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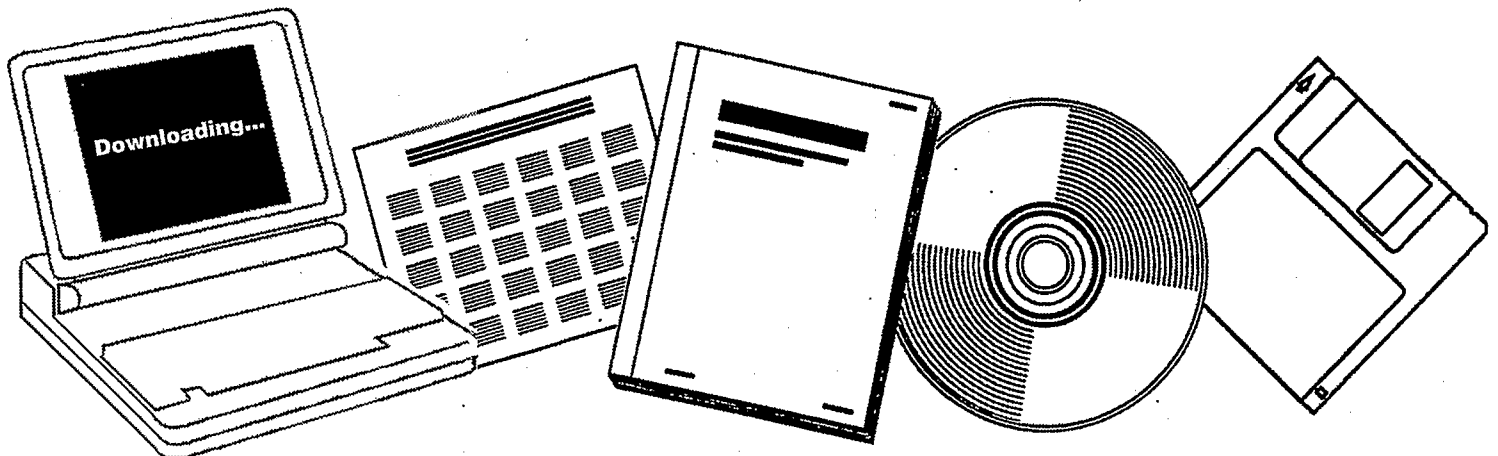
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**PROPERTIES OF LANTHANIDE OXIDES AS
SUPPORTS FOR TRANSITION METAL CATALYSTS.
PROGRESS REPORT, MAY 1, 1984-APRIL 30,
1985**

TEXAS A AND M UNIV., COLLEGE STATION.
DEPT. OF CHEMISTRY

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**PROPERTIES OF LANTHANIDE OXIDES AS SUPPORTS
FOR TRANSITION METAL CATALYSTS**

**Progress Report for the Period
May 1, 1984 to April 30, 1985**

by

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INTRODUCTION

The objective of this research has been to characterize the effect of support variations on the catalytic and surface properties of dispersed Group VIII transition metals. Particular emphasis has been placed on investigating behavior modifications induced by lanthanide oxide supports, in comparison to those of other, more conventional, support materials. Our previous studies of pure lanthanide oxide catalysts, under DOE sponsorship of this project, have demonstrated a surface complexity in these materials that prompted our current interest in their behaviors as metal catalyst supports.

Most of the recently-reported investigations of support effects and so-called "Strong Metal-Support Interactions" (SMSI) have focused on the noble metals, particularly platinum and rhodium, which are easily reducible and can readily be prepared in highly dispersed forms. Few studies, on the other hand, have examined the influence of support variations for the non-noble Group VIII metals, such as iron and cobalt, which are more difficult to reduce and are typically employed in relatively poorly dispersed forms containing large metal particles ($> 100 \text{ \AA}$). Consequently, our investigations have focused primarily on support effects involving dispersed iron and cobalt catalysts. Our most complete and detailed results thus far have been obtained for a series of supported cobalt catalysts, and this progress report has been derived largely from a manuscript entitled "The Influence of Support on the Reduction Behavior of Dispersed Cobalt Catalysts" that we have recently submitted for publication.

Our results demonstrate that the nature of the support has a significant influence on the reduction and surface properties of dispersed cobalt. X-ray photoelectron spectroscopy (XPS) studies show that reduction in H_2 of SiO_2 -supported $\text{Co}(\text{NO}_3)_2$, without prior calcination, results in considerable bulk

metal formation, but that extensive monolayer regions of unreduced Co^{2+} species remain on the surface, even after treatment in H_2 at 500-700°C. If the supported $\text{Co}(\text{NO}_3)_2$ is converted to CoO_x by prior calcination, on the other hand, subsequent treatment in H_2 results in essentially complete reduction to the zero-valent metal. On a TiO_2 support, cobalt is more easily reduced than on SiO_2 , and on the lanthanide oxide supports La_2O_3 , Eu_2O_3 , and CeO_2 , reduction occurs even more readily, but extensive additional interactions exist, particularly with CeO_2 .

EXPERIMENTAL METHODS

Materials

Air Products Co. research purity (99.9995% min.) hydrogen and Matheson purity (99.99% min.) carbon monoxide from Matheson Co. were used for all reduction treatments and CO hydrogenation reactions. Hydrogen and carbon monoxide were passed through separate Messer Griesheim "Oxysorb" columns to reduce the O₂ content to less than 1 ppm, and were then passed through a liquid N₂-cooled trap (-196°C) before use. All supported cobalt catalysts were prepared using Fisher Chemical Co. certified A.C.S. grade Co(NO₃)₂·6H₂O. Supports used for preparing catalysts were SiO₂ from Davison Chemical Co. (grade 57, 310 m²/g), TiO₂ from Johnson Matthey Chemicals Ltd. (puratronic grade, 99.998%, 1 m²/g), and La₂O₃ (99.9%, 12 m²/g), Eu₂O₃ (99.9%, 13 m²/g), and CeO₂ (99.9%, 17 m²/g) from Alfa Chemicals Div. of Ventron Corp. The SiO₂ was washed with 10% HNO₃ to remove base metal impurities and was then calcined at 500°C for 16 hrs to remove organic contaminants. The other four supports were refluxed in deionized water for 16 hrs to achieve maximum surface hydrolyzation prior to impregnation and to increase their surface areas to the values indicated.

Procedures

Catalyst Preparations

All catalysts contained 2.5 wt% cobalt and were prepared by an incipient-wetness technique using aqueous solutions of the corresponding nitrate salts. Unlike the standard incipient-wetness technique, in which the surface is wetted with an amount of solution that it can absorb to saturation, a slight excess of solution was used in the preparations involving TiO₂, La₂O₃, Eu₂O₃,

and CeO_2 because of their low surface areas and consequently small pore volumes. Each wetted catalyst was then dried with continuous stirring at 60-70°C, to assure that an even distribution of the cobalt nitrate on the support was attained. After drying, the catalysts were transferred to an oven and maintained at 110°C for 48 hours, and were then stored in sealed vials to prevent rehydration by atmospheric water.

Samples used in the x-ray photoelectron spectroscopy (XPS) measurements were pressed into 6 mm wafers to fit the sample holder and sample probe of the spectrometer. All reduced cobalt catalysts used for CO hydrogenation reactions and surface characterizations were prepared by treatment of supported cobalt nitrate samples in 500 torr of H_2 using a stirred-batch Pyrex reactor system of the closed-loop recirculation type. The temperature of the sample pretreatment was varied in the range 300-700°C. In each case, the temperature was increased at 2°C/min. and then maintained at the desired final pretreatment temperature for 16 hrs. After reduction (or reaction), the wafer was evacuated to 10^{-5} torr in the reaction system before it was transferred, without exposure to the air, to a Vacuum Atmospheres Co. glove box that enclosed the sample probe of the XPS instrument. Water and O_2 were removed from the N_2 used to fill the chamber by a Messer Griesheim "Oxysorb" column. The nitrogen in the glove box was further treated by continuous circulation through a Vacuum Atmospheres Co. DRI-TRAIN HE-493 system to reduce H_2O and O_2 contaminants to less than 5 ppm.

X-ray Photoelectron Spectroscopy Measurements

X-ray photoelectron spectra were recorded on a Hewlett-Packard 5950A ESCA spectrometer using a monochromatic Al $K\alpha$ (1486.6 eV) source operated at a beam power of 800 watts. In order to avoid surface charging effects, which are caused by the loss of electrons from the surface of non-conducting samples

during the photoemission process and which change the binding energies of the observed peaks, an electron flood gun was used to bathe the surface of the samples with low energy electrons. Before scanning the binding energy range of interest, the electron energy and emission levels of the flood gun were appropriately adjusted. A Hewlett-Packard 18523A Flood Gun Controller was utilized to control the energy and emission levels of the electrons. The binding energies of Au 4f_{3/2} and 4f_{5/2} peaks were used as references for the flood gun adjustment. All spectra were corrected for background contributions using a Hewlett-Packard 9825B computer interfaced to the ESCA spectrometer and a software package obtained from Surface Science Laboratories.

RESULTS

Co/SiO₂

XPS spectra in the Co 2p binding energy region are shown in Fig. 1 for Co/SiO₂ samples treated in H₂ at various temperatures. For the unreduced sample, the spectrum showed two major peaks at 797.4 and 781.7 eV, corresponding to Co 2p_{3/2} and Co 2p_{1/2}, with a spin-orbital splitting of 15.7 eV. The peak width at half maximum (PWHM) for the latter peak was approximately 4.2 eV. Each of the two peaks was accompanied by a strong satellite peak at approximately 5.5 eV higher binding energy than the parent peak. The spectrum of the sample reduced at 300°C in H₂ was virtually identical to that of the unreduced sample. For the sample reduced at 400°C, a small shoulder at 776.4 eV was observed, and no further change occurred in the XPS spectrum for a sample reduced at 500°C. However, the Co 2p XPS spectrum for a sample reduced at 700°C exhibited a decrease in binding energy for both Co 2p peaks of approximately 2 eV.

When a Co/SiO₂ sample that had been reduced at 400°C in H₂ was subsequently exposed to 1 atm of a 2/1 H₂/CO mixture at 250°C, no significant change in the XPS spectrum was observed following the reaction (Fig. 2). However, a sample reduced in H₂ at 700°C and then exposed to a H₂/CO mixture exhibited significant changes in its XPS spectrum. A sharp peak with PWHM less than 3 eV developed at 777.0 eV, and the two satellites peaks disappeared. No significant changes, however, occurred in the Si 1s and O 1s peaks.

