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COMPARISON OF BULK AND SUPPORTED TUNGSTEN OXIDE

By

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INTRODUCTION

Interactions with a support can dramatically change the properties of metals or metal oxides. The strong metal support interaction (SMSI) between Group VIII noble metals and certain transition metal supports decreases the H_2 and CO chemisorption abilities of the metals (1). Chromium (VI) oxide supported on silica is stable at temperatures at which bulk chromic anhydride (CrO_3) decomposes (2). Iron oxide on silica does not completely reduce under conditions at which bulk Fe_2O_3 rapidly converts to metallic iron (3). Recent evidence points to a strong surface complex between WO_3 and γ-Al_2O_3 which influences the chemical and physical properties of both WO_3 and γ-Al_2O_3 (4, 5). The interaction inhibits both the conversion of γ-Al_2O_3 to α-Al_2O_3 (5) and the reduction of tungsten oxide to tungsten metal (6). In the current study, thermal gravimetry (TG) provides a quantitative determination of the reduction resistance of WO_3/γ-Al_2O_3. In-situ X-ray photoelectron spectroscopy (ESCA) suggests differences in the reduction mechanism of supported versus bulk WO_3.

EXPERIMENTAL

Samples of nominal 4, 6, 10 and 25 wt % tungsten oxide on γ-Al_2O_3 (Engelhard, Inc., reforming grade, 220 m^2/gm, 325 mesh) were prepared by the incipient wetness impregnation method by adding an aqueous solution of ammonium meta-tungstate to the alumina powder, drying at 393°K and calcining in air at 773°K for 16 hrs.

TG/DSC measurements were conducted on a Mettler TA-2000C. Powder X-ray diffraction determined phase identity. For the reduction experiments, samples of WO_3/γ-Al_2O_3 were heated to 1243°K (at 10°/min) in He and then held isothermally until constant weight was obtained. This precalcination step minimizes overlapping reduction and dehydroxylation weight losses. After cooling to room temperature, H_2 was introduced, and the samples were reheated to a temperature between 873 and 1173°K (at 10°/min) and held isothermally for two hours. The sensitivity and stability of the thermobalance (0.05 mg) establishes a detection limit of between 1 to 2% on the degree of WO_3 reduction to W, or alternatively, around 10% on the amount of detectable W^{+5}. Visual observation of slight gray discolorations indicate trace levels of reduction.

In-situ X-ray photoelectron spectra (XPS or ESCA) were collected on a modified Leybold Heraeus LHS-10 electron spectrometer. A moveable stainless steel block allows transfer in vacuum of a sample from a reactor chamber to the ESCA chamber. The intensities and binding energies of the tungsten $4f_{5/2,7/2}$ signals (AlKα radiation) were monitored and referenced to the Al2p peak at 74.5 eV. The 10% WO_3/γ-Al_2O_3 powder sample was calcined in air at 1223°K for 16 hrs and then pressed (at 30Mpa) onto a gold screen, which in turn was mounted on a moveable stainless steel block. The WO_3/Al_2O_3 was briefly calcined in-situ at 773°K to clean the surface prior to analysis.

For the reduction experiments, the samples were heated for five minutes at the desired temperature in flowing H_2 (25 cc/min), cooled to 523°K in H_2, evacuated and then transferred into the ESCA chamber. Note that the 1173°K sample (f in Figure 1) was reduced for 2 hours.

We also examined by ESCA the 10% WO_3/Al_2O_3 samples that were previously reduced in the TG experiments (at 1073, 1123 and 1173°K in Table I) to determine the extent of surface reduction. Heating these samples briefly to 873°K in flowing H_2 removes the oxygen that is adsorbed on the tungsten surfaces in transporting the samples from the TG apparatus to the ESCA system.

