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Low Take-off Angle XPS of Oxidic Planar Model NiW/γ-Al_2O_3 Catalysts

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Low take-off angle X-ray photoelectron spectroscopy (XPS) was used to study planar models of the oxidic form of the NiW/γ-Al_2O_3 hydrotreating system. Planar alumina films, grown anodically, were sequentially impregnated with solutions containing tungsten and nickel, and then calcined at 200, 350, and 500°C. XPS analyses were done using take-off angles of 90, 65, 40, and 10°. The results from the planar models were compared to XPS results (normal take-off angle) from "real" or powdered catalysts. The powdered catalysts consisted of powders made by sequential impregnation of γ-alumina and of a commercial NiO–WO_3/γ-Al_2O_3 catalyst, both of which were calcined at 450 and 750°C. Compositional effects for the models appear to indicate that the addition of a small amount of Ni dramatically increases the surface tungstate species (as evidenced by the W 4*f*/Al 2*p* ratio at low take-off angles); this is consistent with the powder data in that a small addition of Ni does not decrease the W/Al ratio. Calcination effects truly show similar trends in both the planar models and the powdered catalysts. Nickel appears to migrate into the support at the highest calcination temperatures while tungsten is redistributed on the outermost surface. Oxidic planar models that show quite similar surface spectroscopic characteristics and similar surface chemistry to real hydrotreating catalysts can be feasibly prepared.

INTRODUCTION

The interaction between a metal species and its support and/or a promoter metal is a key question in heterogeneous catalysis. Insight into understanding this structure/activity relationship in a supported metal catalyst can often be gained by observing structural and/or chemical changes induced by compositional or thermal effects on laboratory-prepared or actual commercial catalysts. An important new pathway to knowledge of supported/promoted systems currently being developed is the preparation and use of planar model catalysts (*1–3*). A relevant and important question about these models concerns how well they mimic the structural and chemical characteristics of real catalysts.

The various hydrotreating systems (alumina-supported CoMo, NiMo, and CoW, and NiW) with their high metal loadings are excellent targets for studying these interactive effects. Because of the intrinsically complex surface chemistry of the active hydrodesulfurization (HDS), hydrodenitrogenation (HDN), and hydrogenation catalysts, a major characterization technique of choice is X-ray photoelectron spectroscopy (XPS), which normally gives elemental and chemical state information about the first 7 to 10 atomic layers of a surface. However, if flat, smooth surfaces, which the planar models provide, are used and the take-off angle to the spectrometer analyzer is decreased, the technique's surface sensitivity is increased to the first 1 to 3 atomic layers. The utilization of this low take-off angle XPS has been described in detail by Fadley (*4*). The technique has not been exploited on heterogeneous catalysts since planar morphologies, which have not generally been available, are required.

The CoMo/γ-Al_2O_3 HDS system has been widely studied by a variety of surface techniques including XPS, ion scattering spectroscopy (ISS), and laser Raman spectroscopy (LRS). Delmon and co-workers

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(*5*), Chin and Hercules (*6*), Cocke and co-workers (*7, 9*), and Webster and Wei (*8*) have all produced evidence that for the oxidic form of the catalyst, Mo exists as a monolayer with a Co species lying directly beneath. The NiMo/γ-Al_2O_3 HDS analog has also been investigated by Knözinger and co-workers (*10–13*) with the conclusion that the Ni species, unlike the Co, is incorporated within the surface Mo layer. The NiW/γ-Al_2O_3 system, an active HDS, HDN, and much more active hydrogenation catalyst, however, has not been as widely investigated using such surface techniques. A much stronger interaction between W and the alumina support, compared with the Mo/interaction, exists, as evidenced by several studies involving reduction characteristics of the two systems (*14–17*). One study by Salvati and co-workers (*14*) utilizing ISS did indicate that the Ni promoter in a γ-alumina-supported NiW catalyst did appear to be incorporated within the tungstate layer.

Another ISS study from this laboratory (*9*) indicated that two types of Ni species existed on a commercial catalyst at high calcination temperatures, one associated with a well-dispersed W species, the other a Ni/support interaction species.

