The Influence of Zinc on the Surface Properties of Cobalt–Alumina Catalysts

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Addition of a small quantity of zinc to γ-Al$_2$O$_3$ was studied with respect to influence on the surface properties of a series of Co/Al$_2$O$_3$ catalysts. ESCA and ISS results indicate that at low cobalt concentrations ($\leq 8\%$ Co) the presence of zinc can enhance formation of a cobalt "surface spinel" resulting from the diffusion of Co ions into tetrahedral sites of the γ-Al$_2$O$_3$ support. At higher cobalt loadings a drastic increase in the ESCA and ISS metal/support intensity ratios is seen relative to catalysts without zinc. X-Ray diffraction data indicate that the increases in intensity ratios result from an increase in dispersion, i.e., generation of smaller cobalt oxide crystallites in the zinc-doped catalysts. For a series of catalysts having fixed cobalt concentrations, the influence of particle size on ESCA and ISS intensity ratios was determined.

INTRODUCTION

The effects of calcination temperature and metal loading on the surface properties of a series of Co/Al$_2$O$_3$ catalysts have been investigated by a variety of spectroscopic techniques (*1*). Catalyst surfaces can be described as consisting of three cobalt species: (1) an interaction species resulting from diffusion of Co ions into tetrahedral lattice sites of γ-Al$_2$O$_3$ (Co-t); (2) Co ions in octahedral sites of the support (Co-o); and/or (3) "bulk-like" Co$_3$O$_4$. Above ca. 3% Co, Co$_3$O$_4$ is a significant surface species. Both calcination temperature and metal loading substantially influence the catalyst surface by altering the relative distribution of the cobalt species. This results in catalysts having differing reactivities toward hydrogen reduction, primarily due to the low reactivity of Co-t. The formation of Co-t is limited to the first few atomic layers of the support and closely resembles bulk CoAl$_2$O$_4$, both structurally and chemically; hence, it is often referred to as a "surface spinel" (*2*).

Addition of small amounts of Zn^{2+}, Ga^{3+}, or Ge^{4+} to γ-Al$_2$O$_3$ is known to modify the surface properties of alumina (*3*). Cimino *et al.* have demonstrated that it is possible to enhance formation of the nickel "surface spinel" in Ni/Al$_2$O$_3$ catalysts by addition of small quantities of the above ions (*3*). Lo Jacono *et al.*, using optical reflectance spectroscopy and magnetic susceptibility measurements, have shown this effect to occur also for Co/Al$_2$O$_3$ and Co/Mo/Al$_2$O$_3$ catalysts doped with a small amount of Ga^{3+} (*4*).

The present study focuses attention on the effect of a small quantity of zinc ions on the surface structure of Co/Al$_2$O$_3$ catalysts. Unlike the work of Lo Jacono *et al.* emphasis is placed on surface changes as a function of cobalt concentration up to moderately high loadings of cobalt (16% Co). Using surface spectroscopic techniques it is shown that formation of the Co "surface spinel" can be enhanced by doping with 1% zinc. The dependency of ESCA and ISS intensity ratios on metal particle size is discussed.

METHODS

Catalyst preparation. All catalysts were prepared by wet impregnation. Two series of Co/Zn/Al$_2$O$_3$ catalysts were prepared by initial impregnation of γ-Al$_2$O$_3$ (90 m^2/g) with an aqueous zinc nitrate solution. The sample was dried overnight at 110°C and

subsequently calcined in air at 500°C for 12 hr. Various quantities of cobalt were added in a second impregnation step followed by drying and calcination at 400°C for 5 hr. For the two sets of catalysts the zinc concentrations were fixed at 1 and 2%, respectively, while the cobalt content was varied.

Co/Al₂O₃ catalysts were prepared by wet impregnation of γ-Al₂O₃ with a cobalt nitrate solution followed by drying at 110°C and calcination for 5 hr in air at either 400 or 600°C.

