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REDUCTION OF WO_3/AL_2O_3 AND UNSUPPORTED WO_3: A COMPARATIVE ESCA STUDY

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ABSTRACT

The interaction between tungsten oxide and alumina has a pronounced effect on the properties of the supported tungsten oxide monolayer. This strong interaction is reflected in the reduction behavior of the tungsten oxide monolayer supported on alumina. The alumina surface stabilizes the tungsten oxide monolayer as W^{+6} and substantially suppresses its reduction. Furthermore, the tungsten oxide monolayer supported on alumina, unlike bulk WO_3, does not exhibit ESCA observable intermediate tungsten oxidation states (W^{+5}, W^{+4}, and W^{+2}) upon reduction. This is thought to be a consequence of the different reduction mechanism of the highly dispersed tungsten oxide monolayer on the alumina surface which precludes the formation of bulk nonstoichiometric tungsten oxide structures present during the reduction of unsupported WO_3. However, tungsten oxide in excess of monolayer coverage on alumina is present as WO_3 crystallites on top of the tungsten oxide monolayer, and exhibits reduction kinetics and mechanism indistinguishable from bulk WO_3.

INTRODUCTION

Interactions with a support can dramatically change the properties of metals or metal oxides.[1-3] The strong interaction between WO_3 and Al_2O_3 has a pronounced effect on the properties of tungsten oxide.[4-7] The reduction of bulk WO_3 proceeds at relatively mild temperatures (300-600°) and results in the formation of a series of nonstoichiometric tungsten oxides as the lattice oxygen is depleted.[8] Electron spectroscopy analysis (ESCA) of partially reduced tungsten oxide samples reveals that the reduction of bulk WO_3 (W^{+6}) to metallic tungsten (W^0) proceeds through intermediate tungsten oxidation states of +5, +4, and +2.[9-11] In contrast, tungsten oxide supported on alumina is highly resistant to reduction and temperatures in excess of 800°C are required to initiate reduction.[4-6] Recent low temperature (550°C) ESCA reduction experiments of WO_3/Al_2O_3 demonstrated that only the tungsten oxide in excess of monolayer coverage is reducible at 550°C.[12] The present high temperature (800-900°C) ESCA experiments were undertaken to study the reduction behavior of the tungsten oxide monolayer on the alumina support. For comparative purposes, the reduction of bulk WO_3 and WO_3/Al_2O_3 containing more than a monolayer of tungsten oxide were also examined with ESCA.

EXPERIMENTAL

A 10% tungsten oxide on γ-Al_2O_3 (Engelhard, Inc., reforming grade, 220 m^2/gm, 325 mesh) catalyst was prepared by the incipient wetness impregnation method by adding an aqueous solution of ammonium metatungstate to the alumina powder. The catalyst was subsequently dried at 110°C and calcined in air at 500°C for 16 hrs. The 10% WO_3/Al_2O_3 catalyst was further calcined at 950°C for 16 hrs. prior to the reduction experiments to assure that only changes due to reduction will be monitored at the high temperatures required for reduction of the tungsten oxide monolayer. Laser Raman spectroscopy confirmed that after the above "conditioning" step only the tungsten oxide monolayer species were present on the alumina support, and that crystallites of WO_3 were absent.[13] The 60% WO_3/Al_2O_3 catalyst was similarly prepared, but was only calcined at 500°C for 16 hrs. because partial reduction of this sample occurs at mild temperatures. The bulk WO_3 sample was prepared by oxidizing a metallic tungsten foil (Goodfellow, 99.999%) at 450°C in flowing O_2 for 30 minutes.

Subsequent catalyst treatments were performed in a reactor furnace directly attached to the ultrahigh vacuum chamber housing the Leybold-Heraeus LHS-10 electron spectrometer. This arrangement allowed the transfer of the catalyst sample from the reactor to the ESCA chamber in UHV. The base pressure of the ESCA chamber was usually in the 10^{-10} Torr range. The x-ray source was obtained from an aluminum anode operated at 12 kV and 25 mA, and the intensities and binding energies of the tungsten $4f_{5/2,7/2}$ signals were referenced to the Al 2p peak at 74.5 eV.[14] The WO_3/Al_2O_3 samples were pressed (~5,000) psi) onto gold screens, and the gold screens were mounted on a stainless steel block that was transferable between the reactor and the ESCA chamber. The tungsten foil was mounted directly onto the stainless steel block. The WO_3/Al_2O_3 samples were briefly calcined in-situ at 500°C to clean the catalyst surface prior to the surface analysis.