Another question that arises in attempting to model a catalytic system is whether to design the catalyst in a form similar to a commercial catalyst (powders, extrudates, pellets, etc.) or, since surface information is crucial, to design the model such that it is ideally suited to modern surface analytical techniques such as XPS and ISS. In this study, both designs were employed: powder *and* planar models. The uses and advantages of planar aluminas as model catalyst supports have been reviewed in detail (*1*); their flatness allows for low take-off angle XPS to be utilized, thereby effectively increasing the surface sensitivity of the technique. A series of "real" (i.e., powder-type) and planar model oxidic NiW/γ-Al_2O_3 catalysts was prepared with different Ni loadings (constant W content) and varying calcination temperatures. These compositional and thermal effects upon the surface structure as seen by surface dispersion (metal/support ratios) and component location and migration were monitored using normal XPS for the powders and low take-off angle XPS for the planar models.

METHODS

Sample Preparation

Planar models. The support material used was 0.5-mm-thick aluminum foil (99.999% from Johnson-Matthey), which was punched into $\frac{1}{2}$-in. disks and sequentially polished with decreasing grit size diamond paste (50, 30, 15, 5, 1, and $\frac{1}{4}$ μm) until smooth and shiny. The alumina films were anodically grown in 1 : 1 boric acid : sodium borate buffer (pH 8.4) in an electrochemical cell at 10 mA/cm^2 current density and varying the applied voltage to 40 V. Barrier films were approximately 550 Å thick. After drying at 110°C for 1 h, the disks were then calcined in a tube furnace at 450°C in flowing air for 5 h to give the γ- or γ'-alumina support (*1*).

Solutions of ammonium metatungstate (Fluka $(NH_4)_6H_2W_{12}O_{40}$) and nickelous nitrate (Fluka $Ni(NO_3)_2 \cdot 6H_2O$) were used to dope the planar aluminas. A constant amount of W corresponding to theoretical full or "monolayer" coverage was used for each model while the amount of Ni varied from full coverage down to zero coverage. The supports were impregnated with the W-containing solution, dried at 110°C for 1 h, calcined in flowing air at 200, 350, or 500°C for 1 h, and then impregnated with the Ni-containing solution, dried at 110°C again, and finally calcined for 2 h at 200, 350, or 500°C. See Table 1 for a complete description of compositions and calcination temperatures.

Powdered catalysts. The support material used was a 200 m^2/g γ-alumina (Strem Chemical) in the form of extrudates. Solutions of ammonium metatungstate and nickelous nitrate were again used to impregnate

TABLE 1

Preparation of Planar Models

Sample designation	% Ni corresponding to full coverage[a]	Calcination temperature (°C)
PNTA.M00	0	350
PNTA.M01	25	350
PNTA.M02	50	350
PNTA.M03	75	350
PNTA.M04	100	350
PNTA.H00	0	500
PNTA.H01	25	500
PNTA.H02	50	500
PNTA.H03	75	500
PNTA.H04	100	500
PNTA.L00	0	200
PNTA.L01	25	200
PNTA.L04	100	200

[a] The W content was constant at full coverage.

the support. The amount of W was held constant at 25.7 wt% WO_3 while the amount of Ni added varied from 0 to 8.3 wt% NiO. See Table 2 for compositions and calcination temperatures. As was done with the planar models, the support was sequentially impregnated with the W species, dried, calcined, impregnated with the Ni species, dried, and recalcined for 2 h. The catalysts were then crushed into a powder with a mortar and pestle.

TABLE 2

Preparation of Powdered Catalysts

Sample designation	Wt% NiO added[a]	Calcination temperature (°C)
RNTA.L00	0.0	450
RNTA.L02	2.0	450
RNTA.L04	4.2	450
RNTA.L06	6.2	450
RNTA.L08	8.3	450
RNTA.H00	0.0	750
RNTA.H02	2.0	750
RNTA.H04	4.2	750
RNTA.H06	6.2	750
RNTA.H08	8.3	750
CNTA.L[b]	6.0	450
CNTA.H	6.0	750

[a] "R" series all contain 25.7 wt% WO_3.

[b] "C" series, commercial catalyst with 19 wt% WO_3.

A commercial catalyst (Strem Chemical) containing 6 wt% NiO and 19 wt% WO_3 on γ-alumina was calcined in flowing air for 2 h at 450 or 750°C and then also crushed into a powder.

