the metal and an atomically dispersed surface phase exist on the catalyst surface. The indication of the presence of metal oxide crystallites can be obtained separately using X-ray diffraction or electron microscopy. An accurate species distribution can be calculated, however, through use of the Kerkhof–Moulijn monolayer model (*15*). The fraction of metal present as a surface phase can be obtained from the ESCA spectrum of a reduced catalyst by using Eq. (1), but substituting the ESCA peak intensity predicted by the Kerkhof–Moulijn monolayer model, (I_M mono), for the total peak intensity as shown by

$$[M_{sp}] = (I_M \text{ unred})/(I_M \text{ mono}). \qquad (3)$$

Using the total peak intensity that is predicted by the Kerkhof–Moulijn monolayer model in place of the measured total intensity ratio eliminates effects due to a poorly dispersed metal oxide phase. The fraction of metal oxide is again calculated by difference using Eq. (2). Also, the percentage of metal oxide is equal to the percentage reduction of the catalyst.

A similar approach can be used for sulfided catalysts to determine the extent of sulfidation, corrected for particle size effects. The ESCA spectrum of a supported metal catalyst treated in H_2/H_2S exhibits peaks due to the metal sulfide and oxidic surface phase. As an example, the ESCA Co $2p_{3/2}$ spectrum of a sulfided 3% Co/Al_2O_3 catalyst is shown in Fig. 1b. This spectrum exhibits a peak at 777.7 eV due to cobalt sulfide, in addition to the oxidic surface phase peak and shake-up satellite at 781.5 and 785.6 eV, respectively. It should be noted that cobalt metal and cobalt sulfide are not distinguishable based on ESCA binding energy measurements alone. The assignment of the 777.7-eV peak in the ESCA spectrum of the sulfided catalyst is based on reported gravimetric and X-ray diffraction results for Co/Al_2O_3 catalysts treated in a similar fashion (*5*).

The fraction of oxidic surface phase can be determined from the ESCA spectrum of a sulfided catalyst using Eq. (4), for the case where all metal species are atomically dispersed, or Eq. (5) when particle size corrections are necessary:

$$[M_{sp}] = (I_M \text{ unsulf})/(I_M \text{ tot}), \qquad (4)$$

$$[M_{sp}] = (I_M \text{ unsulf})/(I_M \text{ mono}). \qquad (5)$$

The fraction of metal sulfide is calculated by difference using the equation

$$[M_{sulf}] = 1 - [M_{sp}]. \qquad (6)$$

The percentage sulfidation of the catalyst is equivalent to the percentage of metal sulfide.

It should be stressed that the metal to carrier ESCA intensity ratio of the oxidic, surface phase portion of the spectrum of a treated catalyst must be used as the basis for calculating the fractions of supported metal species. This is done because the surface phase to carrier intensity ratio is an accurate reflection of the fraction of surface phase present on the catalyst. This assumes that there is no correction necessary for the attenuation of the Al signal by the surface phase. Calculations based on the Kerkhof and Moulijn model (*15*) show that this approximation is valid. Thus, changes in metal oxide particle size due to sintering have no bearing on the calculated speciation.

APPLICATION OF THE METHOD TO Co/Al_2O_3 CATALYSTS

To illustrate the use of the above method to determine the distribution of catalyst species by ESCA, a series of Co/Al_2O_3 catalysts was investigated. Alumina-supported cobalt was chosen for several reasons. First, formation of both Co_3O_4 and a Co surface phase is known to occur and the fraction of each phase can vary with Co loading. In addition, formation of Co_3O_4 can occur at low Co loadings and thus a wide range of catalyst compositions can be investigated. Second, Co_3O_4 is not usually well dispersed on alumina making particle size corrections necessary. Finally, the results of the determination of Co speciation by ESCA can be compared with previously published Mössbauer (*11*) and gravimetric work.

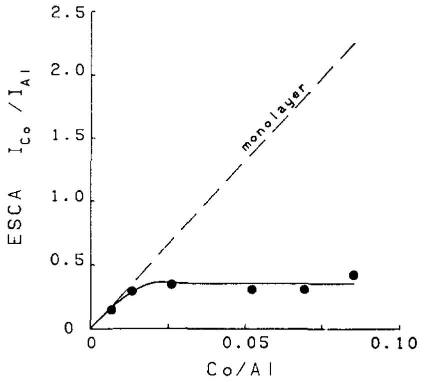

FIG. 2. ESCA total Co/Al intensity ratio as a function of Co content for oxidic Co/Al_2O_3 catalysts.

In the case of Co/Al_2O_3 catalysts, it has been reported that a sulfidable but nonreducible Co phase exists on the catalyst surface (5). This phase has been attributed to Co^{2+} in octahedral coordination. Tetrahedrally coordinated Co^{2+} is niether sulfidable nor reducible. Thus, in addition to determining the fractions of Co_3O_4 and Co surface phase from the ESCA spectra of reduced catalysts, ESCA analysis of sulfided catalysts permits distinction between the octahedral and tetrahedral components of the surface phase.