Co/TiO₂

Fig. 3 shows Co 2p XPS spectra of Co/TiO₂ samples treated in H₂ at various temperatures. As with Co/SiO₂, the spectrum of unreduced Co/TiO₂

exhibited two major peaks, at 797.0 and 781.1 eV, with spin-orbital splitting of about 15.9 eV. Each peak was again accompanied by a strong satellite peak. Slight broadening of both peaks was observed with increasing reduction temperature, and a small shoulder developed at 778.9 eV for the sample reduced at 500°C. The spectrum of the sample reduced at 700°C exhibited two new peaks at 794.2 and 779.1 eV, with spin-orbital splitting of only 15.1 eV and a PWHM of less than 3 eV. No satellite peaks remained. Unlike the case of Co/SiO₂, for which essentially no change in Co 2p spectra occurred after exposure to an H₂/CO mixture at 250°C of a sample reduced in H₂ at 400°C, distinct peaks at 794.2 and 779.1 eV developed after exposure to H₂/CO mixtures of Co/TiO₂ that had been reduced in H₂ at 400°C (Fig. 4). For the sample reduced in H₂ at 700°C, no further change in the Co 2p XPS spectrum was observed after exposure to an H₂/CO mixture.

The influence of treatment conditions on the TiO₂ support is exhibited in Fig. 5. The Ti 2p_{1/2} and 2p_{3/2} peaks for a pure TiO₂ sample treated in H₂ at 700°C are shown in spectrum (a), which is identical to that of a TiO₂ sample that had received no treatment in H₂. The binding energies corresponding to Ti 2p_{1/2} and 2p_{3/2} were 465.0 and 459.2 eV, respectively. Although no evidence for valency changes in the TiO₂ support was observed in the XPS spectrum, a color change from white to dark blue occurred following H₂ treatment at 700°C. Ti 2p XPS spectra for Co/TiO₂ samples treated at various temperatures showed no significant differences from that of a pure TiO₂ sample, except for the sample treated in H₂ at 700°C. In the latter case, a marked peak broadening occurred, as shown in spectrum (c). However, subsequent exposure to an H₂/CO mixture (spectrum (b)) completely eliminated the species generated by the H₂ treatment at 700°C.

Co/La₂O₃ and Co/Eu₂O₃

The reduction behaviors and XPS spectra of Co/La₂O₃ and Co/Eu₂O₃ closely resembled each other, and, for the sake of brevity, detailed results will be presented only for Co/La₂O₃. Fig. 6 summarizes XPS spectra obtained for Co/La₂O₃ that had been treated in H₂ at various temperatures. Unlike Co/SiO₂ and Co/TiO₂, which exhibited marked satellite peaks whose intensities were 30-50% as great as those of their Co 2p_{1/2} and 2p_{3/2} parent peaks, Co/La₂O₃ and Co/Eu₂O₃ showed relatively weak satellite peaks (< 10%). However, the 2p_{1/2}-2p_{3/2} spin-orbital splittings (15.7 eV) and PWHM were comparable to those for Co/SiO₂ and Co/TiO₂. In addition to the differences observed in satellite peak intensities, the color of Co(NO₃)₂-impregnated La₂O₃ and Eu₂O₃ was dark blue, rather than the light pink color observed in the cases of SiO₂ and TiO₂ supports. With increase in H₂ reduction temperature, a slight decrease in spin-orbital splitting occurred. For samples reduced in H₂ at 400°C, significant broadening toward lower binding energy of the Co 2p peaks, together with depression in satellite intensity, was observed. However, when Co/La₂O₃ samples were treated in H₂ at 500°C, the PWHM decreased and the Co 2p peaks shifted toward higher binding energies again. Further increase in binding energy and spin-orbital splitting occurred following H₂ treatment at 700°C.

Exposure of Co/La₂O₃ samples reduced at either 400°C or 700°C in H₂ to an H₂/CO mixture at 250°C resulted in the development of a new peak in the Co 2p_{3/2} region at 777.5 eV having a PWHM of less than 3 eV and spin-orbital splitting of only 15.0 eV, as shown in Fig. 7. A similar peak developed in the cases of Co/SiO₂ (Fig. 2) and Co/TiO₂ (Fig. 4) only for samples that had been reduced in H₂ at 700°C prior to H₂/CO exposure.

Fig. 8 shows that significant changes also occurred in the O 1s XPS spectra of Co/La₂O₃ following H₂ treatment and H₂/CO exposure. For unreduced samples, only a single broad peak at 529.0 eV was observed. However, when samples were treated in H₂ at 400°C, two O 1s peaks developed at 528.0 and 530.5 eV. The relative intensities of these two peaks reversed after exposure to H₂/CO mixtures, the former decreasing and the latter increasing. O 1s spectra of pure La₂O₃ and La₂(CO₃)₃ pretreated in H₂ at 400° and 700°C are shown in Figs. 9 and 10 for comparison. Both compounds exhibited a single O 1s peak at 530.5 eV before H₂ treatment, but two O 1s peaks, at 528.0 and 530.5 eV, following H₂ pretreatment. In the case of La₂O₃, an overall increase in intensity of both peaks occurred in going from an H₂ treatment temperature of 400° to one of 700°C, but the relative intensities of the two peaks remained essentially unchanged. With La₂(CO₃)₃, on the other hand, the relative intensities of the two peaks were reversed when the H₂ treatment temperature was increased from 400° to 700°C.

Co/CeO₂

Fig. 11 shows Co 2p XPS spectra for Co/CeO₂ samples pretreated in H₂ at various temperatures. In behavior similar to that observed for Co/SiO₂ and Co/TiO₂, intense satellite peaks were observed for the Co 2p peaks of Co/CeO₂. However, unlike all the other supported cobalt catalysts studied, which showed little change in Co 2p XPS spectra for samples pretreated in H₂ at or below 400°C, significant peak broadening toward lower binding energy was observed with Co/CeO₂ samples pretreated in H₂ at only 300°C, and a new peak at 778.9 eV with PWHM < 3 eV, as well as marked depression of satellite peak intensity, were observed with samples pretreated in H₂ at 400°C. The spin-orbital splittings were also decreased with increasing reduction temperature. However, for samples treated in H₂ at 500°C, a new peak, different from all

those observed previously, was generated. The binding energy of this peak was 781.0 eV, with a PWHM of approximately 3.6 eV and a spin-orbital splitting of 15.3 eV. Concurrent with the development of this new peak, the Co 2p satellite peaks also disappeared. When samples were treated in H₂ at 700°C, the resulting spectrum resembled that of the sample treated at 400°C. As seen in Fig. 12, no significant changes were observed with samples pretreated in H₂ at 400°C and then exposed to an H₂/CO mixture at 250°C following the H₂ treatment. However, for samples previously treated in H₂ at 700°C, significant increase in the 778.9 eV peak intensity and complete disappearance of the satellite peaks occurred after exposure to H₂/CO mixtures.

O 1s spectra of Co/CeO₂ samples were quite similar to those observed with Co/La₂O₃ and pure La₂O₃ treated at various conditions. Only the relative intensities of the peaks at 528 and 531 eV were smaller than those observed with Co/La₂O₃ at all pretreatment conditions. Fig. 13 shows that, following treatment of pure CeO₂ in H₂ at 700°C, a new Ce 3d_{5/2} peak appeared at 886.1 eV, and the peak at 889.8 eV, observed previously in the untreated sample, was greatly reduced in intensity. The color of the CeO₂ sample also changed from pale yellow to light blue following the high-temperature H₂ treatment. Unlike Co/TiO₂, no further change in the spectrum of the CeO₂ support was observed following exposure to H₂/CO mixtures.

Reduction by CO

A detailed study of sample reduction by carbon monoxide was not performed. However, fragmentary XPS spectra revealed that, with only one exception, a sharp, relatively intense Co 2p peak developed at approximately 777 eV following sample treatment in CO at 400°C. Only in the case of Co/SiO₂ did CO treatment at 400°C fail to produce the peak at 777 eV.

DISCUSSION

As shown in a previous XPS study (1), Co $2p_{3/2}$ binding energies in cobaltous (Co^{2+}) compounds normally vary between 780 and 782 eV, while those in cobaltic (Co^{3+}) compounds are typically in the range 779 to 782 eV, varying somewhat according to chemical environment. Hence, it is very difficult to identify the oxidation state of cobalt solely on the basis of the chemical shift of the binding energy. It is well known that paramagnetic species of some first-row transition metal compounds show satellite(s) for the 2p lines as a result of a shake-up process, e.g., a $3d \rightarrow 4s$ transition, while diamagnetic compounds do not exhibit such satellite peaks (2). Among all the Co^{2+} compounds examined by Okamoto and co-workers, most showed intense 2p satellite peaks, but no such strong satellites were found for Co^{3+} compounds or zero-valent cobalt metal. Satellite-parent splittings (S.S.) and spin-orbital splitting (dE) of the Co $2p_{1/2}$ - $2p_{3/2}$ levels are also very useful indicators for distinguishing among Co^{2+} , Co^{3+} and Co^0 species. Values of S.S. for the Co $2p_{1/2}$ and Co $2p_{3/2}$ levels of Co^{2+} are typically in the range 5.0 to 6.7 eV and 3.7 to 5.6 eV, respectively; the corresponding values for Co^{3+} are 8.4 to 9.3 eV and 8.9 to 10.3 eV. However, the satellite peaks of Co^{3+} are usually very weak, the intensity ratio of the satellite to its parent peak being typically less than 0.1, so it is difficult to obtain accurate S.S. values for Co^{3+} . In the case of zero-valent cobalt metal, no value for S.S. has been reported since no satellite peaks exist. Values of dE for Co^{2+} , Co^{3+} and Co^0 are 15.7 to 16.1 eV, 14.7 to 15.1 eV and 15.1 eV, respectively.

The XPS results obtained for supported cobalt catalysts in the present investigation clearly demonstrate that the support not only influences the reducibility of dispersed cobalt, but may also greatly alter the surface properties of the metal. In order to compare the effects of support, the

oxidation state(s) of cobalt metal observed on all of the supports studied, following various pretreatments, are summarized in Table 1. The oxidation states listed were assigned on the basis of Co $2p_{1/2}$ - $2p_{3/2}$ spin-orbital splittings, satellite peak intensities, and PWHM values, the 2p peak width of Co^0 being invariably at least 1 eV less than those of Co^{2+} and Co^{3+} .

Treatment in H_2

SiO_2 -supported cobalt showed only trace amounts of XPS-detectable reduced Co^0 following treatment in H_2 at $\geq 400^\circ C$ (Fig. 1), and most of the surface cobalt appeared in the XPS spectra as Co^{2+} even after H_2 treatment at $700^\circ C$. Moreover, the Co^{2+} remained primarily in the high-spin state (i.e., three unpaired 3d electrons), as shown by the relatively high intensities of the $2p_{1/2}$ and $2p_{3/2}$ satellite peaks (1).