Instrumentation

All XPS data were recorded using a Kratos XSAM800 spectrometer with a DS3090 PDP11 operating system. The Mg anode ($K\alpha$ = 1253.6 eV) was operated at 12 kV and 20 mA. The pressure in the analysis chamber with the samples loaded was better than 1×10^{-8} Torr. The planar models were analyzed using take-off angles of 90, 65, 40, and 10° with respect to the spectrometer. The powders were sprinkled onto double-sided tape on a sample holder. XPS areas were calculated for the following regions using the total integrated area of that region: Al $2p$, O $1s$, C $1s$, W $4f$, and Ni $2p_{3/2}$. Areas were normalized using atomic sensitivity factors (*18*) and the total number of scans. Peak positions were adjusted using the carbon $1s$ photoelectron peak at 285.0 eV as a reference.

RESULTS AND DISCUSSION

Typical XPS spectra for the commercial, powder model, and planar model catalysts are shown in Fig. 1. All spectra in this figure were taken at a normal (90°) take-off angle. Note that the spectra of the planar models, especially the W $4f$ and Al $2p$ regions, tend to show more detail and are better resolved than the spectra of the powdered catalysts. Charging and inelastic energy losses seem to be less severe with the planar models. This may be one area in which the planar models are superior to the powders. Figure 2 shows typical spectra from all four experimental take-off angles of the W $4f$ and O $1s$ regions of a planar model. There is the expected loss of intensity at the lowest take-off angle (10°). Results for the powders will be discussed

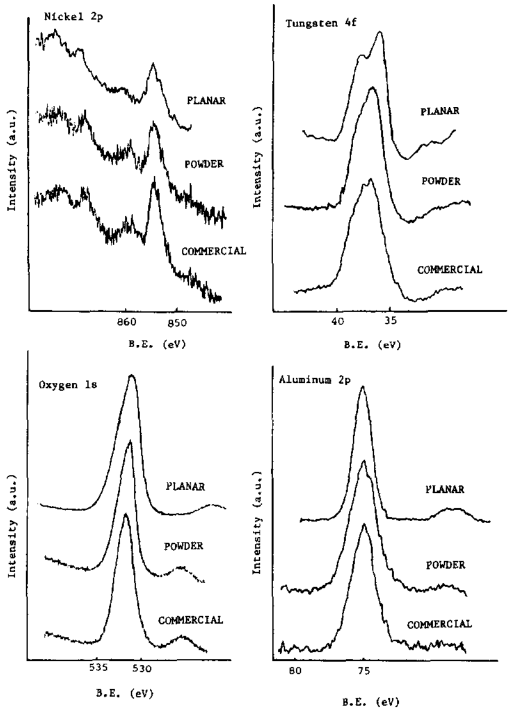

FIG. 1. Typical XPS spectra of the Ni 2*p*, W 4*f*, O 1*s*, and Al 2*p* regions for the commercial, powder, and planar model catalysts. The FWHM of the O 1*s* region for the planar model is very nearly equal to those of the commercial and powder catalysts; the peak appears broader because a different scale was used.

first in order to provide a framework of reference for the planar models.

Commercial Catalyst

The effects of different calcination temperatures are seen for the commercial catalyst in Table 3. Table 3 shows the XPS metal/support ratio ((W or Ni)/Al) at 450 and 750°C. At the 450°C mark, the W/Al ratio is at its lowest value while the Ni/Al ratio is at its highest value. As the calcination temperature is raised from 450 to 750°C, the W/Al ratio increases steadily to reach its highest value, while the Ni/Al ratio decreases to its lowest value. Similar results are seen for the W/O and Ni/O ratios. These ratios appear to indicate that the Ni does indeed migrate into the alumina support as temperature is increased. This supports a previous ISS study by Horrell *et al.* (*9*). This loss of Ni (approximately 21% from Ni/Al ratios) to the support apparently causes a redistribution of tungsten, as indicated by a 30% enhancement of surface tungstate. Note the increases in the W/Al and W/O ratios. This would also seem to