Spectroscopic techniques. ESCA spectra were obtained on a Hewlett–Packard 5950A electron spectrometer using monochomatized Al$K\alpha$ radiation and an AEI ES200A spectrometer employing non-monochromatized Al$K\alpha$ radiation (1486.6 eV). Catalysts in their oxidic state were analyzed with the Hewlett–Packard spectrometer to obtain precise binding energies. ESCA studies of samples reduced in hydrogen necessitated use of the AEI spectrometer, where a sealable sample probe allowed transfer of the reduced catalyst from an external reaction chamber to the spectrometer without exposure to air. Low-energy ion scattering measurements were done on a 3M model 520 spectrometer. ⁴He at a pressure of 1.8×10^{-5} Torr and 2.0 kV was used to produce the incident ion beam for the ISS studies. Primary-ion current density was ca. 5×10^{-9} A/cm². Details of operation for the above instrument have been described previously (*1, 5, 6*). ESCA binding energies and intensity ratios reported are the average of three to five separate determinations, and ISS results are the average of five to ten separate determinations.

Particle size analysis. Particle size analyses were performed only for the oxidic catalysts, due to experimental limitations. Determination of the metal oxide crystallite size was based on X-ray diffraction line broadening. A Diano recording diffractometer employing a Co source (1.78892 Å) and an Fe filter was used for the measurements. The scan rate was 0.4°/min (in 2θ)

and the Co 311 line was used in the calculations. Mean crystallite, $\bar{d}$, was calculated from the Scherrer equation:

$$\bar{d} = \frac{K\lambda}{\beta \cos \theta},$$

where λ is the X-ray wavelength, K is the Scherrer constant (0.89), and β is the FWHM of the Co 311 line. Because of signal-to-noise considerations, accurate measurement of the FWHMs was only obtainable for samples having cobalt concentrations of 8% or greater. No corrections were made for instrumental broadening, as only relative comparisons were sought. Thus the results are reported as relative particle size.

RESULTS AND DISCUSSION

Oxidic Catalysts

The Co $2p_{3/2}$/Al $2p$ ESCA intensity ratios as a function of bulk Co content, calcination temperature, and zinc doping are shown in Fig. 1. For catalysts containing no zinc, the intensity ratios are lower for catalysts calcined at 600°C than for those calcined at 400°C. As was shown previously (*1*) the decrease in the intensity ratios at the higher calcination temperature results from greater interaction between the dispersed Co ions and the support for catalysts calcined at 600°C. The results of this metal–support interaction is the formation of subsurface cobalt species by diffusion of Co ions into tetrahedral (Co-t) or octahedral (Co-o) lattice sites of the γ-Al₂O₃. These species are less susceptible to detection by surface spectroscopic techniques than noninteracting surface species (i.e., Co₃O₄), because the interacting species are incorporated into the support, whereas the noninteracting species lie on top of the support. It is well established that the interaction species formed by incorporation of Co ions into tetrahedral sites of γ-Al₂O₃ resemble bulk CoAl₂O₄ both physically and chemically (*3, 7–9*). Hence, CoAl₂O₄ was used to model Co-t. It was determined that
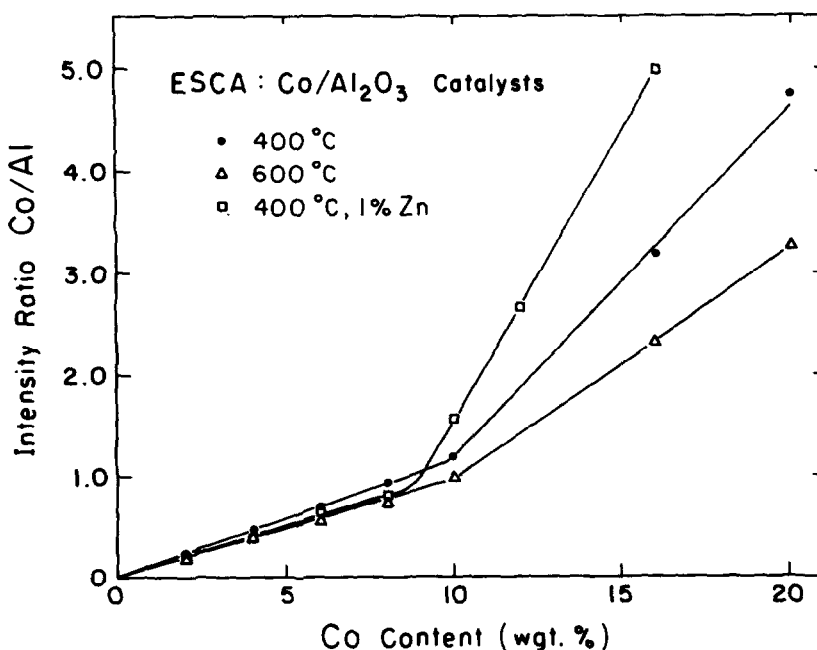
FIG. 1. ESCA peak are intensity ratios (Co/Al) versus metal content for Co/Al₂O₃ and Co/Zn/Al₂O₃ catalysts. Relative standard deviations are ±8%. ●—Co/Al₂O₃ calcined at 400°C. △—Co/Al₂O₃ calcined at 600°C. □—Co/Zn/Al₂O₃ (1% Zn) calcined at 400°C.

