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# X-Ray Photoelectron Spectroscopy Study of Supported Tungsten Oxide

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An X-ray photoelectron spectroscopy study of supported tungsten oxide has indicated that calcination of $WO_3/\gamma\text{-}Al_2O_3$ leads to formation of tungstate. Proof has been obtained that $WO_3/\gamma\text{-}Al_2O_3$ cannot be appreciably reduced in hydrogen at 550°C, whereas $WO_3/SiO_2$ is reduced to lower valence states and unsupported $WO_3$ is completely reduced to tungsten metal under these conditions.

## INTRODUCTION

As part of our study of solid-state reactions between transition-metal oxides and high-surface-area catalyst supports we have investigated the $WO_3/\gamma\text{-}Al_2O_3$ and $WO_3/SiO_2$ systems, using X-ray photoelectron spectroscopy (*1*) (X-PES or ESCA). Earlier work on these systems was done by Sondag *et al.* (*2*). They studied the reduction of pure $WO_3$, $WO_3$ on γ-alumina, $WO_3$ on α-alumina, and $WO_3$ on silica by determining the average tungsten valence by means of a titration technique. The advantage of X-PES over the titration technique used by Sondag *et al.* is that, in principle, it is capable of determining the different tungsten valences separately.

In X-PES the sample is irradiated with (ultrasoft) X-ray photons of a well-defined energy (either 1486.6 or 1253.6 eV), and the photoelectrons ejected from the sample are observed. Part of the photon energy is used for the liberation of the photoelectron from the system, requiring the electron binding energy (BE). The remainder of the photon energy appears as kinetic energy of the ejected photoelectron (energy conservation). The electron spectrometer sorts electrons according to their kinetic energy, and thereby one obtains the quantity of interest, viz. BE. In the present study attention is confined to photoelectrons originally accommodated in the inner shells of the atoms of the sample, i.e., the core electrons. The BE's measured are first of all characteristic of a particular kind of atom. Moreover, when going from an (isolated) atom to an (isolated) positive ion it is found that the BE's of all the core electrons increase, as it requires more energy to remove an electron from a positive center than from a neutral center. This feature, called the chemical shift in BE's, is characteristic also of compounds and is a qualitative measure of the "charge" on a given atom: the BE's measured by X-PES are thus a direct measure of the valence state of the atoms under study (*1*). The potential usefulness of X-PES as an analytical tool in catalysis research has been reviewed by Delgass, Hughes and Fadley (*3*), while recently Miller *et al.* (*4*) have published X-PES evidence for metal–support interaction for the system $MoO_3/Al_2O_3$.

The present study shows the applicability of X-PES as a technique for monitoring valence changes of supported and unsupported tungsten compounds resulting from treatments such as calcination and reduction. Specially, changes in reactivity due to metal–support interaction show up clearly in the spectra.

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## EXPERIMENTAL

### A. *Materials*

A 13 wt% tungsten oxide on γ-alumina (surface area 200 $m^2/g$) catalyst was made by a conventional impregnation technique using a solution of ammonium tungstate. After drying at 120°C, samples were calcined at 550°C in air. Tungsten oxide on silica (Mallinckrodt silica, surface area 600 $m^2/g$) was made in the same way. The $WO_3$-on-$\gamma$-$Al_2O_3$ sample was amorphous according to X-ray diffraction, whereas in the calcined $WO_3$-on-silica sample X-ray powder diffraction lines of $WO_3$ were observed.

### B. *Techniques*

Spectra were measured on a Varian IEE-15 X-ray photoelectron spectrometer. Powdered samples were mounted: (a) on adhesive tape (when no sample treatment was required) or (b) by pressing them into the grooves of a stainless steel cylinder, permitting sample treatment. Hydrogen and nitrogen treatment of the samples was performed in a specially designed flow cell at a controlled temperature and gas flow rate (30 liter/hr). Both nitrogen and hydrogen were dried before use. A specially designed sample holder allowed us to transfer the sample from the flow cell to the spectrometer without exposing it to the atmosphere. Corrections for static charging were made by shifting the spectrum on the BE-axis until the BE for carbon 1*s*-electrons, measured for each sample separately, corresponded to 285.0 eV. This procedure requires electrochemical equilibrium between the sample and the hydrocarbon overlayer. Its widespread use is justified merely by the internal consistency of the data.