RESULTS

γ-Al_2O_3, on programmed heating (10°/min) to 1373°K in the presence of oxygen, continuously lost weight as a result of dehydroxylation: the percent weight loss between 473 and 1373°C equaled about 3.5%. In addition, a weak exotherm with an onset near 1323°K occurred during the transition to α-Al_2O_3. A 10% WO_3 on γ-Al_2O_3 sample showed very different behavior. When this sample was heated in an oxygen atmosphere, a larger exotherm occurred at 1323°K as some of the Al_2O_3 and WO_3 reacted to form $Al_2(WO_4)_3$. X-Ray diffraction confirmed the phase identification. The remaining WO_3/γ-Al_2O_3 transforms to WO_3/θ-Al_2O_3: only a trace of α-Al_2O_3 appeared. Thus, the surface WO_3 on Al_2O_3 complex inhibited the transition to α-Al_2O_3.

TABLE I

REDUCTION BEHAVIOR OF TUNGSTEN OXIDE ON ALUMINA

After 1173°K H_2 Treatment (2 hr)

% WO_3	4	6	10	25	100
% Reduction of $WO_3 \rightarrow W$	-0-	2.5%	49%[a]	85%[b]	black
Color after treatment	white	lt. gray	black	black	black

After 873°K H_2 Treatment (2 hr)

% WO_3	4	6	10	25	100
% Reduction of $WO_3 \rightarrow W$	-0-	-0-	-0-	~22%[a]	-100-
Color after treatment	white	white	white	black	black

10% WO_3/γ-Al_2O_3 (2 hr at reduction temperature)

Temperature (°K)	% Reduction $WO_3 \rightarrow W$	Color
873	-0-	white
973	-0-	white
1073	-0-[c]	tint of gray-slight discoloration
1123	17%[a]	gray
1173	49%[a]	black

a. Reduction still continuing after 2 hr.
b. Some α-Al_2O_3 present.
c. Detection limit of 1 to 2 %.

TG and ESCA experiments indicated the resistance of WO_3/γ-Al_2O_3 to reduction. Table I shows the degree of reduction (expressed as percent WO_3 reduced to W°) of the different loaded samples after two hour treatments at 873° or 1173°K. The 10% sample was tested at several intermediate temperatures as well. The retardation of WO_3 reduction depends on loading levels. With low loading levels, little or no reduction occurs. The 10% WO_3/Al_2O_3 showed the first trace of reduction at 1073°K. Even though no weight loss could be detected by TG, the slight greyish discoloration after the heat treatment indicated some reduction had occurred. In contrast, bulk WO_3 completely reduced in these experiments at 873°K after 2 hours. For the 1123°K and 1173°K reductions of 10% WO_3/Al_2O_3, X-ray diffraction indicated that the reduced tungsten sintered.

Figure 1 shows the ESCA W 4f signal for the 10% WO_3/γ-Al_2O_3 sample calcined in-situ in oxygen at 773°K. The binding energy of the W $4f_{7/2}$ peak measures 36.0 eV, indicative of W^{+6} and identical to the value recently reported by Salvati et al. (7). For the samples partially reduced in-situ (Figure 1b-1e), a new tungsten peak at a binding energy of 31.0 eV appeared: indicative of metallic tungsten (W°) (8). Increasing the extent of reduction increased the intensity of the ESCA tungsten peak at 31.0 eV (W^{+6}). After two hours at 1173°K (Figure 1f), the ESCA tungsten peak at 36.0 eV (W^{+6}) disappeared. The total intensity of the ESCA 4f signal also decreased about 70%. Independent X-ray diffraction examinations showed the presence of large particles of tungsten metal.

Deconvolution of the

$W_{4f_{5/2,7/2}}$

ESCA spectra in Figure 1 shows the presence of only W^{+6} and W°: intermediate tungsten oxidation states are not detected on the partially reduced samples (9). This behavior sharply contrasts with that of bulk WO_3, which passes through ESCA-observable intermediate oxidation states of +5, +4 and +2 (10, 11, 12).