the Co $2p_{3/2}$ ESCA spectrum of CoAl₂O₄ was substantially different in terms of binding energy and peak shape than Co₃O₄. At high cobalt loadings the dominant Co surface species is expected to be Co₃O₄ (1, 10, 11).

Examination of Fig. 1 reveals that catalysts doped with 1% Zn and calcined at 400°C have ESCA Co/Al intensity ratios slightly lower than undoped catalysts calcined at the same temperature, up to a concentration of 8% Co. BET surface area measurements indicate no substantial differences among the catalysts. From Table 1 it can be seen that for the three catalysts having 8% Co, relative particle sizes of the Co oxide crystallites are essentially constant. Thus, it can be assumed that for concentrations below 8% Co no significant differences in particle size exist among the catalysts at a given cobalt concentration. However, due to instrumental limitations of the diffractometer, this assumption could not be verified. It is also worth noting that

ESCA binding energies of the peak maxima are within experimental error for the three samples. These values lie between the binding energies of CoAl₂O₄ and Co₃O₄ and indicate a surface comprised of a mixture of species (Co-t, Co-o, and Co₃O₄) as shown previously (1).

The slopes of the ESCA intensity ratios vs Co content plots in Fig. 1 are constant up to 8–10% Co for the three series of catalysts. Above 8% Co, the curve for the Co/Zn/Al₂O₃ samples undergoes a dramatic increase in slope. A similar change in slope is seen for catalysts without Zn^{2+}; however, the enhancement in the intensity ratios occurs at 10% Co. It is significant to note that the discontinuity in the 1% zinc-doped ESCA curve occurs at ca. 1% lower cobalt loading than for the two sets of undoped catalysts. For Co/Al₂O₃ (1) and Zn/Al₂O₃ (12) catalysts "monolayer" coverage occurs at a metal content of ca. 10% by weight. Hence, the change in slope in the ESCA curve of the doped catalysts at

TABLE 1

Spectroscopic and Particle Size Results for Oxidic Catalysts

Catalyst[a]	Binding energy[b] (eV)	Co/Al (ESCA)[c]	Co/Al (ISS)[d]	Relative particle size[e]
Co/Al$_2$O$_3$, 8% (400°C)	781.0	0.95	0.12	162
Co/Al$_2$O$_3$, 8% (600°C)	781.2	0.65	0.10	157
Co/Zn/Al$_2$O$_3$, 8%, 1% (400°C)	781.1	0.77	0.10	157
Co/Al$_2$O$_3$, 16% (400°C)	780.7	3.05	0.28	170
Co/Al$_2$O$_3$, 16% (600°C)	781.2	2.28	0.17	233
Co/Zn/Al$_2$O$_3$, 16%, 1% (400°C)	780.6	4.82	0.61	123
Co$_3$O$_4$	780.6			
CoAl$_2$O$_4$	781.8			

[a] Values in parentheses represent calcination temperature.