## RESULTS AND DISCUSSION

### A. *X-PES of Tungsten and Tungsten Oxide*

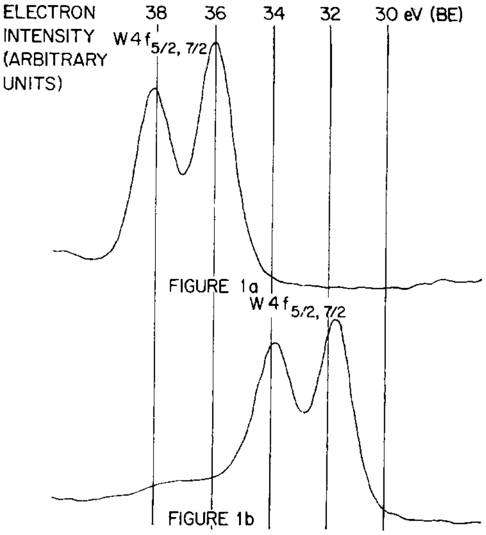

FIG. 1. (a) $WO_3$; (b) W-metal.

The spectrum of tungsten 4*f*-electrons in $WO_3$ is shown in Fig. 1a. For a single type of tungsten atoms or ions we observe a split line (doublet): the full width of the individual lines at half height (fwhm) is approximately 1.1 eV, the double splitting being 2.1 eV. The line splitting is due to spin-orbit coupling (1). The magnitude of the splitting and the relative line intensity are the same for different tungsten compounds. In the following we will, therefore, refer only to the position of one of the two lines. We have chosen the one at lower BE, the tungsten $4f_{7/2}$ line. In Fig. 1a, we observe for $WO_3$ a binding energy BE $(4f_{7/2}) = 36.0$ eV. In the spectrum of tungsten metal shown in Fig. 1b we find BE $(4f_{7/2}) = 31.8$ eV. The chemical shift between $WO_3$ and W-metal is thus 4.2 eV.

### B. *X-PES of Calcined Supported Tungsten*

**$WO_3/\gamma$-$Al_2O_3$.** The spectrum of the calcined $WO_3/\gamma$-$Al_2O_3$ catalyst (cf. Sect. II.A) is shown in Fig. 2a. For comparison we brushed a small amount of $WO_3$ onto a sample of pure $\gamma$-$Al_2O_3$; the spectrum obtained is shown in Fig. 2b.

The spectrum of the calcined product is broader than that of $WO_3$. The tungsten ions are obviously distributed over many nonequivalent sites, pointing to an ill-defined, i.e., defective, structure around the individual tungsten ions. The BE in the calcined product is somewhat larger than that of unsupported $WO_3$: 0.5 eV ± 0.2 eV.

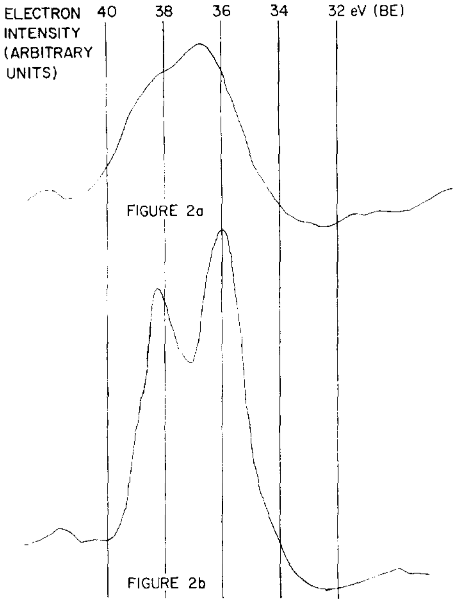

FIG. 2. (a) $W/\gamma\text{-}Al_2O_3$; 2 hr/air/550°C; (b) $WO_3$ as a thin film brushed onto $\gamma\text{-}Al_2O_3$.