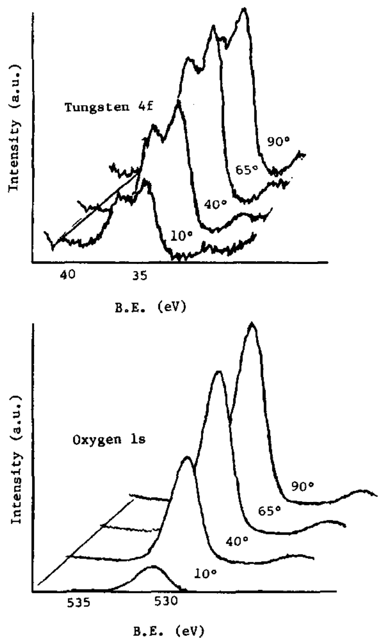

FIG. 2. Typical XPS spectra of the W 4*f* and O 1*s* regions of the planar models at the four different take-off angles. Each spectrum of oxygen region is the sum of 10 scans. For the tungsten region, 100 scans were accumulated at the 90, 65, and 40° angles, but 200 were taken at the 10° angle.

TABLE 3

XPS Peak Area Ratios[a] of Commercial Catalyst Calcined at 450 and 750°C

Peak ratio	450°C	750°C
W 4*f*/Al 2*p*	7.9	10.3
W 4*f*/O 1*s*	3.8	4.8
Ni 2*p*/Al 2*p*	5.8	4.6
Ni 2*p*/O 1*s*	2.7	2.1
Ni 2*p*/W 4*f*	0.75	0.45

[a] All ratios (except Ni/W) multiplied by 100.

indicate that there is a strong competition for sites between Ni and W at lower temperatures, but driving the Ni into the support thermally allows the W to redisperse. There is also a 40% decrease in the Ni/W ratio as the catalyst is calcined from 450 to 750°C.

Powders

Temperature effects for the laboratory-prepared catalysts (RNTA series) are seen in Table 4, which shows the various XPS peak area ratios for the catalysts calcined at 450 and 750°C. The Ni/Al and Ni/O ratios for the catalysts of varying Ni content show that the Ni migrates toward the support as the temperature is increased from 450 to 750°C. Meanwhile, the W/Al and W/O ratios increase steadily with increasing calcination temperature. In fact, at 750°C, the W/Al ratio is seen to be at or above the level for an unpromoted catalyst. This would seem to manifest the dispersion-enhancing effect of the active metal by the promoter metal. It also raises the possibility of increasing dispersion of the Group VIB metal by thermally driving a small portion of the Group VIIIB promoter into the support. The W/O ratio at 750°C, however, seems to converge near the value for an unpromoted catalyst. This may indicate an oxygen surplus near the surface. The loss of W dispersion at 450°C, when compared to the unpromoted catalyst, is readily understood due to the competition for sites between the added Ni promoter and the already present W. The Ni appears to replace some of the W, or perhaps cause the W to form clusters. It may be this replaced or clustered W that is redispersed on the surface as Ni moves inward at high calcination temperatures. The values also show the expected decrease in the Ni/W ratio as temperature is increased. All these trends are similar to those observed in the commercial catalyst.

Planar Models

The relative flatness of the models is important in subsequent XPS interpretations. Powder models, of course, have extremely rough surfaces. The morphology of various planar models (a, dried-only oxide, b, calcined oxide, c, PNTA.L04, and d, PNTA.H04) is seen in the backscattered electron images shown in Fig. 3. All images are 850× magnified. The dried-only oxide, representing a fresh film, seen in Fig. 3a, exhibits many small particles, which, upon calcination at 450°C for 5 h, greatly diminish in quantity (Fig. 3b).

Although remnants of the polishing process are seen, evidenced by small grooves in the film, the images of the calcined and doped oxide films are fairly nondescript. They do appear to be flat in character, with few contaminant particles observed.

Also important is the oxidation behavior of the films under the calcination condi-

TABLE 4

XPS Peak Area Ratios[a] for Lab-Prepared Catalysts Calcined at 450 and 750°C

Wt% NiO added	Ni/Al		Ni/O		W/Al		W/O		Ni/W	
	450°C	750°C	450°C	750°C	450°C	750°C	450°C	750°C	450°C	750°C
0.0					7.8	7.8	4.7	4.8		
2.0	1.3	0.9	0.75	0.6	6.3	8.5	3.8	5.1	0.21	0.11
4.2	2.3	1.8	1.3	1.1	4.3	8.7	2.8	5.0	0.53	0.20
6.2	3.0	2.3	1.8	1.4	5.7	7.8	3.5	4.6	0.53	0.27
8.3	3.3	2.8	2.0	1.6	5.1	8.6	3.1	4.7	0.65	0.32

[a] All ratios (except Ni/W) multiplied by 100.