[b] Binding energies were measured with a precision of ±0.15 eV.

[c] ESCA ratios are measured to ±8% r.s.d.

[d] ISS ratios are measured to ±12% r.s.d.

[e] Particle size measurements were done by XRD but are not corrected for instrumental broadenning. Thus, absolute values are not meaningful, but relative comparisons are valid. Values given are in angstroms.

ca. 9% may be attributed to complete saturation of surface sites since the total metal content is constant and is that required for monolayer coverage.

It can be seen also that the increase in slope of the zinc-doped catalysts is much greater than that for the undoped catalysts above monolayer coverage. At a loading of 16% Co, the Co/Zn/Al$_2$O$_3$ catalyst has an intensity ratio much higher than either of the Co/Al$_2$O$_3$ catalysts (Table 1). Examination of ESCA binding energies indicates that at this concentration major compositional changes are occurring for both Co/Zn/Al$_2$O$_3$ (400°C) and Co/Al$_2$O$_3$ (400°C). The data indicate that the dominant Co species is Co$_3$O$_4$. Since this species probably occupies sites on the surface of the support, increases in the slopes of the curves would be expected. In fact, changes in slopes of plots like Fig. 1 constitute firm evidence for phase changes on catalyst surfaces. For Co/Al$_2$O$_3$ (600°C) no detectable change in binding energy is observed with an increase in loading. Although an increase in slope is seen, its magnitude is

much smaller than that for the other two series of catalysts.

The ESCA results are supported by the ISS data shown in Fig. 2. The peak height intensity ratios of Co/Al are plotted against metal content for Co/Al$_2$O$_3$ (400°C) and Co/Zn/Al$_2$O$_3$ (400°C). Again it is observed that at concentrations below 8% Co, the intensity ratios for zinc-doped catalysts are slightly lower than those for catalysts without zinc. At 10% Co, the intensity ratios are approximately equal but large differences exist for concentrations of 12 and 16% Co; similarly to the ESCA data, the Co/Zn/Al$_2$O$_3$ catalysts have the higher intensity ratios. Catalysts calcined at 600°C given an ISS plot that is completely linear over the range 0–20% Co. This effect has been discussed elsewhere (1).

The ISS and ESCA results obtained in the lower concentration range (0–8%) are in qualitative agreement with the results of Lo Jacono et al. (4). However, the maximum cobalt concentration studied in that work was 5.29% Co (wt%). It is apparent that the ability of zinc to enhance Co ion
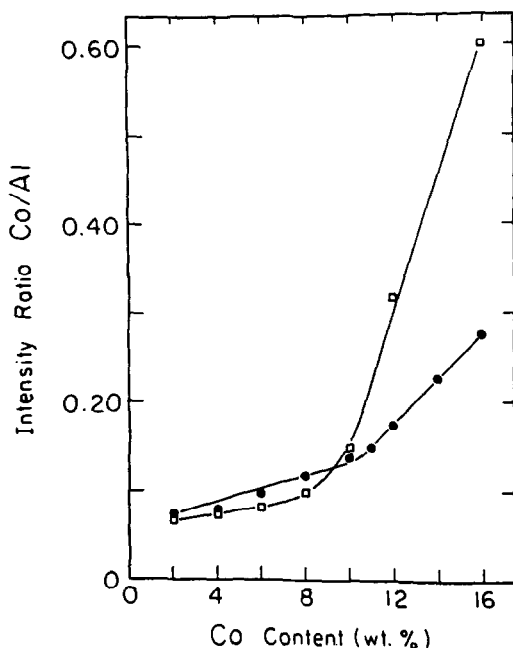
FIG. 2. ISS peak height intensity ratios (Co/Al) versus metal content for Co/Al$_2$O$_3$ calcined at 400°C (●) and Co/Zn/Al$_2$O$_3$ (1% Zn) calcined at 400°C (□). Relative standard deviations are ±12%.

diffusion into γ-Al$_2$O$_3$ lattice sites extends to monolayer coverage. Formation of the subsurface Co-t species leads to a slight decrease in ESCA and ISS intensity ratios relative to the undoped samples. Because the catalysts contain both Co-t and Co$_3$O$_4$ (and probably Co-o) it is difficult to assign any specific cause to this small change in intensity ratio.