TABLE 1

TUNGSTEN $4f_{7/2}$ BINDING ENERGIES FOR SOME SELECTED TUNGSTEN COMPOUNDS

| Compound | Binding energy,[a] eV | Remarks |
|---|---|---|
| $\gamma\text{-}Al_2O_3/WO_3$ calcined | 36.5 | broadened |
| $SiO_2/WO_3$ calcined | 36.0 | broadened; tail to lower BE |
| $H_2WO_4$ | 36.4 | |
| $(NH_4)_6W_7O_{24}\cdot 4H_2O$ | 36.5 | para-ammonium wolframate |
| $Al_2(WO_4)_3$ | 36.5 | 500°C sample; broadened |
| $Al_2(WO_4)_3$ | 36.2 | 900°C sample |
| $Na_{0.1}WO_3$ | 35.8 | semiconducting sodium-tungsten bronze |
| $Na_{0.6}WO_3$ | 36.0 | metallic conducting sodium-tungsten bronze |
| $WO_3$ | 36.0 | |
| $W_{18}O_{49}$ | 34.5 | shoulder on side of 36.0 signal |
| $WO_2$ | 34.4 | shoulder on side of 36.0 signal |
| W-metal | 31.8 | |

[a] Tungsten $4f_{7/2}$; C $1s \equiv 285.0$ eV.

This suggests an interaction between the $WO_3$ and the alumina support.

Miller *et al.* (*4*) observe a similar broadening and shift in BE for the $MoO_3/Al_2O_3$ system. They propose an explanation based upon electron transfer from the molybdenum to the alumina. However, it may also be possible that the shift in BE for both $WO_3/\gamma\text{-}Al_2O_3$ and $MoO_3/Al_2O_3$ is an artifact, brought about by line broadening.

An interaction between $WO_3$ and the alumina support shows up clearly in the difference in chemical behavior between bulk $WO_3$ and the calcined product (cf. Section D).

Hoping to learn more about the nature of the tungsten compound(s) formed during calcination, we measured the X-PES spectra of a number of different tungsten compounds; the BE's found are given in Table 1. All but the tungstates, $H_2WO_4$, $(NH_4)_2WO_4$, and $Al_2(WO_4)_3$, have a BE equal to or lower than that of $WO_3$. Comparison of spectra of the sample before and after calcination shows that at least 90% of the nitrogen escapes during calcination. Therefore, our results point to $Al_2(WO_4)_3$ formation during calcination. It should be mentioned that this conclusion relies entirely on the validity of the static charging correction.

To check this conclusion further we measured the X-PES spectra of the two different $Al_2(WO_4)_3$ samples: Fig. 3a, b. Going from the 500°C to the 900°C sample the spectrum sharpens. The spectrum of the catalyst sample calcined at 550°C is closer to that of the $Al_2(WO_4)_3$ sample obtained by heating the $Al(NO_3)_3/(NH_4)_2WO_4$ mixture at 500°C.

We also tried to establish whether, during calcination, the tungsten diffuses into the support. To this end we very carefully measured the tungsten-to-aluminium line intensity ratio $Q$ (W/Al), because diffusion of tungsten into the support was expected to result in a decrease in $Q$ (*5*). From the experimental finding that

$$Q^{\text{before}}_{\text{calcination}} = (1.00 \pm 0.01) \times Q^{\text{after}}_{\text{calcination}},$$

we conclude that diffusion of tungsten into

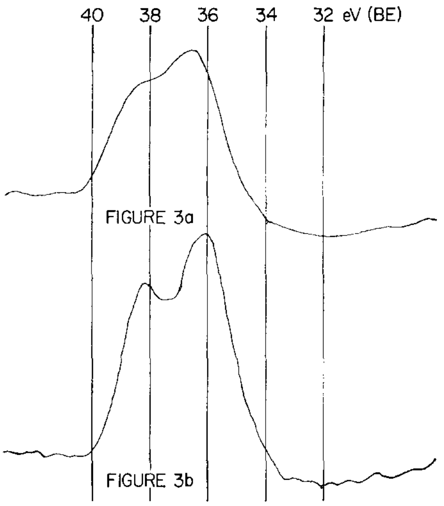

FIG. 3. (a) $Al_2(WO_4)_3$ heated at 500°C (yellow); (b) $Al_2(WO_4)_3$ heated at 900°C (white).

the $\gamma$-$Al_2O_3$ support over distances larger than a few Ångstroms is highly improbable and that all the effects reported here are surface effects.