It quite unexpected to observe supported cobalt remain principally as unreduced Co^{2+} following H_2 pretreatments at temperatures of $400^\circ C$ or above, since the study by Okamoto et al. (1) and a more recent study by Santilli and Castner (3) both reported complete reduction of Co/SiO_2 in H_2 at about $400^\circ C$, based on XPS measurements. However, it should be noted that the metal loading levels (viz., 10 wt% by Okamoto et al. and 5 wt% by Santilli and Castner), used in both of these studies are considerably higher than that (2.5 wt%) of our catalysts. Metal loading levels have been widely reported to have a significant influence on the reducibility of supported cobalt (3-5). A recent XPS study of silica-supported cobalt catalysts by Sato et al. (6) demonstrated that surface cobalt in 7.5 wt% Co/SiO_2 can be easily reduced to zero-valent Co^0 in H_2 at $450^\circ C$, while no zero-valent cobalt could be detected on a 3.35 wt% Co/SiO_2 surface following the same treatment. The low apparent reducibility of our Co/SiO_2 samples may be due to more extensive support interactions caused by the low metal loading. Furthermore, the Co/SiO_2

catalysts studied by Okamoto et al. and by Santilli and Costner were calcined in O_2 prior to the H_2 treatments, which may have caused a significant decrease in dispersion, due to agglomeration of cobalt oxides, and prevented the support interaction. These factors may have contributed to the greater ease of reduction of their Co/SiO_2 samples. It is worth noting, in this regard, that Bartholomew also observed incomplete metal reduction in recent studies of supported cobalt catalysts that had been treated in H_2 without prior calcination in O_2 , a finding that is consistent with our observation (4,7).

A possible explanation for this observed behavior of Co/SiO_2 , which may be applicable to other supports as well, is that prior calcination in O_2 generates a uniform, highly agglomerated CoO_x phase that reduces readily to Co^0 upon exposure to H_2 at $\geq 400^\circ C$. Treatment in H_2 of uncalcined $Co(NO_3)_2/SiO_2$, on the other hand, involves both direct reduction of Co^{2+} and thermal decomposition of the nitrate salt, yielding CoO_x and NO_x . The presence of both NO_x and gaseous HNO_3 , resulting from H_2 reduction of $Co(NO_3)_2$, may promote an interaction between the support surface and either the unreduced Co^{2+} species and/or Co^0 that leads to the formation of monolayer regions of highly stable Co^{2+} species that are quite resistant to reduction by H_2 . Substantial amounts of reduced, metallic cobalt may indeed exist on the surface, but as very large particles whose net contribution to an observed XPS spectrum is disproportionately small compared to that of the unreduced Co^{2+} regions. Recent temperature-programmed reduction measurements of Co/SiO_2 catalysts have demonstrated that samples which had been previously calcined in O_2 at $500^\circ C$ are more readily reducible in H_2 than $Co(NO_3)_2/SiO_2$ that had not been calcined (8). The latter samples still underwent at least 80-90% reduction to the zero-valent metal, however, based on cumulative H_2 consumption at $550^\circ C$, confirming that the relative amounts of Co^0 and Co^{2+}

species on the support surface are not those suggested by the XPS spectra. For the catalysts studied in the present investigation, therefore, it appears that the XPS spectra are best used to compare differences in surface behavior of the dispersed cobalt, rather than as quantitative indicators of actual distributions of metal oxidation states on the support surfaces.

The increase in Co 2p binding energy observed with Co/SiO₂ samples treated in H₂ at 700°C may be due to Si-Co alloy formation. Evidence of alloy formation in silica-supported metal catalysts at high reduction temperatures has been observed previously by Praliaud and Martin by specific saturation magnetization measurements of 20 wt% Ni/SiO₂ catalysts (9). The temperature reported for the formation of Ni-Si alloy was 1180 K; however, since the metal loading level was much smaller in our case, this type of metal-support interaction may occur at a considerably lower temperature. It was also reported that formation of the alloy only occurred at the low heating rate of 20°C/min.; a Ni/SiO₂ catalyst heated at 20°C/min. to 1180 K showed no Ni-Si alloy formation. The heating rate used for our reduction of Co/SiO₂ was also 20°C/min., so formation of a Co-Si alloy may have been attained at 700°C in H₂.

TiO₂-supported cobalt showed similar reducibility behavior to that of SiO₂-supported cobalt (Fig. 3). Significant reduction of surface cobalt was not observed even at a H₂ treatment temperature of 500°C, at which point Co/TiO₂ exhibited approximately the same amount of XPS-detectable zero-valent cobalt as did Co/SiO₂ samples treated at the same temperature. Following treatment of a Co/TiO₂ sample in H₂ at 700°C, however, the disappearance of 2p satellites, the decrease in 2p binding energy from 781.1 to 779.1 eV and in the value of dE from 15.9 to 15.1 eV, and the marked decrease of PWHM from 4.5 to less than 3.0 eV all confirm the formation of zero-valent, metallic cobalt.

Accompanying the reduction of detectable surface cobalt from Co^{2+} to Co^0 at 700°C reduction temperature was evidence of surface TiO_2 reduction from Ti^{+4} to Ti^{+3} , as shown by the substantial broadening of the Ti 2p_{3/2} peak in spectrum (c) of Fig. 5 when compared to the same peak in the cases of pure TiO_2 and Co/TiO_2 treated in H_2 at lower temperatures. Although partial reduction of TiO_2 is considered to be an essential feature of the so-called SMSI effect (10-13), none of the previously-reported studies have conclusively demonstrated surface reduction of TiO_2 in TiO_2 -supported metal catalysts by H_2 pretreatment alone; most such assertions have been based on the color change of samples (from white to blue) following H_2 treatment. XPS spectra that have previously been used to demonstrate the formation of a lower oxidation state of titanium on a surface have been obtained using TiO_2 -supported metal films (14). As shown in spectrum (a) of Fig. 5, no evidence for the formation of a lower oxidation state titanium species was observed on the pure TiO_2 surface treated at 700°C. However, a color change from white to blue following this treatment suggests that bulk reduction of the TiO_2 may have occurred. The surface reduction of TiO_2 observed in the case of Co/TiO_2 reduced at 700°C suggests that the presence of supported cobalt may catalyze or stabilize formation of the lower oxidation state titanium species on the surface. Comparison of the XPS results obtained for TiO_2 - and SiO_2 -supported cobalt catalysts suggests that the partial reducibility of TiO_2 may be responsible for the somewhat more facile reducibility of surface cobalt on TiO_2 than on SiO_2 .

Due to the evidently weak interaction between cobalt metal and TiO_2 support, the Co^{2+} on TiO_2 support appeared to be predominantly in the high-spin form, as was observed for Co/SiO_2 . La_2O_3 - and Eu_2O_3 -supported cobalt, by contrast, produced much weaker satellite structures for the Co 2p_{1/2} and Co

2p_{3/2} peaks than did Co/TiO₂ and Co/SiO₂ (Fig. 6). It is very unlikely that oxidation of surface Co²⁺ to Co³⁺ (which, as noted previously, has very weak Co 2p satellite peaks) would occur under the mild conditions used in the impregnation process, and the observed dE value (15.7 eV) also indicates that the surface cobalt remained as Co²⁺. As reported by Okamoto and co-workers, Co²⁺ compounds, such as Co(CN)₂, that involve strong crystal-field ligands also exhibit virtually no Co 2p satellite peaks (1). Since the electronic configuration of Co²⁺ in Co(CN)₂ is the low-spin state, i.e., one unpaired electron, and the unpaired spin may be distributed over the cyano ligands because of their large nephelauxetic effect, Co(CN)₂ may behave like diamagnetic compounds in the XPS study of 2p satellites. The relatively weak satellite structures of Co 2p XPS spectra for Co/La₂O₃ and Co/Eu₂O₃ indicate that the surface Co²⁺ in these cases is present primarily in the low-spin (i.e., one unpaired 3d electron) state, due to a relatively strong interaction with the basic lanthanide oxide supports. Additional evidence for the formation of a low-spin Co²⁺ complex on these oxides was provided by the color change from pink to dark blue that was observed during catalyst preparation. The color of Co²⁺ low-spin compounds such as Co(CN)₂ is also blue.

There was clear indication of Co²⁺ reduction to Co⁰ on Co/La₂O₃ and Co/Eu₂O₃ pretreated in H₂ at 400°C. Broadening of the Co 2p_{1/2} and 2p_{3/2} peaks toward lower binding energy which is due to the overlapping of Co⁰, Co²⁺ and, possibly, Co³⁺ peaks, was observed following H₂ treatment at this temperature, and, when combined with the decrease in area of the Co 2p_{3/2} satellite peak, suggests that extensive reduction to zero-valent cobalt metal had occurred. With further increase in pretreatment temperature, however, reoxidation of cobalt appeared to occur, since the Co 2p_{1/2} and 2p_{3/2} peaks narrowed again, and dE decreased from 15.9 eV at 400°C to 15.5 eV at 700°C.

Reoxidation of surface Co^0 in H_2 above 400°C has also been observed on LaCoO_3 (15), and was attributed to surface dehydroxylation above 500°C that reoxidized the Co^0 .

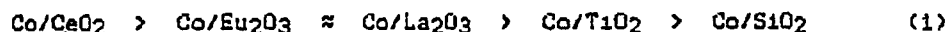
Evidence of support change for $\text{Co}/\text{La}_2\text{O}_3$ with variation in H_2 treatment temperature is presented in Fig. 8. Prior to reduction (spectrum (a)) a single O 1s peak at 529.2 eV was present, but after H_2 pretreatment at 400°C (spectrum (b)) this peak had disappeared and was replaced by separate O 1s peaks at 530.5 and 528.0 eV. In order to further investigate the nature of surface oxygen-containing species on $\text{Co}/\text{La}_2\text{O}_3$, samples of pure La_2O_3 (containing a virtual monolayer of surface hydroxyls) and $\text{La}_2(\text{CO}_3)_3$ were treated in H_2 at 400°C and 700°C , and were then examined by XPS. As shown in Figs. 9 and 10, both materials showed a decrease in the intensity of a peak at 530-531 eV (resulting from the oxygen atoms in surface OH and CO_3 species) with increasing treatment temperature, and an accompanying increase in the relative intensity of a peak at 528 eV (corresponding to surface O^{2-} ions in the La_2O_3 lattice). Thus, the reoxidation of surface cobalt on La_2O_3 support following H_2 pretreatment at higher temperatures was most likely caused by decarbonation and/or dehydroxylation of the La_2O_3 support under reduction conditions.

In the case of Eu_2O_3 -supported cobalt, Co^{2+} again existed mostly in the low-spin state, and a relatively greater amount of Co^0 than that observed with SiO_2 , TiO_2 and La_2O_3 supports was evident after H_2 treatment at 400°C . The XPS-detectable $\text{Co}^0/\text{Co}^{2+}$ ratio increased at 500°C reduction temperature, and then decreased at 700°C , due to apparent reoxidation of surface cobalt in a manner similar to that observed for $\text{Co}/\text{La}_2\text{O}_3$.