The data of Table 1 show substantial differences in average particle size of the Co oxide crystallites among the three oxidic catalysts at a loading of 16% Co. This is in marked contrast to the lower-loading catalysts (≤8% Co) where no significant differences were observed at a given metal concentration. Differences in particle size provide a ready explanation for the dramatic differences in ESCA and ISS intensity ratios in the range 8–16% Co. The effect of particle size or dispersion for supported catalysts has been studied by a number of researchers (13–15). For example, Brinen et al. (15) have correlated

ESCA peak area ratios with metal crystallite sizes for a series of 12% Rh/C catalysts. It was observed that decreases in the Rh/C ESCA intensity ratio resulted concurrent with decreases in dispersion, i.e., the formation of large Rh crystallites during hydrogen reduction of the catalysts. In the present study significant differences in particle size at the 12 and 16% Co levels were found for the catalysts. For undoped catalysts the particle size of the Co$_3$O$_4$ crystallite increased dramatically with an increase in calcination temperature. However, the addition of 1% Zn to the 16% Co/Al$_2$O$_3$ (400°C) catalyst caused a significant decrease in the Co$_3$O$_4$ particle size as significant increases in the ESCA and ISS intensity ratios. Thus, it is clear that the presence of Zn drastically affects dispersion of the Co$_3$O$_4$ particles in the catalyst surface.

Samples impregnated with 2% Zn were also studied. Increases in the ISS intensity ratios were seen for 12 and 16% Co relative to undoped catalysts. The plot of the Co/Al intensity ratio versus Co concentration coincides almost exactly with the curve for 1% Zn samples, except that the change in slope was observed at a concentration of 8% cobalt. This result has two important consequences. First, the presence of additional zinc does not further affect the cobalt dispersion because the intensity ratios are essentially the same. Second, the break in the ESCA curve occurs at a total metal content of 10% as would be predicted. This adds support to the proposition that only a finite number of surface sites on the γ-Al$_2$O$_3$ are available for occupation by metal ions.

Reduced Catalysts

It was of interest to investigate the effect of zinc doping on the reducibility of catalysts measured by ESCA. Samples doped with 1% Zn were compared to samples without zinc, but having identical cobalt loadings and calcination temperatures. Fig-
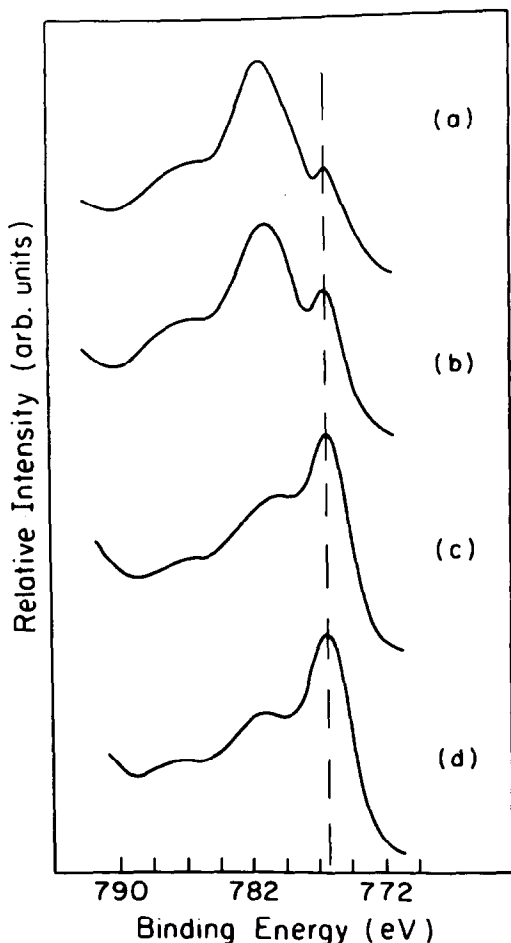
FIG. 3. Co $2p_{3/2}$ ESCA spectra for catalysts reduced at 350°C for 4 hr in hydrogen: (a) 8%, 1% Co/Zn/Al$_2$O$_3$ (400°C); (b) 8% Co/Al$_2$O$_3$ (400°C); (c) 16% Co/Al$_2$O$_3$ (400°C); (d) 16%, 1% Co/Zn/Al$_2$O$_3$ (400°C). Calcination temperatures are in parentheses.