The reduction of the WO_3/Al_2O_3 samples was performed by heating the sample in flowing H_2 (26 SCCM) in the reactor section, maintaining the catalyst at the desired temperature, cooling the sample to ~250°C, and transferring the catalyst in vacuum to the ESCA chamber. The reduction of the oxidized metallic tungsten foil was performed by heating the sample in vacuum to 800°C and introducing flowing H_2 for very short periods of time. This experimental procedure was chosen because of the facile reduction of bulk WO_3.

RESULTS

The reduction of the bulk WO_3 sample was examined as a function of reduction time at 800°C, and the ESCA W $4f_{5/2,7/2}$ spectra are presented in Figure 1. The ESCA W $4f_{7/2}$ binding energy measured for the unreduced foil occurred at ~36 eV and corresponds to tungsten in the +6 oxidation state (WO_3).[9-12,14] Reduction of the bulk WO_3 sample produced very marked changes in the W 4f ESCA spectra. The resolution of the W $4f_{5/2,7/2}$ doublet decreased and the peaks became progressively broader. The partially reduced tungsten oxide samples exhibited a major ESCA W

$4f_{7/2}$ peak at a binding energy of ~33 eV. The completely reduced sample possessed two major ESCA W 4f peaks at ~32 and ~34 eV which correspond to metallic tungsten.[12,14] Essentially the same series of ESCA W $4f_{7/2,5/2}$ spectra were obtained by increasing the reduction time and varying the reduction temperature from 256 to 700°C.

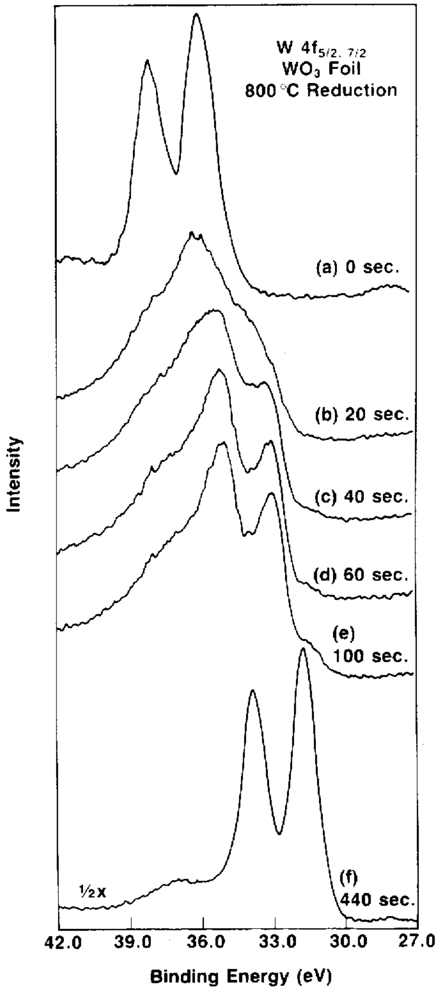

Figure 1 ESCA W $4f_{5/2,7/2}$ spectra for reduction of bulk WO_3.

Deconvolution of the ESCA W 4f signal from the partially reduced tungsten oxide samples revealed that five oxidation states of tungsten exist in these samples. The deconvoluted spectrum for the tungsten oxide sample reduced for 10 seconds at 800°C is shown in Figure 2. The ESCA W $4f_{7/2}$ binding energies for the five tungsten states occur at 36.1, 35.3, 34.5, and 33.2, and 31.8 eV, and are in excellent agreement with that reported by Haber et al.[9] Haber et al. assigned these W $4f_{7/2}$ binding energies to W^{+6}, W^{+5}, W^{+4}, W^{+2}, and W^{0}. Thus, the reduction of bulk WO_3 (W^{+6}) to metallic tungsten (W^{0}) proceeds through ESCA observable intermediate tungsten oxidation states of W^{+5}, W^{+4}, and W^{+2}.

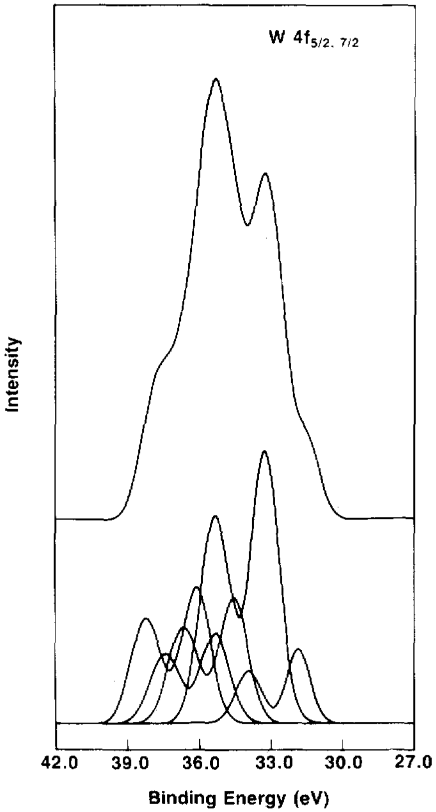

Figure 2 Deconvolution of ESCA W $4f_{5/2,7/2}$ spectrum for partially reduced bulk tungsten oxide (800°C for 100 seconds).