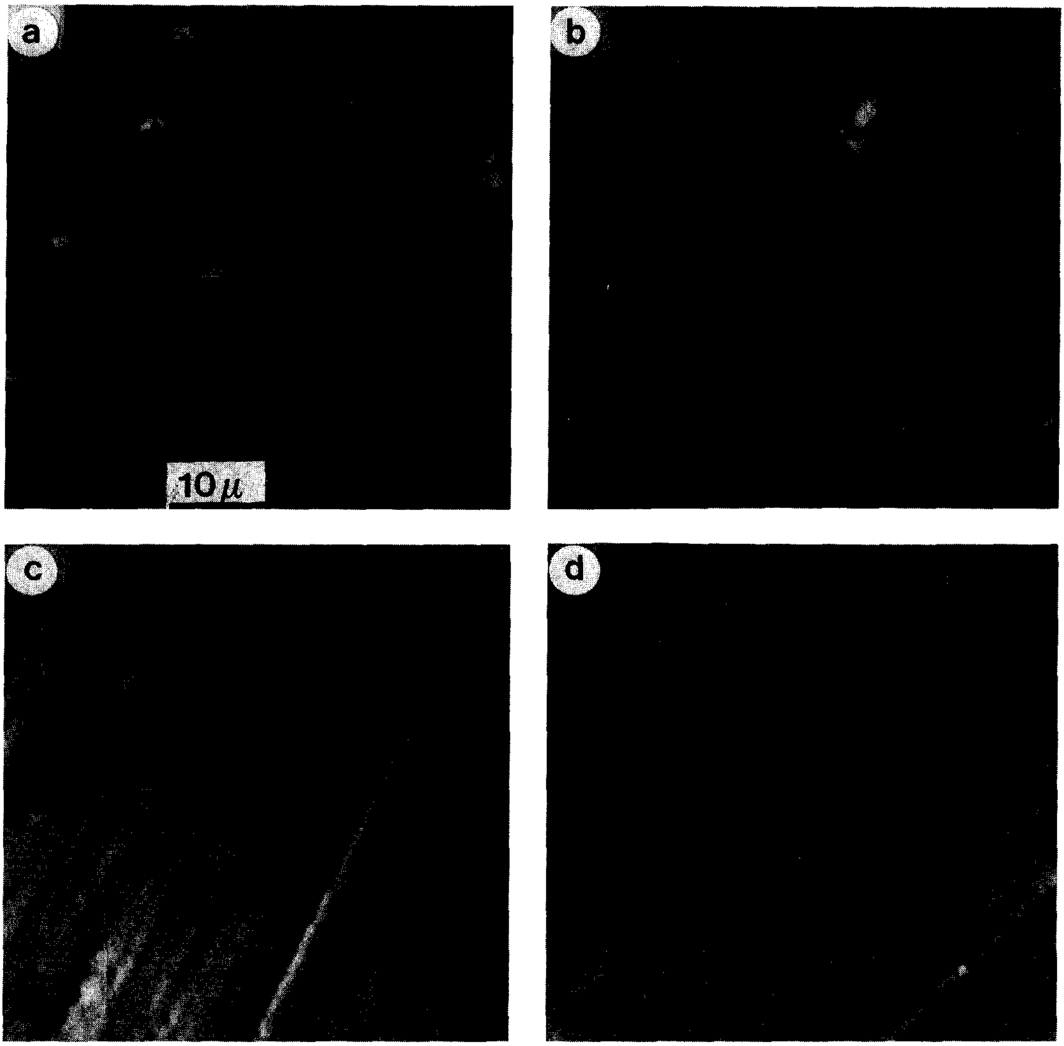

FIG. 3. Backscattered electron images (850×) of planar models of (a) "fresh" alumina dried at 110°C for 1 h; (b) alumina calcined at 450°C for 5 h; (c) PNTA.L04; and (d) PNTA.H04.