ures 3a and 3b show the Co $2p_{3/2}$ ESCA spectra of 8% Co/1% Zn/Al$_2$O$_3$ (400°C) and 8% Co/Al$_2$O$_3$ (400°C), respectively, after reduction in flowing H$_2$ for 4 hr at 350°C. The 8% Co catalyst containing zinc showed 15% reducible cobalt while the 8% catalyst without zinc showed 20% reducible cobalt. The reproducibility of percentage reduction measured by ESCA is ±10% r.s.d. at 20% reducibility, so the difference of 5% reduction is probably significant ($P = 0.97$ by t test). This difference in reducibility cannot be attributed to differences in cobalt oxide particle sizes in the fresh (before reduction)

catalysts. Instead it is more likely a manifestation of relative differences in the distribution of the various cobalt species on the catalyst. As shown previously (1), the Co-t species was found to be chemically inert toward hydrogen reduction but Co-o and Co$_3$O$_4$ were reducible. The decreased reducibility of the zinc-doped catalyst probably results from increased formation of the unreactive Co-t species relative to the catalyst without zinc. This result is rather surprising and needs to be checked further, for it implies that the presence of zinc may be affecting the distribution of Co between tetrahedral and octahedral lattice sites on the γ-Al$_2$O$_3$. Another possibility would be changes in particle size on reduction, but this seems unlikely as will be discussed later.

The 16% Co/Al$_2$O$_3$ (400°C) and Co/Zn/Al$_2$O$_3$ (400°C) catalysts show higher reducibility under the same reaction conditions as can be seen from Figs. 3c and 3d. However, the difference between the two is not significant ($P < 0.7$ by t test), the Co/Al$_2$O$_3$ catalyst showing 42% reducibility and the Co/Zn/Al$_2$O$_3$ catalyst showing 45%. From the data of Table 1 it is clear that the dominant species on the surfaces of both catalysts is Co$_3$O$_4$, on the basis of ESCA binding energy data. It is also evident from Table 1 that the Co$_3$O$_4$ particle sizes on the two catalysts are quite different (123 vs 170 Å) as discussed above.

Influence of Particle Size on Intensity Ratios

In order to determine the physical significance of ESCA and ISS intensity ratios, a relationship must be established between these quantities and metal oxide particle size. In the present study it was found that calcination temperature and/or the presence of Zn^{2+} was a significant factor in determining the size of the Co oxide crystallites formed on the catalysts. By varying the calcination temperature for doped and undoped samples, it is possible to generate particles of various sizes. The relationship

between the relative Co oxide particle size and the observed ESCA and ISS intensity ratios is shown in Fig. 4 for catalyst samples having a constant loading of 16% Co. This figure is only a qualitative example of the relationship since no calibration using particle size standards was performed.

It is evident that for both ESCA and ISS the measured Co/Al intensity ratio is inversely proportional to the size of the Co_3O_4 particles. The shape of the ESCA curve is in qualitative agreement with the results of Brinen et al. (15) and the theoretical treatment of Fung (13). The decreases in the measured ESCA intensity ratios due to sintering may be rationalized by the fact that a greater volume of metal atoms becomes inaccessible to ESCA detection as the oxide particle becomes larger. Since the electron escape depths for oxides are 30 Å or less, atoms in the center of large metal particles will not be detected. The results

obtained for ISS are qualitatively similar to those for ESCA. However, changes in particle size exert a greater influence on ISS intensity ratios than on ESCA. This is evident by comparing the change in the intensity ratios as a function of particle size for both ESCA and ISS. Over the particle size range measured, the ESCA Co/Al intensity changes by a factor of 2, while the ISS ratio changes by a factor of 3.4. This result is consistent with the greater surface sensitivity of ISS.