The 10% WO_3/Al_2O_3 TG sample previously reduced at 1073°K did not contain a measurable amount of surface W° (<5%), whereas the TG samples reduced at 1123 and 1173°K did contain significant amounts of surface W°. These observations agree with the TG results. A small but measureable amount of W°, however, formed during the in-situ ESCA reduction study at 1073°K (Figure 1b). The slightly faster rate of reduction observed in the in-situ ESCA studies probably results from the higher hydrogen pressure used in the ESCA experiments (3 atmospheres) than in the TG experiments (1 atmosphere).

DISCUSSION

The strong interaction of WO_3 on a γ-Al_2O_3 surface modifies the behavior of both the tungsten oxide and the alumina. γ-Al_2O_3 itself will transform from a series of closely related transitional alumina phases with a defect spinel structure, containing both tetrahedral and octahedral aluminum ions, to α-Al_2O_3, a corundum structure containing only octahedral aluminum ions (19). The γ to α-Al_2O_3 transformation occurs following the condensation of all the surface hydroxyl groups to form H_2O. Our TG and X-ray studies indicate an inhibiting of the γ to α-Al_2O_3 phase transformation in WO_3/γ-Al_2O_3 samples. The presumed bonding of WO_3 with the hydroxyl surface of γ-Al_2O_3 blocks the transformation to α-Al_2O_3. At sufficiently high temperatures and WO_3 concentrations (~1323°, 10% WO_3), some of the surface tungsten oxide reacts with alumina forming $Al_2(WO_4)_3$.

The reduction behavior of tungsten oxide supported on γ-Al_2O_3 also differs from that of bulk WO_3. Bulk WO_3 crystallizes in a distorted ReO_3-type structure, consisting of a three-dimensional corner shared array of linked octahedra (13). The reduction of bulk WO_3 proceeds through the formation of shear phases WO_{3-x} in which octahedra along certain planes cooperatively displace to share edges while maintaining the tungsten, in an octahedral coordination. On further reduction, a discrete WO_2 (distorted rutile) phase, also containing octahedral tungsten exists and can form its family of shear structures on reduction. Further reduction proceeds through WO_3 to tungsten metal. During the reduction of WO_3, ESCA observes several intermediate oxidation states (+5, +4 and +2).

The reduction of $WO_3/\gamma Al_2O_3$ depends strongly on tungsten oxide loading level. Low concentrations (4 or 6 wt %) of WO_3 do not significantly reduce at temperatures hundreds of degrees above those at which bulk WO_3 completely reduces. At intermediate concentrations (10 wt %), WO_3 reduces slowly and partially. At high concentrations (25 wt %) some of the supported WO_3 behaves like bulk WO_3. The isolated tetrahedral tungstate groups (7, 13) on the low loaded samples do not reduce through intermediate structures but, as our ESCA results indicate, the reduction proceeds directly to W°. This reduction occurs only at very high temperature. Once formed, the W° rapidly sinters. Similarly, a 10% WO_3/γ-Al_2O_3 sample partially reduced at 1173°K contains only W^{+6} and W°.

Our high temperature ESCA reduction experiments agree with the recent low temperature reduction experiments by Salvati, et al. (15), who also found a loading level dependence on reduction and the presence of bulk like WO_3 species above a critical coverage. Our study indicates that at the temperature necessary to reduce the surface tungsten oxide, the reduced tungsten rapidly sinters.

The critical coverage for non-reducibility of WO_3 on an alumina surface corresponds to approximately one WO_3 group per seven surface anion sites. Titarelli et al. report a similar WO_3 loading as the optimum concentration to suppress transformation of transitional aluminas (5). Apparently, this close-packed arrangement of isolated tetrahedral tungstate groups possesses a remarkable stability. Further, significant additions of WO_3 will result in formation of a bulk-like WO_3 species.