Unlike the behavior of $\text{Co}/\text{La}_2\text{O}_3$ and $\text{Co}/\text{Eu}_2\text{O}_3$, Co^{2+} on the much less basic CeO_2 support remained in the high-spin form as shown by the intense 2p

satellite peaks that closely resemble those observed with SiO_2 and TiO_2 supports (Fig. 11). Alone among the five catalysts studied in this investigation, CeO_2 -supported cobalt showed evidence for a substantial amount of XPS-detectable cobalt reduction following H_2 treatment at only 400°C . But at 500°C reduction temperature, all evidence for Co^0 disappeared, and Co^{3+} became the predominant cobalt species observed by XPS on the surface, indicating that CeO_2 reduction by H_2 , accompanied by cobalt oxidation, had occurred. This result is consistent with the disappearance of catalytic activity for carbon monoxide hydrogenation that was observed with a Co/CeO_2 catalyst that had been pretreated at 500°C (16). H_2 treatment at 700°C showed evidence for partial re-reduction of Co^{3+} to Co^0 . However, catalytic activity for hydrogenation of CO was still not observed with a Co/CeO_2 catalyst pretreated at the same condition, indicating that the re-reduced zero-valent cobalt may have become encapsulated in a thin layer of a partially-reduced CeO_x phase that migrated onto the metal particles in a manner similar to that suggested for TiO_2 (11,12). XPS evidence of CeO_2 reduction is presented in Fig. 13. After reducing Co/CeO_2 in H_2 at 700°C , a new peak developed in the $\text{Ce } 3d_{5/2}$ region at 886.0 eV , a binding energy which is in good agreement with those previously reported in the $3d$ region for Ce(III) (17). Although no surface reduction of Ce(IV) could be observed in the XPS spectra of Co/CeO_2 treated in H_2 at 500°C , the observed oxidation of cobalt metal indicated that bulk reduction of Ce(IV) may have occurred.

The extent of XPS-detectable reduction of surface cobalt on the five supports studied, following H_2 treatment at 400°C , may be summarized as follows:



Although the reducibility of the support itself appeared to have some influence on the reducibility of supported cobalt, no clear correlation of reducibility of supported Co with that of the support could be made. For example, although Eu_2O_3 is reported to be partially reducible at $\geq 650^\circ\text{C}$ in H_2 atmosphere (18), no evidence for surface reduction of Eu^{3+} to Eu^{2+} was observed in our XPS spectra of $\text{Co/Eu}_2\text{O}_3$ samples treated in H_2 at 700°C . La_2O_3 is quite irreducible in the temperature range studied, yet both the Eu_2O_3 - and La_2O_3 -supported catalysts showed considerable evidence of reduced Co^0 following H_2 treatment at 400°C , while SiO_2 -supported cobalt showed only trace amounts of Co^0 under the same pretreatment conditions. The relative amount of surface Co^0 observed for H_2 -treated $\text{Co/Eu}_2\text{O}_3$ at 400°C was higher than that for Co/TiO_2 . TiO_2 is evidently much more easily reduced in H_2 than is Eu_2O_3 , as shown by the observed color change from white to blue of the pure TiO_2 sample treated at 500°C in H_2 , and by the peak broadening of the $\text{Ti } 2p_{3/2}$ peak in the XPS spectrum for Co/TiO_2 treated in H_2 at 700°C (see Fig. 5). These results indicate that other effects, besides reducibility of the support (or electronic effects), may also play a significant role in influencing the reducibility of supported cobalt. Such additional factors might include structural (i.e., morphological) effects or support basicity.

Exposure to H_2/CO Mixture

Although differences in the extent of reduction of supported cobalt were observed following H_2 treatment, further changes in the surface properties of supported cobalt following exposure to H_2/CO reaction mixtures were evidenced by the XPS measurements. In the case of Co/SiO_2 pretreated in H_2 at 400°C , no evidence for further reduction of the cobalt was observed after subsequent

exposure to an H₂/CO mixture at 250°C. However, when the sample had been pretreated in H₂ at 700°C, substantial further reduction of cobalt occurred following subsequent H₂/CO exposure at 250°C (Fig. 2). The difference in cobalt reduction behavior for Co/SiO₂ between the samples pretreated in H₂ at 400°C and at 700°C and then exposed to an H₂/CO mixture at 250°C may be due to a structural effect caused by the SiO₂ support. The XPS data showed a chemical shift of the Co 2p peaks toward lower binding energy for the sample pretreated in H₂ at 700°C, which may indicate Co-Si compound formation. Such a structural change may be responsible for the relatively greater ease of reduction by exposure to an H₂/CO mixture of the sample reduced at 700°C.

TiO₂-supported Co, after reduction in H₂ at 400°C and following exposure to a 2/1 H₂/CO mixture, showed considerably more Co⁰ than did the H₂-treated sample before H₂/CO exposure (Fig. 4), presumably due to Co²⁺ reduction by the CO, as shown by XPS evidence for CO reduction of TiO₂-supported cobalt. The lower oxidation state titanium formed by H₂ pretreatment of Co/TiO₂ at 700°C was destroyed following exposure to H₂/CO reaction mixtures, as shown in Fig. 5. This may be due to the reoxidation of surface Ti³⁺ caused by the H₂O produced during CO hydrogenation.

Although a substantial amount of Co⁰ was observed by XPS on the La₂O₃ support after reduction in H₂ at 400°C, an even further increase in reduced Co⁰ was observed after the sample had been exposed to an H₂/CO mixture. Similar behaviors were also observed with Co/Eu₂O₃ and Co/CeO₂. Again, these may all be due to Co²⁺ reduction by CO. It is worth noting that, unlike surface Ti³⁺ on Co/TiO₂, surface Ce³⁺ observed with Co/CeO₂ reduced in H₂ at 700°C did not reoxidize after subsequent exposure to H₂/CO reaction mixtures (Fig. 13). Apparently, surface Ce³⁺ is more stable under these conditions than is Ti³⁺.

It is apparent that the tendency toward further cobalt reduction by H₂/CO mixtures among the five supports is similar to that summarized in equation (1) for reducibility by H₂. CeO₂-, Eu₂O₃-, and La₂O₃-supported cobalt underwent more extensive reduction than did Co/TiO₂, which, in turn, underwent more extensive reduction than did Co/SiO₂, following exposure to an H₂/CO mixture at 250°C. One of the significant differences between La₂O₃, Eu₂O₃, and CeO₂ supports on the one hand and SiO₂ and TiO₂ on the other are that the former undergo extensive decarbonation/dehydroxylation during H₂ reduction, and carbonation and/or hydroxylation during the H₂/CO reaction (see Figs. 8 to 10), while the latter do not. The structural changes involved in the reduction and reaction processes for the lanthanide oxide supports caused by these behaviors may have a significant impact on the reducibility of supported Co. The reduction and agglomeration of supported cobalt metal may be very susceptible to such environmental changes. However, direct interaction, i.e., a localized interaction between supported cobalt and lanthanide oxides cannot be ruled out, particularly in the case of La₂O₃ and Eu₂O₃ supports, since significant changes in the Co 2p XPS spectra were observed with the non-H₂-treated samples indicating that a strong interaction between the metal and the support may have occurred.

REFERENCES

1. Okamoto, Y., Nakano, H., Imanaka, T., and Teranishi, S., *Bull. Chem. Soc. Japan* 48, 1163 (1975).
2. Frost, D. C., McDowell, C. A., and Woolsey, I. S., *Mol. Phys.* 27, 1473 (1974).
3. Castner, D. G., and Santilli, D. S., in "Catalytic Materials: Relationship between Structure and Reactivity," ACS Symposium Series, No. 248, p. 39 (1984).
4. Reuel, R. C., and Bartholomew, C. H., *J. Catal.* 85, 78 (1984).
5. Chin, R. L., and Hercules, D. M., *J. Phys. Chem.* 86, 360 (1982).
6. Sato, K., Inoue, Y., Kojima, I., Miyazaki, E., and Yasunori, I., *J. Chem. Soc., Farad. Trans. I* 80, 841 (1984).
7. Reuel, R. C., and Bartholomew, C. H., *J. Catal.* 85, 63 (1984).
8. Rosynek, M.P. and Li, C., unpublished data.
9. Praliaud, H., and Martin, G. A., *J. Catal.* 72, 394 (1981).
10. Tauster, S.J., Fung, S.C., Baker, R.T.K., and Horsley, J.A., *Science* 211, 1121 (1981).
11. Belton, D.N., Sun, Y.-M., and White, J.M., *J. Phys. Chem.* 88, 5172 (1984).
12. Resasco, D.E. and Haller, G.L., *J. Phys. Chem.* 88, 4552 (1984).
13. Horsley, J.A., *J. Am. Chem. Soc.*, 101, 2870 (1979).
14. Fung, S.C., *J. Catal.* 76, 225 (1982).
15. Lombardo, E. A., Tanaka, K., and Toyoshima, I., *J. Catal.* 80, 340 (1983).
16. Rosynek, M.P. and Chen, S.-S., unpublished data.
17. Koel, B. E., Praline, G., Lee, H. I., and White, J. M., *J. Electron Spectrosc. Relat. Phenom.* 21, 31 (1980).
18. Barrett, M. F., and Barry, T. I., *J. Inorg. Nucl. Chem.* 27, 1483 (1965).

Table 1

Summary of Cobalt Surface Species on Various Supports Following H₂, CO, or H₂/CO Treatment *

| <u>Treatment</u> | <u>Support</u> | | | | |
|---|---------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|---|
| | <u>SiO₂</u> | <u>TiO₂</u> | <u>La₂O₃</u> | <u>Eu₂O₃</u> | <u>CeO₂</u> |
| None | Co ²⁺ | Co ²⁺ | Co ²⁺ | Co ²⁺ | Co ²⁺ |
| H ₂ at 300°C | Co ²⁺ | Co ²⁺ | Co ²⁺ | Co ²⁺ | Co ²⁺ , Co ³⁺ |
| H ₂ at 400°C | Co ²⁺ , (Co ⁰) | Co ²⁺ , (Co ⁰) | Co ²⁺ , Co ⁰ | Co ²⁺ , Co ⁰ | Co ⁰ , Co ²⁺ , Co ³⁺ |
| H ₂ at 500°C | Co ²⁺ , (Co ⁰) | Co ²⁺ , (Co ⁰) | Co ²⁺ | Co ²⁺ , Co ⁰ | Co ³⁺ |
| H ₂ at 700°C | Co ²⁺ , (Co ⁰) | Co ⁰ , (Co ²⁺) | Co ²⁺ | Co ²⁺ , (Co ⁰) | Co ³⁺ , Co ²⁺ , Co ⁰ |
| CO at 400°C | Co ²⁺ , (Co ⁰) | Co ⁰ , Co ²⁺ | — | — | Co ⁰ , (Co ²⁺) |
| H ₂ at 400°C, H ₂ /CO at 250°C | Co ²⁺ , (Co ⁰) | Co ²⁺ , Co ⁰ | Co ⁰ , (Co ²⁺) | Co ⁰ , Co ²⁺ | Co ⁰ , Co ²⁺ |
| H ₂ at 700°C, H ₂ /CO at 250°C | Co ⁰ , Co ²⁺ | Co ⁰ , (Co ²⁺) | Co ⁰ , (Co ²⁺) | Co ²⁺ , Co ⁰ | Co ⁰ , (Co ²⁺) |

* Where more than one species is indicated, the predominant one in the XPS spectrum is listed first. Species shown in parentheses were present in only barely observable amounts.