If oxide particles of different sizes generate Co–metal crystallites of sizes comparable to the oxide particles, one would expect the percentage reduction of cobalt measured by ESCA to be constant for catalysts having different oxide particle sizes but the same amount of reducible cobalt. This is because reducibility measured by ESCA requires deconvolution of overlapping oxide and metal Co $2p_{3/2}$ lines. If oxide and metal particles are the same size, they will contribute to the overall spectrum in proportion to their concentrations regardless of the absolute particle sizes. This argument assumes that all of the Co_3O_4 on the surface is reduced. However, if the metal particle sizes generated are independent of oxide particle size, variations in percentage reduction would be expected. This is because the relative contributions of oxide and metal to the summed spectrum will vary as the particle size of one or the other changes.

The ESCA Co/Al intensity ratios measured for reduced 16% Co/Al_2O_3 (400°C) and 16% $Co/Zn/Al_2O_3$ (400°C) catalysts are 1.01 and 1.63, respectively. The Co_3O_4 oxide particle sizes measured for the same catalysts before reduction are 233 and 123 Å, respectively. These results are consistent with both larger metal and oxide particles on the 16% Co/Al_2O_3 (400°C) catalyst. Because the percentages reduction measured for the two catalysts is essentially the same (42 and 45%), one may conclude that the size of the metal particle formed or reduced is related to the size of the initial
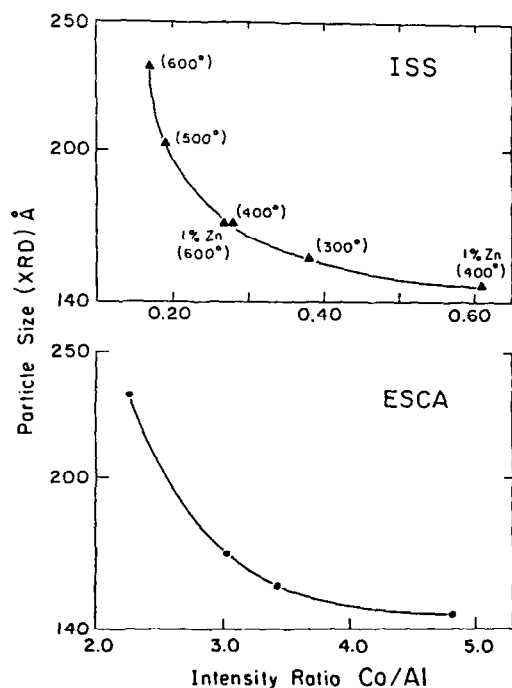

FIG. 4. ISS (upper curve) and ESCA (lower curve) intensity ratio versus relative particle size for catalysts having a metal loading of 16% Co. The values in parentheses represent calcination temperatures. ESCA data were obtained for undoped catalysts only.

oxide particle. On the basis of Brinen's results for Rh/C, the Co particle size on the Co/Al_2O_3 catalyst is the larger, consistent with the reduction studies above. A similar result has been obtained in an ESCA study of W/Al_2O_3 catalysts, indicating that metal particle size formed on reduction is related to the size of the oxide particle (16).

CONCLUSIONS

The influence of a small quantity of zinc on the surface properties of Co/Al_2O_3 catalysts appears to be twofold. At low cobalt concentrations (0–8% Co) the presence of Zn^{2+} enhances the formation of the Co-t interaction species. This is reflected by decreases in the ESCA and ISS intensity ratios relative to catalysts without Zn^{2+}. Above 8% Co, dramatic differences in dispersion of oxide were observed for doped and undoped catalysts. This presumably resulted from stabilization of the Co oxide particles against sintering (during calcination) when zinc was present.

ACKNOWLEDGMENTS

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