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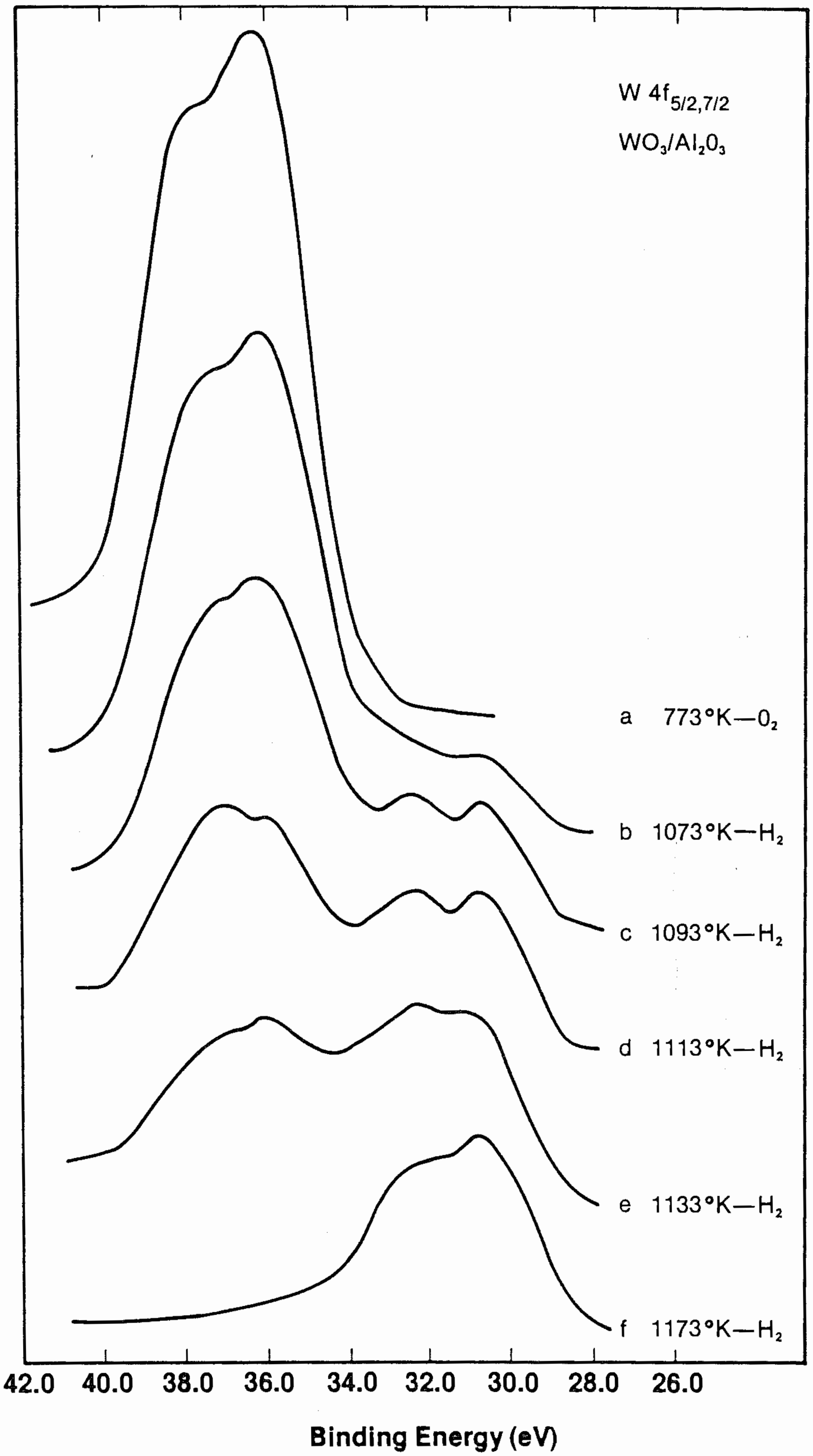

Figure 1. Influence of reduction temperature on W_{4f} ESCA spectra of 10% WO_3/Al_2O_3 precalcined at 1223°K, 16 hour in air. Sample (a) was calcined in-situ in oxygen at 773°K. Samples (b–e) were reduced 5 min, sample f, for 2 hours.

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