FIGURE CAPTIONS

- Figure 1 XPS spectra of Co/SiO₂ catalysts in Co 2p_{1/2} and 2p_{3/2} regions. Reduction at the indicated temperatures involved treatment with 500 torr of H₂ for 16 hrs.
- Figure 2 XPS spectra of fresh and used Co/SiO₂ catalysts in Co 2p_{1/2} and 2p_{3/2} regions. Used catalysts had been exposed at 250°C to a 2/1 H₂/CO mixture at 1 atm for 4 hrs.
- Figure 3 XPS spectra of Co/TiO₂ catalysts in Co 2p_{1/2} and 2p_{3/2} regions. Reduction at the indicated temperatures involved treatment with 500 torr of H₂ for 16 hrs.
- Figure 4 XPS spectra of fresh and used Co/TiO₂ catalysts in Co 2p_{1/2} and 2p_{3/2} regions. Used catalysts had been exposed at 250°C to a 2/1 H₂/CO mixture at 1 atm for 4 hrs.
- Figure 5 XPS spectra in Ti 2p_{1/2} and 2p_{3/2} regions. (a) TiO₂ treated in 500 torr of H₂ at 700°C; (b) Co/TiO₂ treated in 500 torr of H₂ at 700°C and then exposed to 1 atm of 2/1 H₂/CO mixture at 250°C for 4 hrs; (c) Co/TiO₂ treated in 500 torr of H₂ at 700°C.
- Figure 6 XPS spectra of Co/La₂O₃ catalysts in Co 2p_{1/2} and 2p_{3/2} regions. Reduction at the indicated temperatures involved treatment with 500 torr of H₂ for 16 hrs.
- Figure 7 XPS spectra of fresh and used Co/La₂O₃ catalysts in Co 2p_{1/2} and 2p_{3/2} regions. Used catalysts had been exposed at 250°C to a 2/1 H₂/CO mixture at 1 atm for 4 hrs.
- Figure 8 XPS spectra of Co/La₂O₃ in O 1s region. (a) unreduced; (b) treated in 500 torr of H₂ at 400°C; (c) treated in 500 torr of H₂ at 400°C and then exposed to 1 atm of 2/1 H₂/CO mixture at 250°C for 4 hrs.
- Figure 9 XPS spectra of La₂O₃ in O 1s region. (a) without pretreatment; (b) treated in 500 torr of H₂ at 400°C; (c) treated in 500 torr of H₂ at 700°C.
- Figure 10 XPS spectra of La₂(CO₃)₃ in O 1s region. (a) without pretreatment; (b) treated in 500 torr of H₂ at 400°C; (c) treated in 500 torr of H₂ at 700°C.

Figure 11 XPS spectra of Co/CeO₂ catalysts in Co 2p_{1/2} and 2p_{3/2} regions. Reduction at the indicated temperatures involved treatment in 500 torr of H₂ for 16 hrs.

Figure 12 XPS spectra of fresh and used Co/CeO₂ catalysts in Co 2p_{1/2} and 2p_{3/2} regions. Used catalysts had been exposed at 250°C to a 2/1 H₂/CO mixture at 1 atm for 4 hrs.

Figure 13 XPS spectra of CeO₂ in Ce 3d_{5/2} region. (a) without pretreatment; (b) treated in 500 torr of H₂ at 700°C.