tions. Table 5 shows the Al 2*p* peak position and the O 1*s*/Al 2*p* peak area ratio as seen by XPS at normal and low take-off angles for a "blank" planar model which has been analyzed while "fresh," calcined at 450°C for 5 h and then further calcined at 200 or 500°C for 2 h each. In all cases it is observed that a more highly oxidized alumina exists on the outer surface for two reasons: (i) the O/Al ratios at the 10° angle are significantly higher than those at normal angle, and (ii) the binding energy of the Al 2*p* peak is slightly higher at the 10° angle. It does appear that the 500°C calcination results in a small increase in the O/Al ratio at the 10° angle, which may signify an oxygen buildup at the surface. This may mean that metal/oxygen ratios must be interpreted carefully for the 500°C temperatures, especially if comparisons with the 200°C calcination temperature are to be made. However, the position of the Al 2*p* is not significantly greater at the 10° take-off angle for the 200 and 500°C samples, so

TABLE 5

XPS Al 2*p* Peak Positions and O 1*s*/Al 2*p* Area Ratios at 10 and 90° Take-off Angles for Planar Supports

Sample description	Al 2*p* binding energy (eV)		O 1*s*/Al 2*p*	
	10°	90°	10°	90°
Dried 110°C 1 h	74.45	74.30	2.29	2.00
Calcined 450°C 5 h	74.55	74.40	2.31	2.05
Calcined 200°C 2 h[a]	74.55	74.40	2.24	2.08
Calcined 500°C 2 h[a]	74.60	74.45	2.46	2.08

[a] Support already experienced the 450°C, 5-h treatment.

comparisons using the metal/aluminum ratio can prove useful.

Figure 4 shows the W/Al ratios at the four take-off angles for five planar models of varying Ni concentrations calcined at 350 and 500°C, respectively. Note in Fig. 4a that the W/Al ratio for zero added, Ni, i.e., an unpromoted WO_3/alumina catalyst, stays relatively constant at all four take-off angles. This seems to indicate that the W exists as particles on the support since there is no appreciable difference in the ratio with increasing probe depth. As 1 unit of Ni (representing one-fourth monolayer coverage by Ni) is added to the catalyst, there is little change in the W/Al ratio at the high (65 and 90°) take-off angles, but the 40° angle shows a prominent increase and the 10° angle exhibits an enormous increase. This clearly shows the analytical value of low take-off angle XPS. The analyzed depth at a 10° angle is much smaller than that at a normal angle. This increases surface sensitivity to a point such that information is derived from the first two or three atomic layers of this flat model catalyst. It can be inferred that the W particles have been redistributed due to the promotional effect of the added Ni. Evidently there is a strong tendency for the added Ni to associate with the W, causing the breakdown of some W particles or clusters. As more Ni is added (2, 3, and 4 units), the competition for sites between Ni and W increases and the stronger Ni/support interaction causes the W to start to reassociate into particles, as evidenced by the decrease in the W/Al ratio. The nearly identical profiles and the overall lower W/Al ratios at the 90 and 65° angles indicate that there is little tungsten "deep" in the support; this is reasonable if the W does indeed exist as clustered particles and because the doping level of the W was small.

Note in Fig. 4b that as the catalysts are calcined at 500°C, the W/Al ratios at 10 and 40° remain relatively large even when 2 units of Ni (one-half monolayer) are added. This is in contrast to the same points in Fig. 4a. Apparently the competition for surface sites is not as prevalent at 500°C due to the

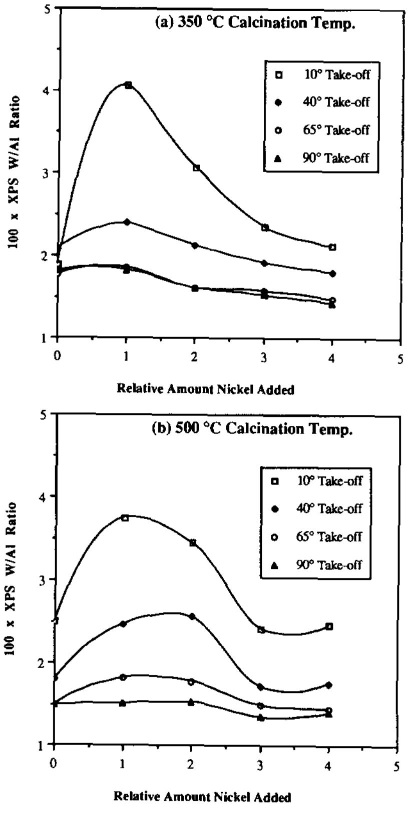

FIG. 4. Take-off angle XPS W 4*f*/Al 2*p* area ratios for planar models of varying nickel content calcined at (a) 350°C and (b) 500°C.

probable migration of some of the Ni into the support. This movement of Ni allows the W to remain in a fairly highly dispersed state at the surface. The decrease in the ratio as 3 and 4 units of Ni are added again gives credence that competition for sites and reassociation into W clusters are occurring.