**$WO_3$–$SiO_2$.** The spectrum of calcined $WO_3$–$SiO_2$ (cf. Sect. II.A) is shown in Fig. 5a. Approximately 70% of the intensity is located at the position of $WO_3$. As in the $WO_3/\gamma$-$Al_2O_3$ system, the spectrum is broader, indicating an ill-defined structure around the tungsten ions. From Guinier X-ray photographs we have positive indication that during calcination $WO_3$ is formed on the silica surface.

Unexpectedly, but clearly observable (Fig. 5a), approx. 30% og the tungsten $4f$-intensity shows up at low BE, approx. 2 eV below the main line. We, therefore, concluded that, despite the oxidizing conditions during calcination, part of the tungsten goes to a lower valence state, which is possibly formed at the boundary layer between the silica support and the $WO_3$ particles.

### *C. Reduction of Unsupported α-Tungsten Oxide*

Pure $WO_3$ was treated for two hours with $H_2$ at 1 bar pressure and different temperatures: 100, 320, 430, and 550°C. X-PES spectra are given in Fig. 4a–e.

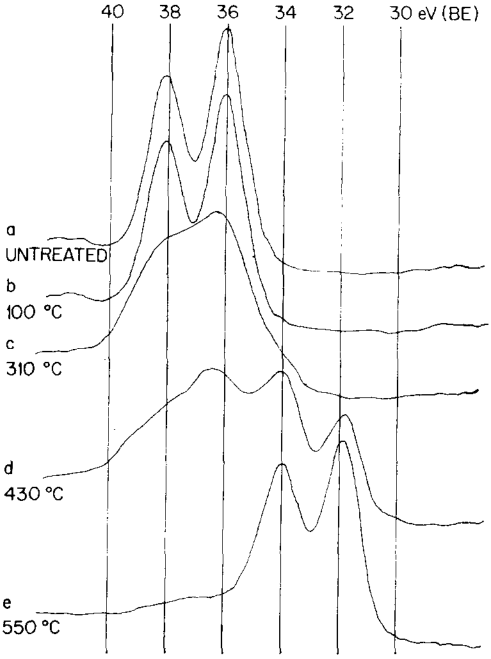

FIG. 4. $WO_3/H_2$; 2 hr/various temperatures.

From the broadening and changes in the X-PES spectra it is evident that the reduction starts at about 310°C. From the oxygen-to-tungsten line intensity ratio we found the oxygen deficiency at 310°C to be low: $x > 2.95$ in the formula $WO_x$ (Fig. 4c). At 430°C tungsten metal is formed, as is evident from the spectrum in Fig. 4d. At the same time a considerable amount of $WO_3$ is still present. Reduction for two hours at 550°C converts $WO_3$ almost completely to tungsten metal (Fig. 4e). Exposure to air for five minutes of the (finely divided) tungsten metal formed upon reduction causes a partial re-oxidation to $WO_3$.

There exist a number of colored tungsten oxides:

$\alpha$-tungsten oxide—$WO_3$ —green-yellow
$\beta$-tungsten oxide—$WO_{2.88}$—blue
$\gamma$-tungsten oxide—$WO_{2.77}$—purple-red
$\delta$-tungsten oxide—$WO_2$ —brown.

We have made the $\gamma$- and $\delta$-tungsten oxides. X-PES spectra of these oxides clearly showed W-valences lower than six: cf. Table 1. From the experiments on unsupported $WO_3$ we conclude that the tendency to form, during the reduction, compounds of valences intermediate between those of $WO_3$ and W-metal is low.