Figure 1

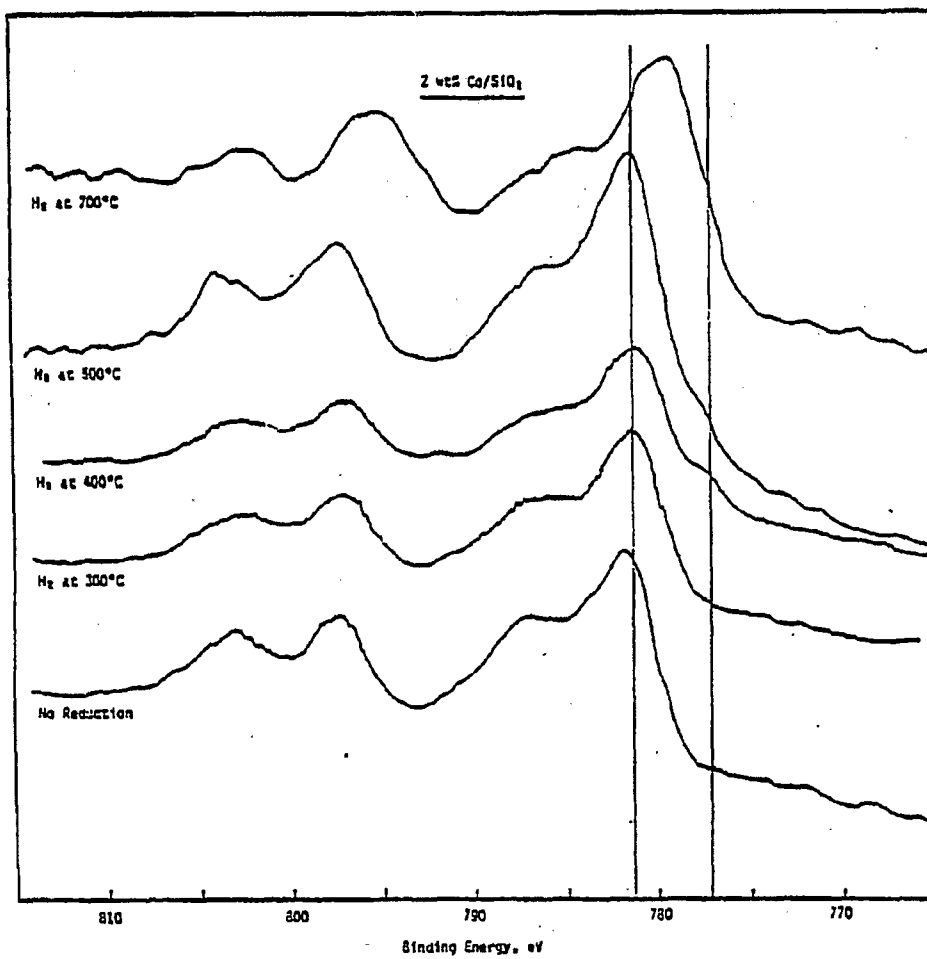


Figure 2

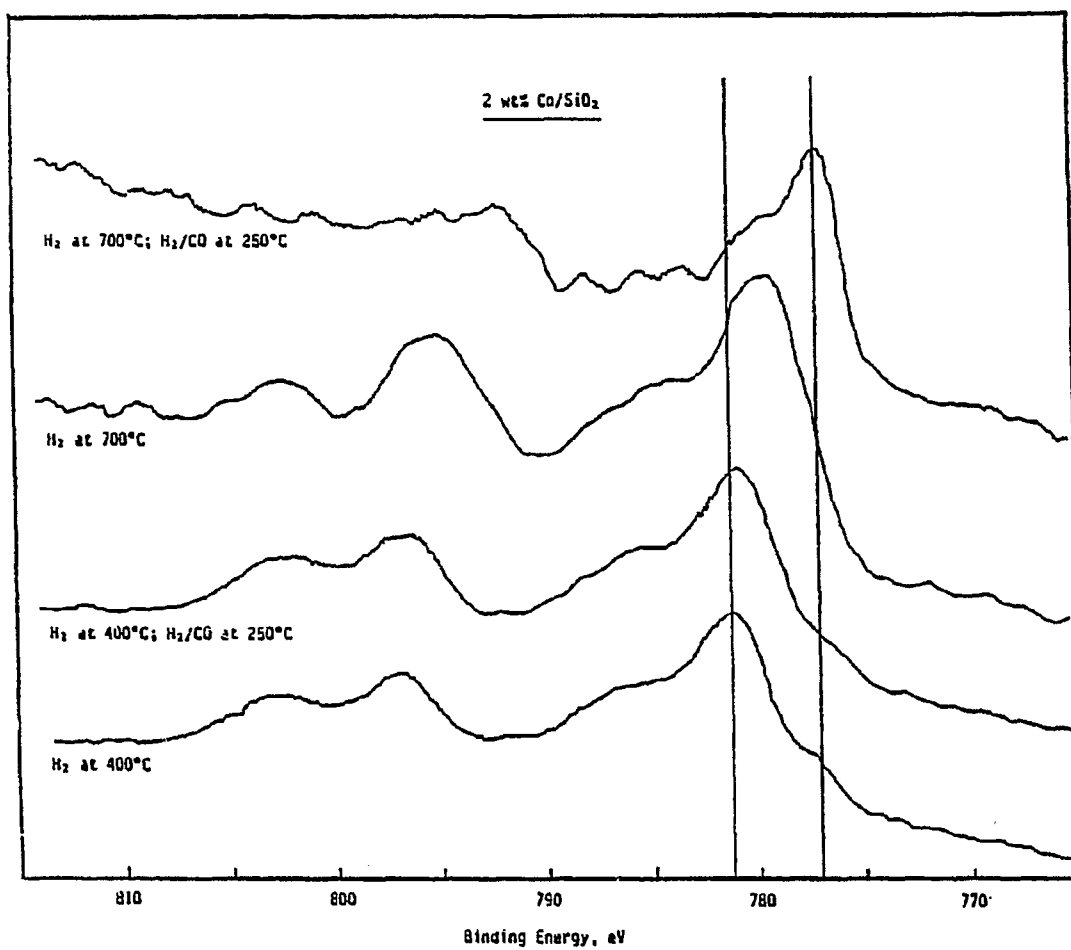


Figure 3

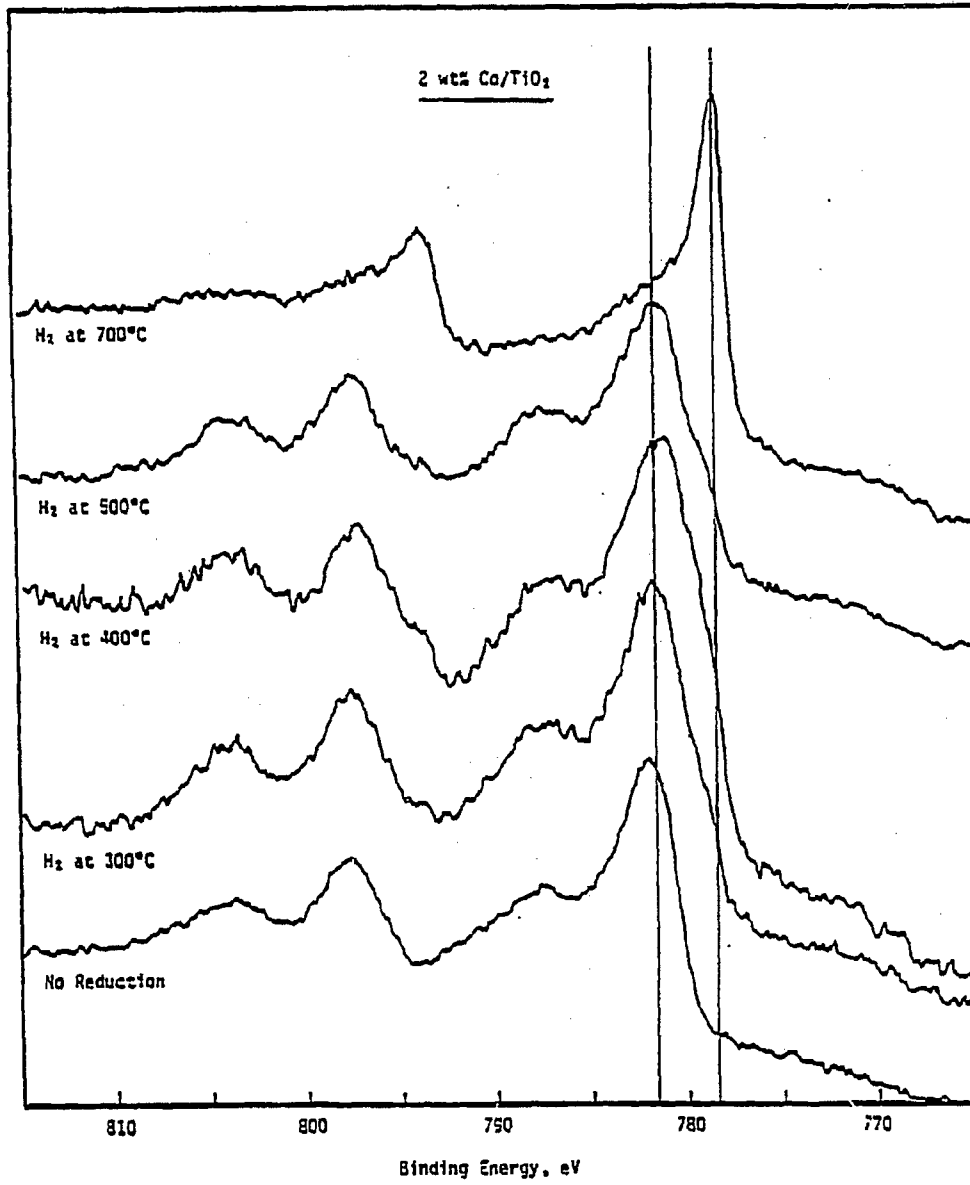


Figure 4

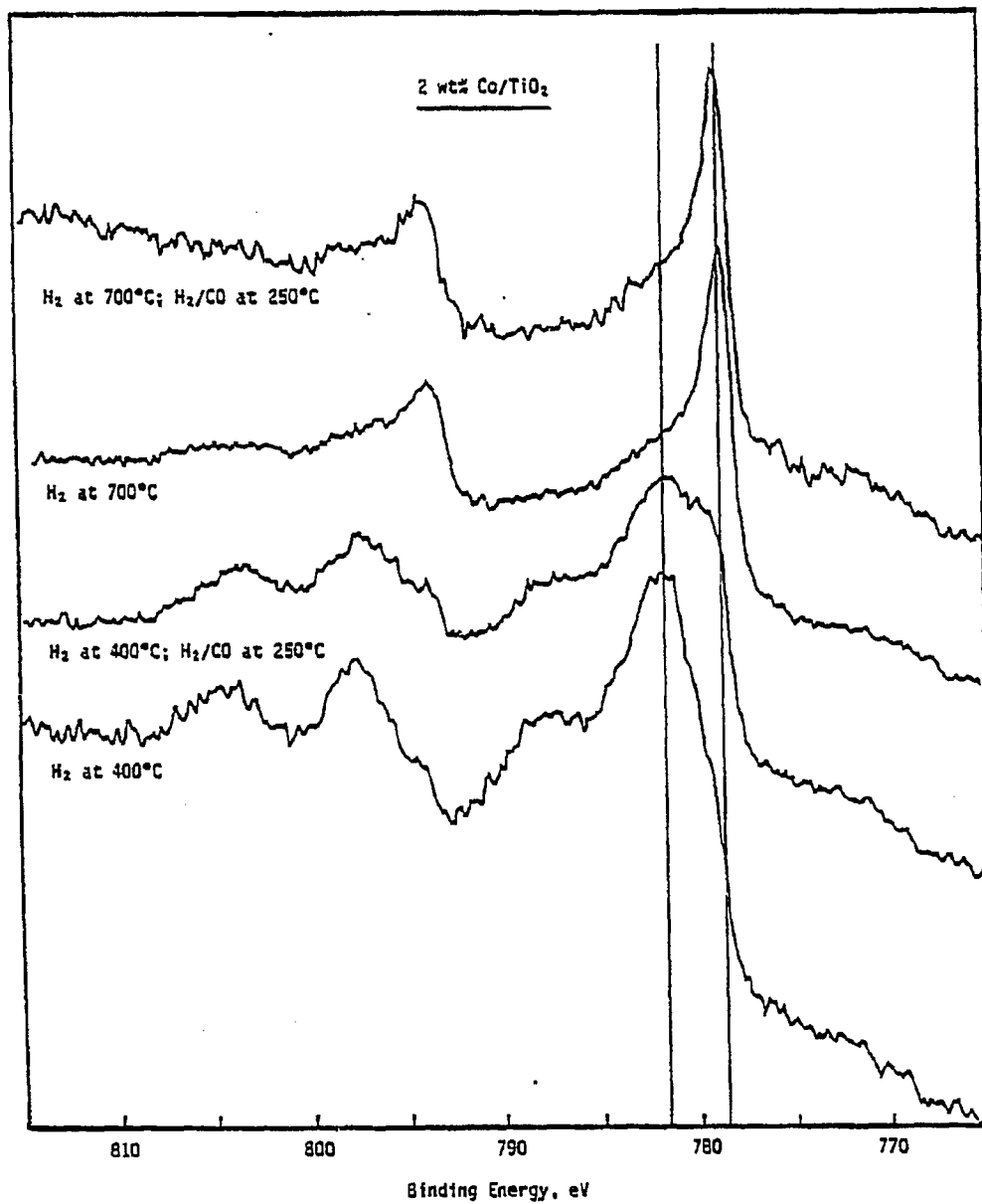