The fraction of Co surface phase, $[Co_{sp}]$, can be determined from the ESCA spectra of reduced catalysts according to

$$[Co_{sp}] = (I_{Co}\ \text{unred})/(I_{Co}\ \text{tot}), \qquad (7)$$

where (I_{Co} unred) refers to the Co/Al intensity ratio using the intensity of the oxidic portion of the Co ESCA spectrum. The fraction of Co_3O_4 can then be calculated by difference:

$$[Co_3O_4] = 1 - [Co_{sp}]. \qquad (8)$$

The fraction of tetrahedrally coordinated Co^{2+}, $[Co_{Td}]$, can be determined from the ESCA spectra of sulfided catalysts according to

$$[Co_{Td}] = (I_{Co}\ \text{unsulf})/(I_{Co}\ \text{tot}), \qquad (9)$$

where (I_{Co} unsulf) refers to the Co/Al intensity ratio of the oxidic portion of the Co ESCA spectrum. The fraction of Co^{2+} in octahedral coordination, $[Co_{Oh}]$, can then be determined using

$$[Co_{Oh}] = [Co_{sp}] - [Co_{Td}]. \qquad (10)$$

Substitution of the Kerkhof–Moulijn intensity ratio for the measured total intensity ratio in Eqs. (7) and (9) will correct for the presence of Co_3O_4 particles in the oxidic catalyst, as shown by

$$[Co_{sp}] = (I_{Co}\ \text{unred})/(I_{Co}\ \text{mono}), \qquad (11)$$

$$[Co_{Td}] = (I_{Co}\ \text{unsulf})/(I_{Co}\ \text{mono}). \qquad (12)$$

The percentage sulfidation of the catalyst is equivalent to the sum of the percentage Co_3O_4 and percentage octahedral Co^{2+}.

RESULTS AND DISCUSSION

Characterization of Oxidic Catalysts

X-Ray powder diffraction analysis of Co/Al_2O_3 catalysts containing loadings of 1.5 wt% Co or less revealed no diffraction lines except for those of γ-alumina. Catalysts having Co loadings greater than 1.5 wt% revealed primary diffraction lines at d spacings of 2.4 and 2.9 Å, indicating the presence of Co_3O_4. The diffraction results presented here are in agreement with those reported previously (*1*).

Figure 2 shows the total ESCA Co $2p_{3/2}$/Al $2s$ intensity ratios for oxidic Co/Al_2O_3 catalysts plotted as a function of Co/Al atomic ratio. Also plotted are the Co/Al intensity ratios predicted by the model of Kerkhof and Moulijn assuming monolayer Co coverage. The Co/Al intensity ratios initially increase with increasing Co loading and agree with those calculated by the monolayer model, indicating a well dispersed Co phase. Catalysts having Co

TABLE 1

Percentage Reduction and Sulfidation of Co/Al_2O_3 Catalysts Determined by ESCA

Co loading		% Reduction[a]	% Sulfidation[a]
wt%	Co/Al at. ratio		
0.7	0.007	0	25
1.5	0.013	22	30
3.0	0.026	63	73
6.0	0.052	83	89
8.0	0.069	82	92
10.0	0.087	89	94

[a] Percentage reduction and sulfidation are ±10% (r.s.d.).

loadings in excess of 1.5 wt% (Co/Al = 0.013) exhibited no significant change in the Co/Al intensity ratio with increasing Co/Al atomic ratio, indicating that Co dispersion decreases with increasing Co content. A constant ESCA Co/Al intensity ratio with increasing Co loading has been reported previously for Co/Al_2O_3 catalysts (*3*).

Characterization of Reduced and Sulfided Catalysts

Determination of the percent reduction and sulfidation of the catalysts required correction for Co_3O_4 particle size effects. The presence of Co_3O_4 lines in the XRD patterns of catalysts containing greater than 1.5 wt% Co indicated that Co_3O_4 particles greater than ca. 4 nm in size were present on the catalysts. The escape depth of a Co $2p_{3/2}$ photoelectron from a the surface of a Co/Al_2O_3 catalyst is approximately 1 nm (*23*). In addition, the Co_3O_4 particle size increased by approximately a factor of 2 for the 10 wt% Co catalyst relative to the 3 wt% Co catalyst, as estimated by XRD line broadening. Evidence for the presence of discrete Co particles is also indicated by the lower experimental ESCA Co/Al intensity ratios for catalysts containing greater than 1.5 wt% Co, compared to those predicted for monolayer Co coverage.