Figures 5, 6, and 7 exhibit angular and thermal effects for planar models containing either 1 or 4 units of added Ni promoter. Figure 5a shows that the W/Al ratio at 200°C and at a 10° angle is significantly lower than the ratios at 350 and 500°C. This implies that the small amount of added Ni (1 unit) does not significantly affect the redistribution of the W until higher calcination temperatures are reached. The ratios at 90, 65, and 40° vary little with calcination temperature and slightly increase with angle, yet the ratio jumps markedly in going from a 40 to a 10° take-off angle. This supports the idea that there is little W deeper in the support and that redistribution of W particles occurs at higher temperatures.

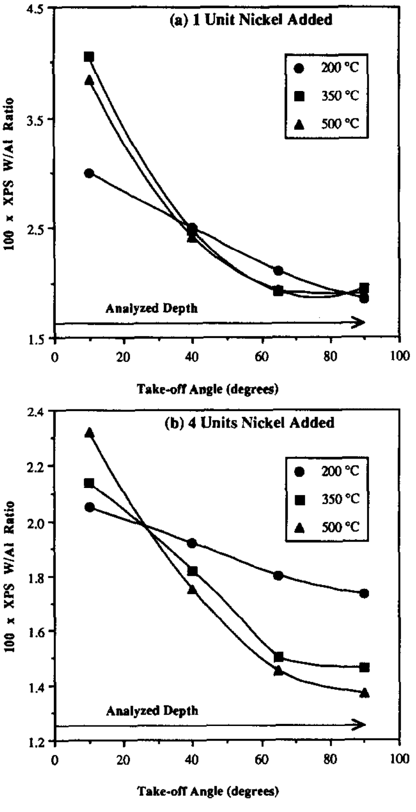

FIG. 5. Take-off angle XPS W 4*f*/Al 2*p* area ratios for planar models calcined at 200, 350, and 500°C: (a) one unit added nickel and (b) four units added nickel.

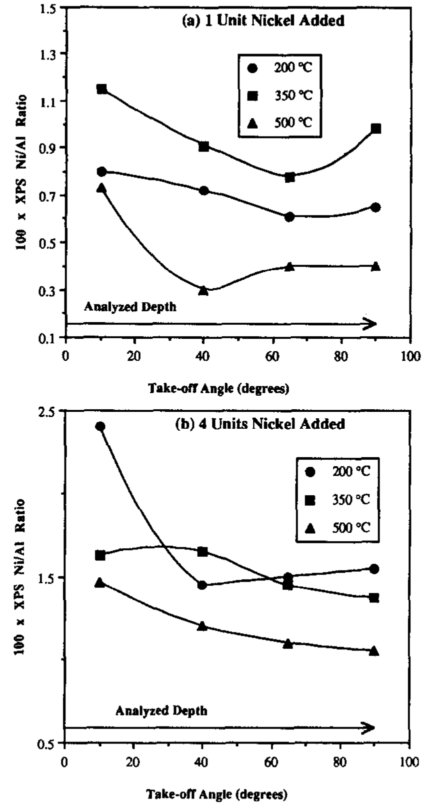

FIG. 6. Take-off angle XPS Ni 2*p*/Al 2*p* area ratios for planar models calcined at 200, 350, and 500°C: (a) one unit added nickel and (b) four units added nickel.

The effect of 4 units of Ni (full monolayer) upon the W/Al ratios are seen in Fig. 5b. The relatively flat profile at 200°C further supports the existence of W clusters. At a 10° angle, there appears to be some fairly well dispersed W, probably associated with the Ni, on the surface. The lower W/Al ratios at 65 and 90° for the 350 and 500°C treatments indicate an absence of W from the support, which may be due to the reformation of W clusters.