Figure 5

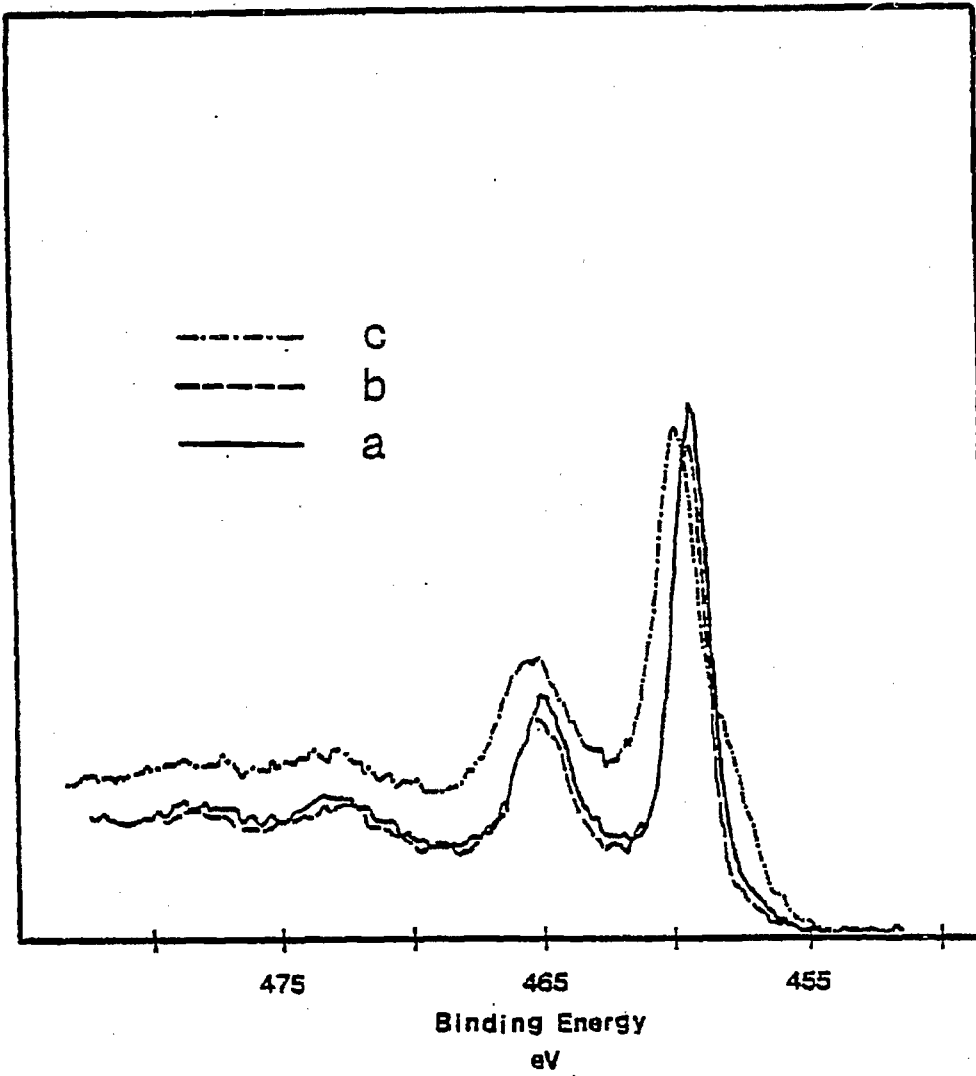


Figure 6

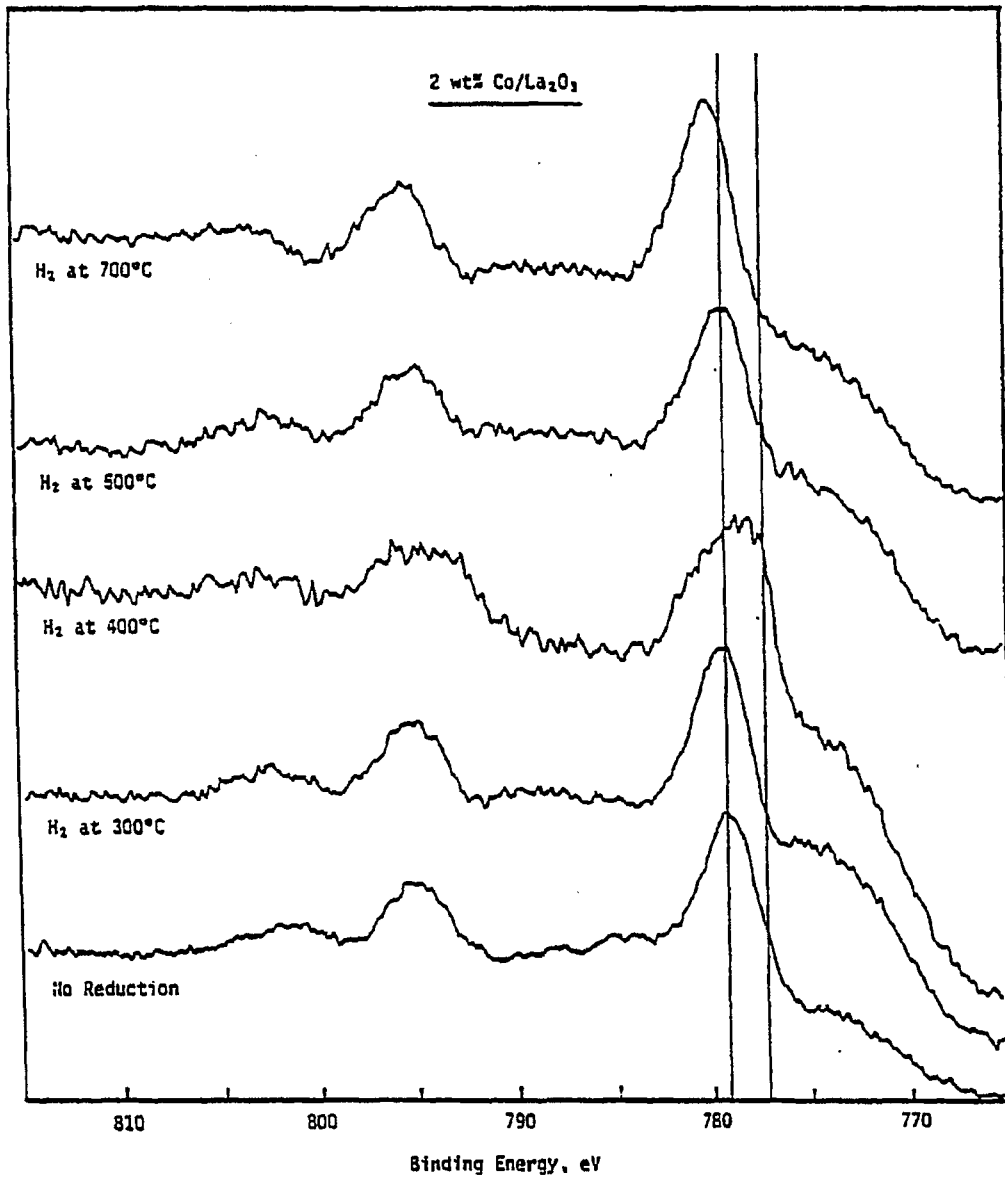


Figure 7

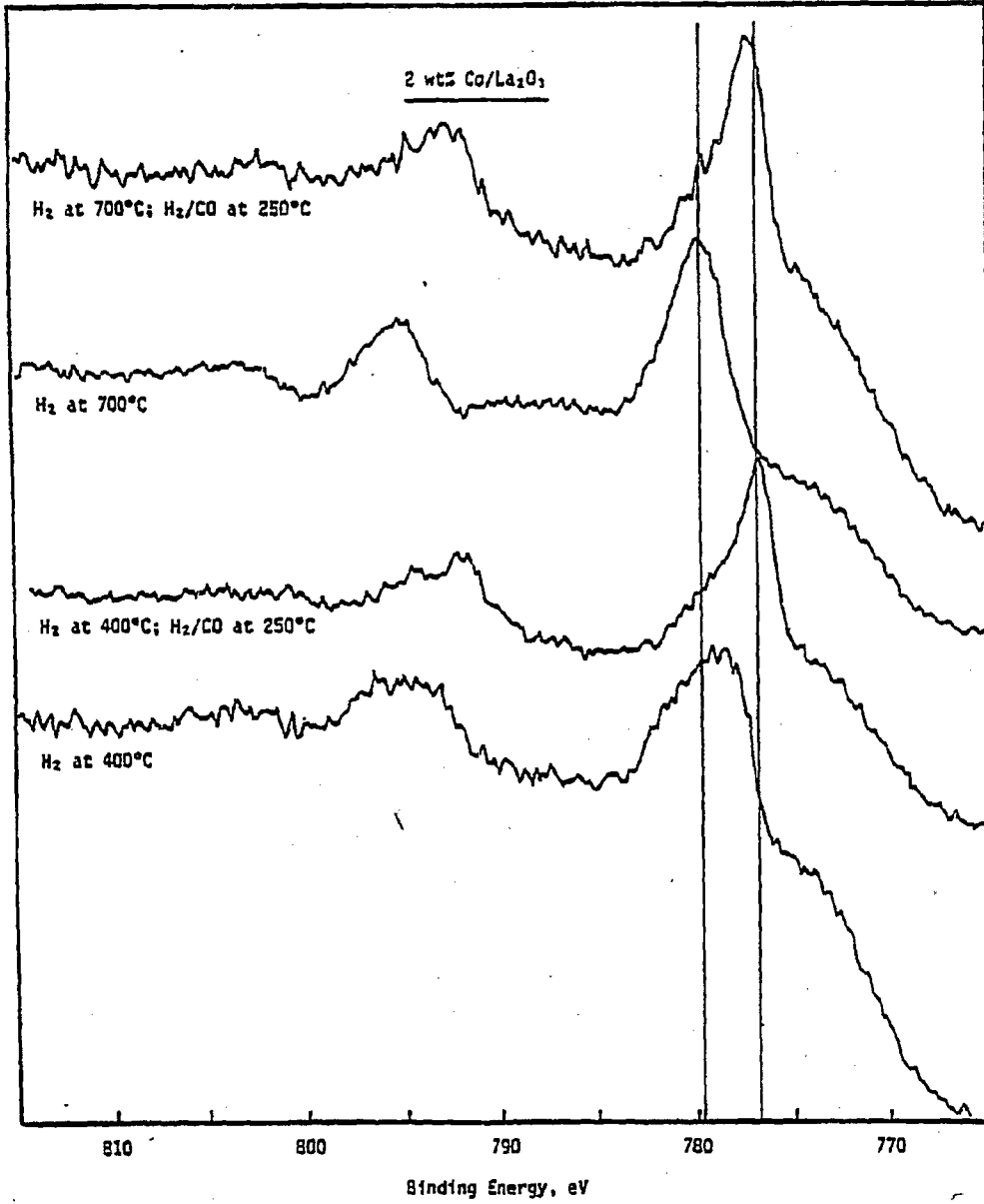


Figure 8

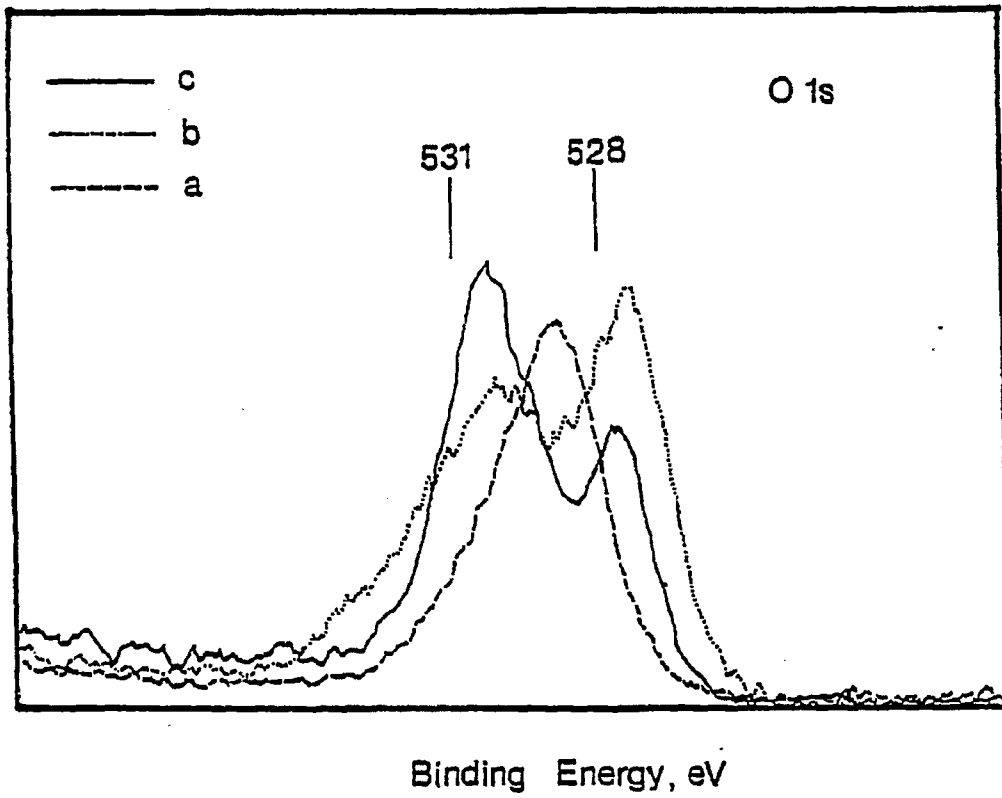


Figure 9