Table 1 lists the percentage reduction for Co/Al_2O_3 catalysts calculated from ESCA data, correcting for Co_3O_4 particle size effects using Eqs. (8) and (11). The Co/Al intensity ratios of the reduced catalysts were not significantly different from those measured for oxidic catalysts, as shown in Table 2. This indicates that no appreciable sintering occurred as a result of sample treatment. The Co $2p_{3/2}$ spectrum of the catalyst containing 0.7 wt% Co did not exhibit a Co metal peak, indicating that the Co present was not reducible under the experimental conditions used (500°C for 12 h in H_2). A Co metal peak was observed for catalysts containing 1.5 wt% Co and greater. This indicates the presence of Co_3O_4, since it is assumed that the metal oxide phase is the only reducible phase on the catalyst. The percent reduction increased with increasing Co loading and ranged from 22 to 89%. Thus, Co_3O_4 is not present on the catalyst at a Co loading of 0.7 wt%, while at higher loadings the fraction of Co_3O_4 increases with increasing Co loading.

The percentage sulfidation of Co/Al_2O_3 catalysts is also presented in Table 1, corrected for Co_3O_4 particle size effects in the oxidic catalysts using Eqs. (8) and (10) through (12). The Co/Al intensity ratios of the sulfided catalysts are also given in Table 2 and were comparable to those of the oxidic catalysts at low Co loadings indicating that particle growth had not occurred dur-

TABLE 2

Total Co $2p_{3/2}$/Al $2s$ Intensity Ratios of Oxidic and Chemically Treated Co/Al_2O_3 Catalysts

Co loading		Oxidic	Reduced	Sulfided
wt%	Co/Al at. ratio			
0.7	0.007	0.15	0.13	0.13
1.5	0.013	0.30	0.35	0.35
3.0	0.026	0.35	0.37	0.36
6.0	0.052	0.31	0.33	0.55
8.0	0.069	0.31	0.33	0.41
10.0	0.087	0.43	0.37	0.45

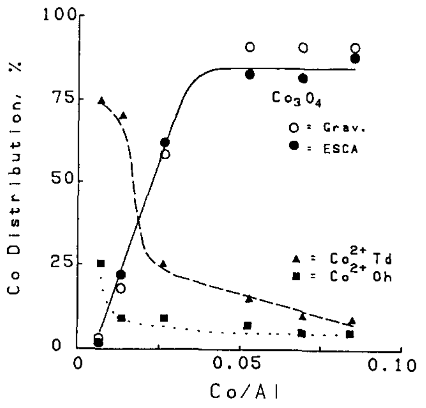

FIG. 3. Distribution of Co species, in percentage, as a function of Co loading from ESCA, using Co_3O_4 particle size correction. Percentage Co_3O_4 versus Co loading determined gravimetrically.

ing treatment. The Co/Al intensity ratios of catalysts with higher Co loadings increased slightly, which indicates some redispersion of Co may have occurred. The pesence of a Co sulfide peak was observed for all catalyst samples, including the 0.7 wt% Co catalyst, indicating a sulfidable Co species exists at all Co loadings. The percent sulfidation increased with increasing Co content from 25 to 94%. The percent sulfidation was greater than the percent reduction at all Co loadings. This indicates that octahedral Co^{2+} is present on the surface of the oxidic catalysts in addition to tetrahedral Co^{2+} and Co_3O_4.

Distribution of Co Species from ESCA Measurements

Figure 3 illustrates the percentage of each Co species plotted as a function of Co loading. It can be seen from Fig. 3 that the percentage of Co_3O_4 increases from 0% at a Co loading of 0.7 wt% to a constant value of approximately 80% at loadings greater than 6 wt% Co. Also plotted in Fig. 3 is the percentage of Co_3O_4 determined gravimetrically. The relative amounts of Co_3O_4 calculated from ESCA data employing the correction for particle size effects are consistent with the percentages of Co_3O_4 determined by gravimetric measurements. The gravimetric results reported here are consistent with data reported by Chung and Massoth (*4*), considering that a higher calcination temperature was used in the present study. It is also evident that the percentages of Co^{2+} in tetrahedral and octahedral coordination decrease with increasing Co loading to levels below 10%. The Co species distribution presented in Fig. 3 indicates that Co_3O_4 formation is favored over Co surface phase formation with increasing Co loading. An increase in Co_3O_4 formation with increasing Co loading has been reported by others for Co/Al_2O_3 catalysts using catalyst preparation procedures similar to those employed in this work (*4*).