Figure 6 examines the effects of temperature and take-off angle upon the Ni/Al ratio

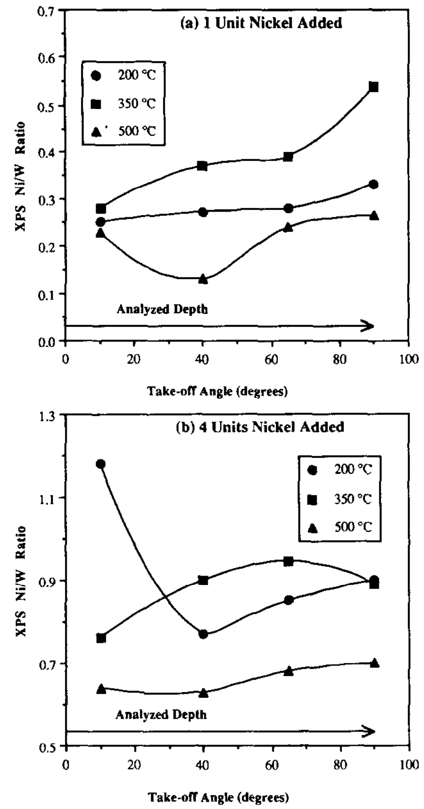

FIG. 7. Take-off angle XPS Ni $2p$/W $2f$ area ratios for planar models calcined at 200, 350, and 500°C: (a) one unit added nickel and (b) four units added nickel.

of the promoted planar models. The relatively constant Ni/Al ratio seen for the 200°C profile indicates that the small amount of Ni exists as clusters. As the calcination temperature is increased to 350°C, a well-dispersed Ni species, redistributed and associated with the W, is observed at the surface (10° angle). The decrease in the ratio is expected as the angle is increased from 10 to 40 to 65°, but in going from 65 to 90°, a significant increase is seen. This can perhaps be credited to an accumulation of Ni at the support interface or to a redistribution and movement of Ni near 350°C, because at 500°C, very little of the Ni is viewed. There is a small amount of Ni near the surface, which is more than likely still associated with the W, but the low ratios at 40, 65, and 90° indicate a large depletion of Ni. This may be due to the movement of the Ni which is associated with the support deeper into the support to a level that is out of the analyzing depth of XPS.

The Ni/W ratios are shown for 1 and 4 units of added promoter in Fig. 7. The fairly constant 200°C profile for 1 added Ni unit (Fig. 7a) reiterates the point that Ni and W both may exist in clusters. The gradual increase in the ratios in going from 10 to 90° take-off angles at both 350 and 500°C in Fig. 7a is explained by the migration of Ni into the support and the small amount of W deeper in the support. The lower ratios at 500°C again imply the migration of Ni through the analysis zone. The same trends are seen in Fig. 7b for the 350 and 500°C profiles. At 200°C, however, the effect of the excess Ni on the surface is again manifested at the 10° take-off angle.

The W/O ratio as a function of temperature and take-off angle shows little difference in any of the profiles, which indicates that oxygen exists in vast quantities on the surface. This piling up of oxygen prohibits gaining much useful information from metal/oxygen ratios. Using metal/support metal ratios give a better indication of surface compositions and dispersion.

CONCLUSIONS

It is apparent from this study that planar model catalysts do mimic the characteristics of real and powdered catalysts. The trends seen for the planar models are quite similar to those seen on the powder models, and both are consistent with the commercial powder. This study also shows the advantage of the planar models over powders for more sensitive surface information. Other conclusions are:

(i) The W/Al ratio generally increases with increasing calcination temperatures due to a redistribution of the W. This higher dispersed W is probably associated with some of the Ni which does not migrate into the support. Because most of the Ni does move inward at the high calcination temperatures, the Ni/Al ratio decreases with increasing temperature. The competition for sites between Ni and W is manifested by lower W/Al ratios at low calcination temperatures, indicating a preference for the stronger Ni/support interaction and the clustering of W when an excess of Ni is added.

(ii) The information gained from a 10° take-off angle is extremely valuable as a surface analytical tool. Surface sensitivity is greatly enhanced as evidenced by the data from this angle. Correlation with ISS data taken so far is complementary.

(iii) The combined use of planar model catalysts and low take-off angle XPS shows promise as an effective way to "depth profile" a flat or planar sample; the increased surface sensitivity gained by low take-off angles may prove to be a method of understanding chemistry at the surface of these complex promoted/supported systems. Reduction and activity studies are underway on these planar model catalysts to examine the chemistry at the extreme surface and to also correlate the viability of the planar models as working catalysts.

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