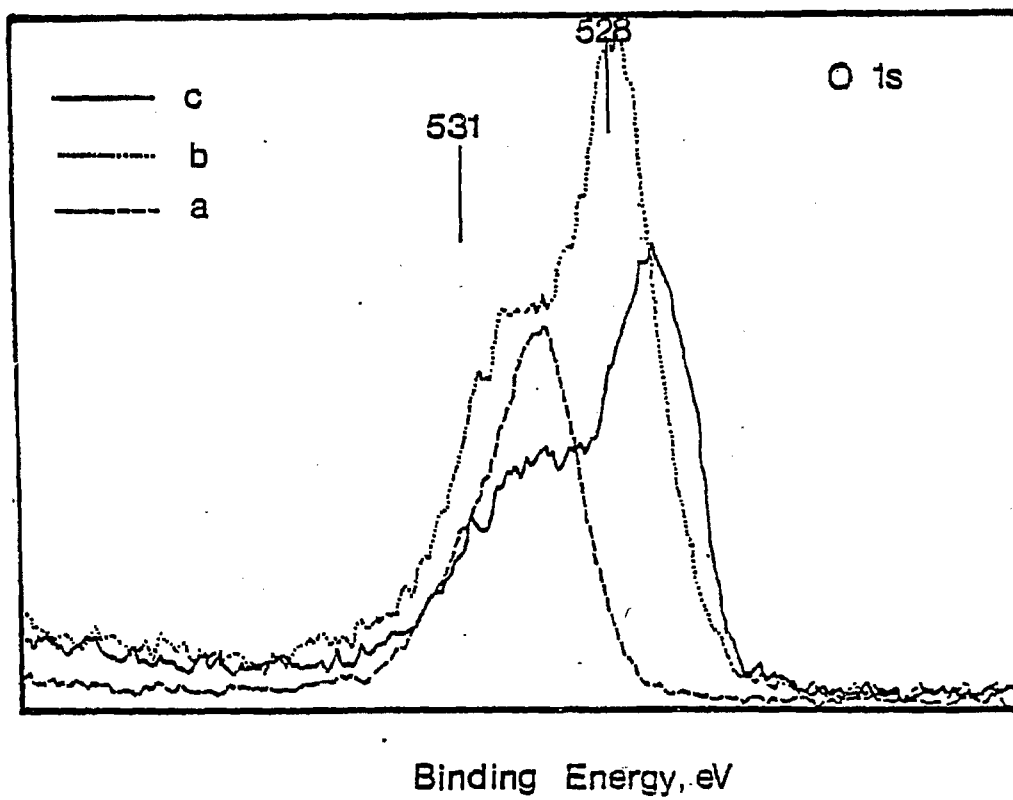


Figure 10

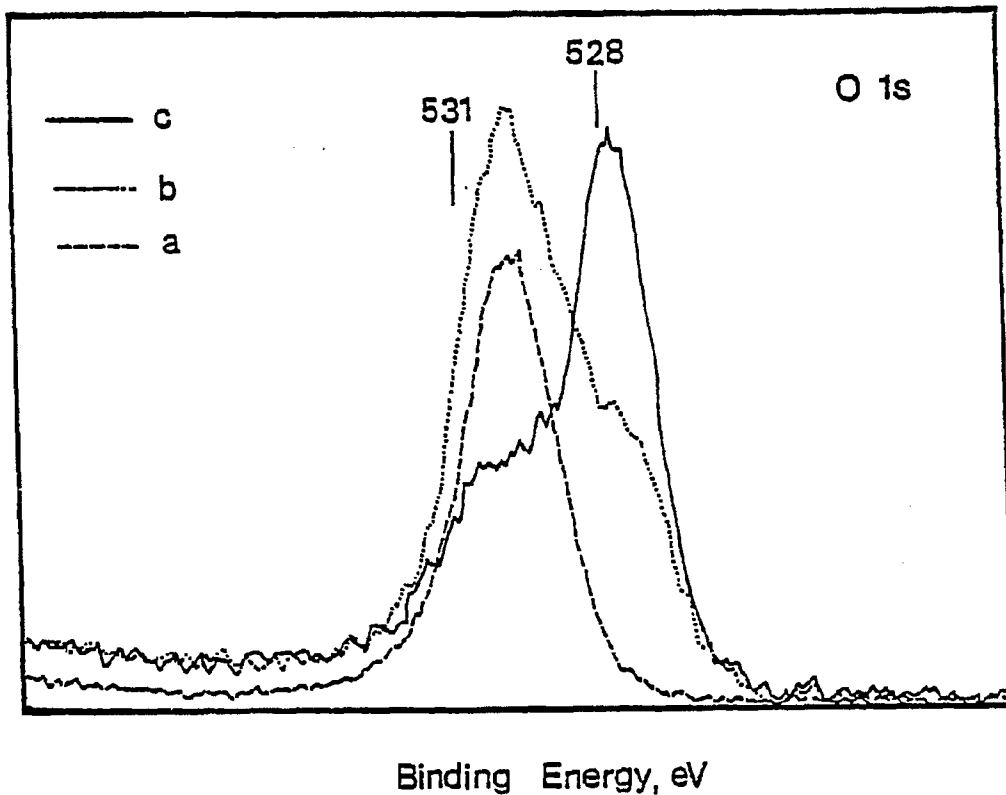


Figure 11

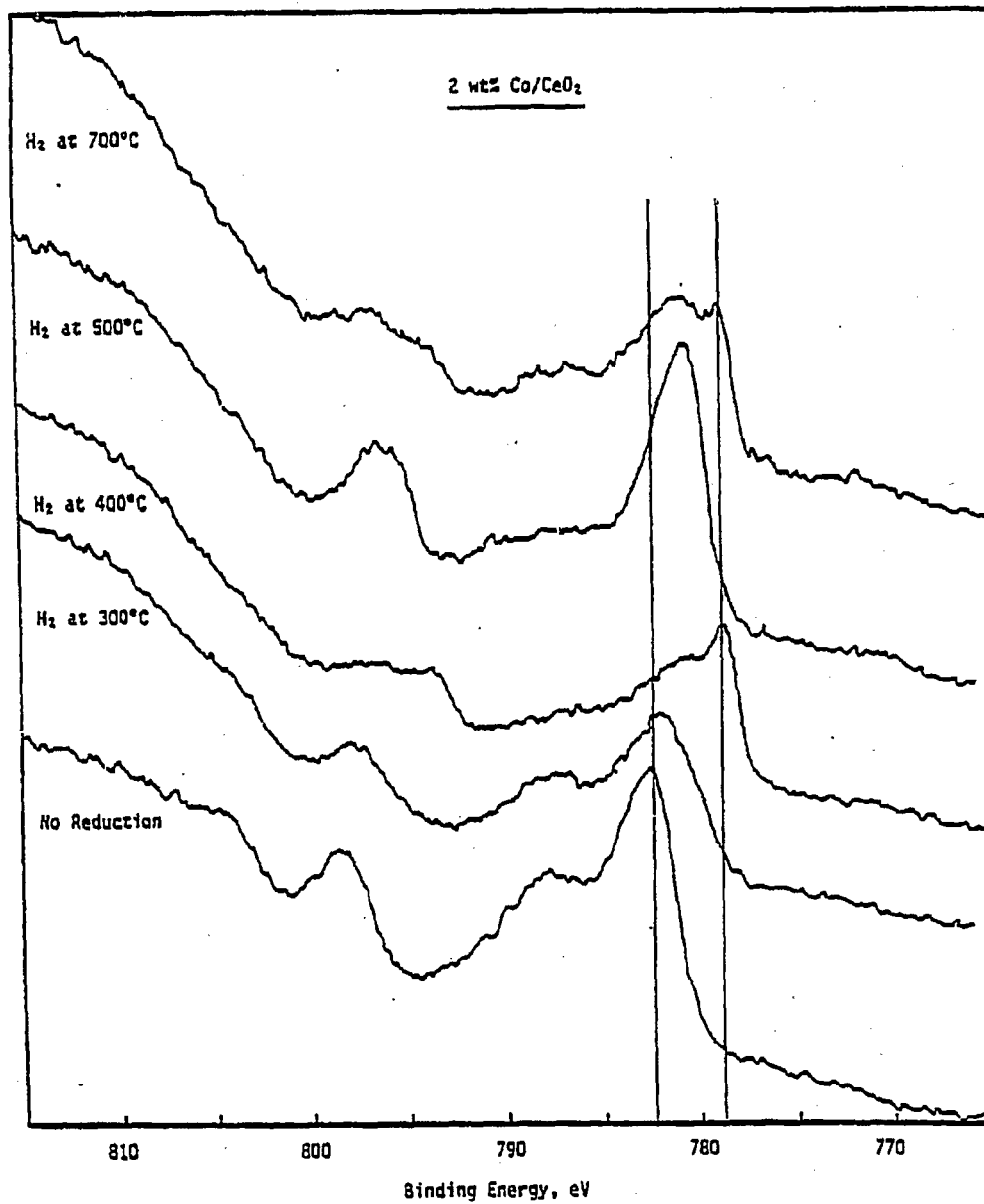


Figure 12

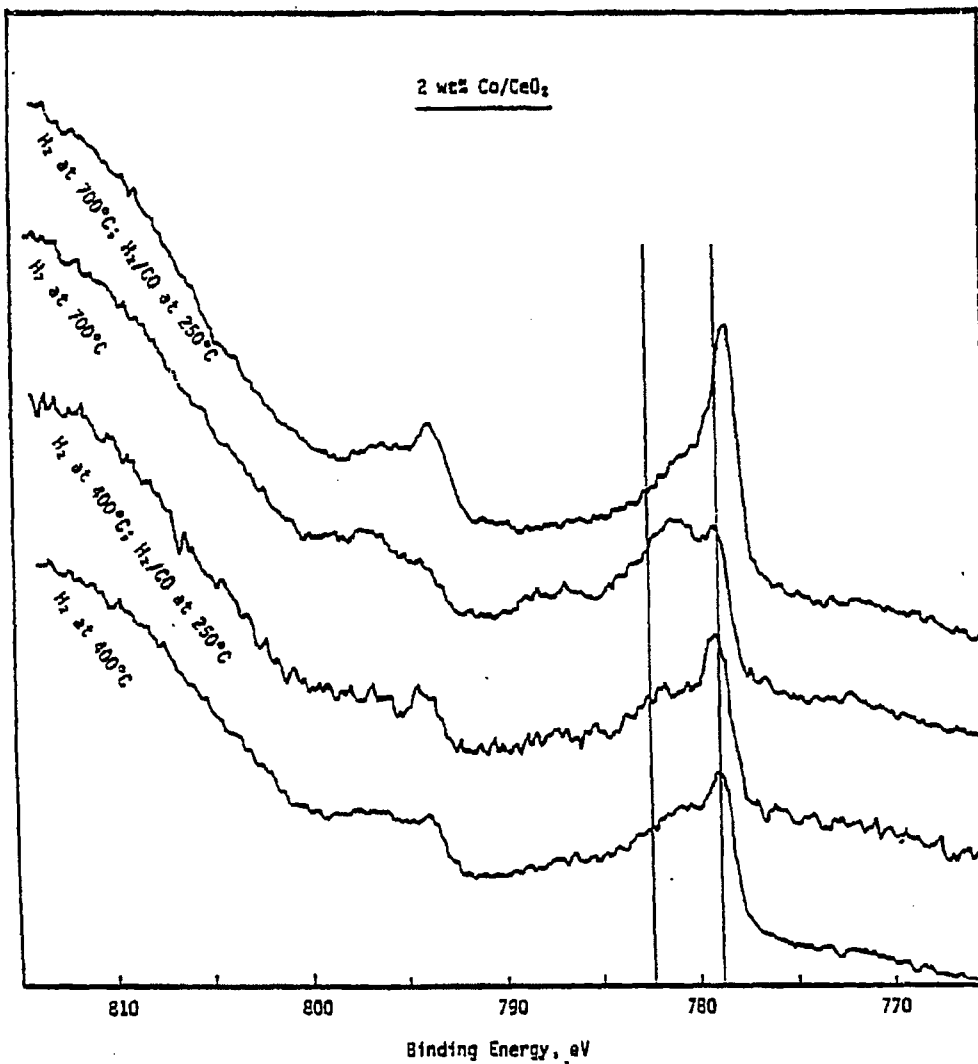


Figure 13