Figure 4 shows the Co species distribution which would have been obtained from ESCA data if no correction was applied for Co_3O_4 particle size effects. In Fig. 4 the amount of Co_3O_4 on the catalyst surface is underestimated by ESCA, while the fraction of Co^{2+} surface phase is overestimated for catalysts containing Co loadings greater than 0.7 wt%. The species distribution shown in Fig. 4 was calculated using the measured total Co ESCA peak intensities, as in Eqs. (7) through (10), instead of the monolayer Co intensities from the Kerkhof–Moulijn model. Comparison of

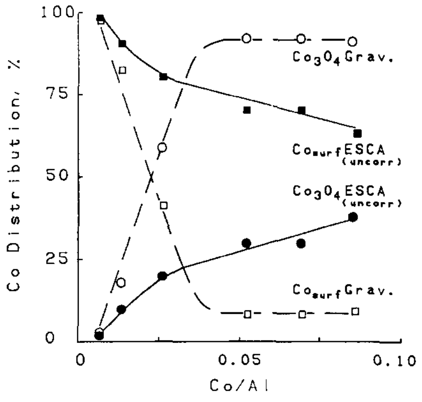

FIG. 4. Distribution of Co species, in percentage, as a function of Co loading from ESCA, neglecting the correction for Co_3O_4 particle size effects. Percentage Co_3O_4 and Co surface phase versus Co loading determined gravimetrically.

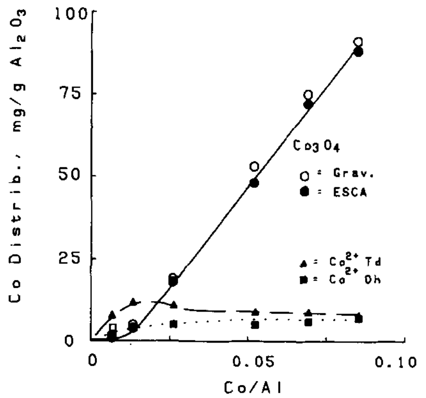

FIG. 5. Distribution of Co species, in mg/g Al_2O_3, as a function of Co loading from ESCA, using Co_3O_4 particle size correction. Co_3O_4 content, mg/g Al_2O_3, versus Co loading determined gravimetrically.

the uncorrected species distribution with the gravimetric results, also shown in Fig. 4, illustrates the magnitude of the error caused by neglecting the correction for Co_3O_4 particle size. The percent of Co_3O_4 is underestimated by as much as 60% compared to the corrected ESCA and gravimetric results, while the percentage of Co surface phase is overestimated by as much as a factor of 7.

Figure 5 shows the Co species distribution in mg Co species/g Al_2O_3, the same units used by Wivel *et al.* (*11*) in reporting the Co species distribution determined from Mössbauer measurements. It can be seen that the amount of Co_3O_4 present on the catalyst surface increases with increasing Co loading, after a threshold amount of Co has been added to the catalyst. The amount of Co^{2+} in tetrahedral coordination reaches a maximum level at Co loadings between 1 and 2 wt%. The amount of octahedrally coordinated Co^{2+} increases slightly with increasing Co loading. Comparison of Fig. 5 with the Mössbauer work of Wivel (*11*), for similar Co/Al_2O_3 catalysts reveals good agreement between the two methods of determining Co distribution. Both Mössbauer and ESCA indicate that the Co_3O_4 content increases above approximately 1 wt% Co with similar Co_3O_4 contents determined for catalysts having similar Co loadings. In addition, both techniques reveal a maximum in the amount of the Co surface phase, the sum of the amounts of tetrahedral and octahedral Co^{2+}, at approximately 1 to 2 wt% Co, with the major surface component at a loading of 1 wt% being tetrahedrally coordinated Co^{2+}.

ASSESSMENT OF THE METHOD

In the present work, a method has been described for the use of ESCA to determine the distribution of metal species on alumina supported catalysts. For catalysts containing both a metal oxide phase and a surface phase, the method can correct for the effects of poorly dispersed metal oxide particles in determining the catalyst species distribution. If particle size effects are not taken into account an inaccurate species distribution may result.

Application of the method for determining the distribution of catalyst species was presented for Co/Al_2O_3 catalysts. It should be noted that the Co/Al_2O_3 catalyst system served only as an example to establish the utility of the method for determining the correct species distribution from ESCA data. For catalysts containing only one supported metal, a similar species distribution could be obtained gravimetrically. The utility of ESCA in catalyst speciation should be realized for multicomponent catalysts, such as $Co-Mo/Al_2O_3$ or $Ni-W/Al_2O_3$ catalysts, where gravimetric determination of the distribution of catalyst species is not possible.

The primary drawback to the method is that the distribution of catalyst species determined by ESCA is inferred from the reactivity of the active phase under reducing and sulfiding conditions. Mössbauer spectroscopy, on the other hand, can determine the catalyst species distribution directly. Although the catalyst species distribution determined by ESCA is an indirect method, the results were consistent with those determined by Mössbauer spectroscopy and gravimetric analysis. In addition, the time required for data acquisition in ESCA is often much shorter than for Mössbauer spectroscopy and ESCA is useful for a wider range of elements.

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