Analogous to the $H_2$ treatments, we performed $N_2$ treatments. $N_2$ treatment of unsupported $WO_3$ up to 550°C led to only small changes in the spectrum; the most significant feature was a slight broadening of the peaks. From the broadened spectra we deduce the creation of ill-defined tungsten sites. This is accompanied by a clearly visible (blue) coloration of the sample. As the β-tungsten oxide $WO_{2.88}$ is known to be blue, this may be the product formed in the surface of the $WO_3$ crystallites during $N_2$-treatment at elevated temperatures.

### *D. Reduction of Supported Tungsten Oxide*

**$WO_3/SiO_2$.** A calcined catalyst was treated with hydrogen: 1 bar $H_2$/2 hr/550°C. The X-PES spectra before and after hydrogen treatment are shown in Fig. 5a,b. According to the spectra, hydrogen treatment causes an intensity redistribution to lower BE in the already broadened W-4*f* lines. Schematically, the observations are: (a) contrary to bulk $WO_3$, no tungsten metal is formed (cf. Fig. 4d, e); (b) some reduction of W(VI) to a valence of approx. III–IV takes place. Smaller amounts of these "lower-than-six" valences were already present after calcination.

**$WO_3/\gamma$-$Al_2O_3$.** The calcined catalyst (2 hr/air/550°C) was treated with hydrogen: 2 hr/1 bar $H_2$/550°C. The X-PES spectra of the sample before and after calcination are shown in Fig. 6a, b. According to these spectra, treatment with hydrogen does not cause any detectable tungsten (VI) reduction. This behavior is in striking contrast with that of bulk $WO_3$ and points to tungstate formation on the surface (cf. Sect. III.B).

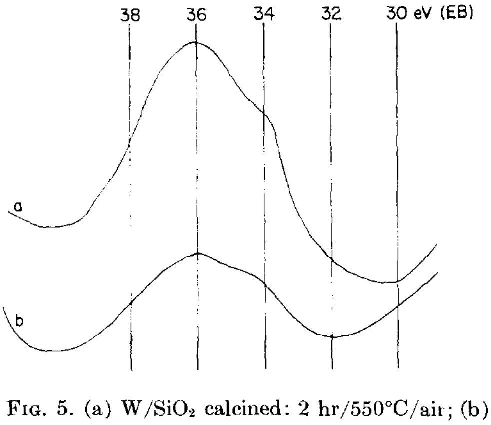

FIG. 5. (a) $W/SiO_2$ calcined: 2 hr/550°C/air; (b) $W/SiO_2$ sample a reduced: 2 hr/550°C/1 bar $H_2$.

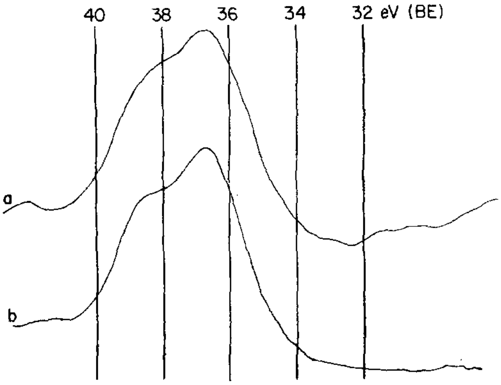

FIG. 6. (a) $W/\gamma$-$Al_2O_3$ calcined: 2 hr/550°C/air; (b) $W/\gamma$-$Al_2O_3$ reduced: 2 hr/550°C/1 bar $H_2$.

### CONCLUSIONS

The X-PES spectra clearly show the different behavior of supported and unsupported $WO_3$. Whereas pure unsupported $WO_3$ is reduced to tungsten metal at temperatures of 430°C and higher, $WO_3$ on $SiO_2$ reduces only to intermediate valences and $WO_3$ on $\gamma$-$Al_2O_3$ does not reduce at all. These results, obtained with X-PES, are in agreement with those on supported $WO_3$ obtained by Sondag *et al.* (1) and on unsupported $WO_3$ by other workers using various techniques. From our results we have evidence of a solid-state reaction between $WO_3$ and the support to form a kind of poorly crystallized and defective structure, $Al_2(WO_4)_3$. The $WO_4^{2-}$ ion is very stable and difficult to reduce, supporting the idea of tungstate formation.

### ACKNOWLEDGMENTS

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