The reduction behavior of the tungsten oxide monolayer on the alumina support was examined as a function of temperature by successively increasing the reduction temperature after each in situ ESCA measurement. The ESCA W 4f spectra for the 10% WO_3/Al_2O_3 sample are presented in Figure 3 as a function of the reduction temperature. Note the much longer reduction times required to initiate reduction for the supported tungsten oxide compared to the bulk WO_3 sample. The ESCA tungsten $4f_{5/2,7/2}$ doublet for the supported tungsten oxide is broader than that for bulk WO_3

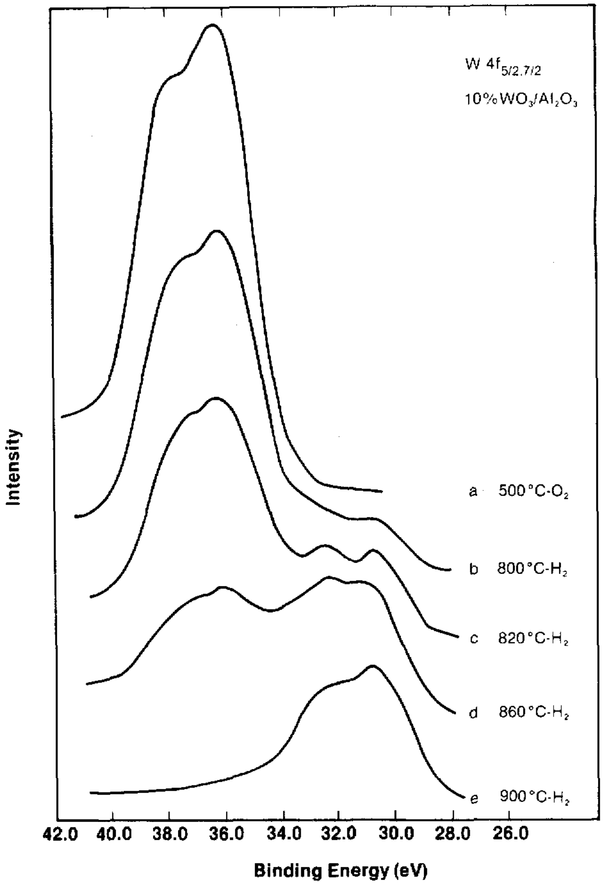

Figure 3 ESCA W $4f_{5/2,7/2}$ spectra for reduction of 10% WO_3/Al_2O_3. Samples b-d were reduced for 5 minutes, and sample e was reduced for 2 hours.

because of the sample charging present for the 10% WO_3/Al_2O_3.[12] The ESCA spectrum of the unreduced 10% WO_3/Al_2O_3 sample, calcined in situ at 500°C, is shown in Figure 3a. The W $4f_{7/2}$ binding energy for the unreduced sample occurs at ~36 eV and reveals that tungsten is present on the alumina support as W^{+6}. Metallic tungsten, binding energy of ~31 eV, is present on the alumina support at reduction temperatures of 800°C and above. As the temperature of reduction is increased the intensity of the W^{+6} peak decreases and the intensity of the W^0 peak increases. After 2 hours of reduction at 900°C - the extended reduction was performed to completely reduce the supported tungsten oxide - the ESCA W^{+6} doublet is completely absent and only the ESCA W^0 doublet is present. The total intensity of the ESCA W 4f signal is ~70% smaller after reduction of the supported tungsten oxide at 900°C. X-ray diffraction analysis of the 900°C reduced sample shows the presence of bulk W^0. Thus, the high temperature reduction of the tungsten oxide monolayer on alumina is accompanied by agglomeration of the reduced tungsten on the alumina support.

Detailed analysis of the 10% WO_3/Al_2O_3 ESCA W $4f_{5/2,7/2}$ spectra in Figure 3 only reveals the presnece of W^{+6} and W^0 on the alumina support after partial reduction. The ESCA W 4f spectra for the unreduced 10% WO_3/Al_2O_3 sample, Figure 3a, and the samples reduced at 800 and 820°C, Figures 3b and c, were normalized with respect to their intensities at 36.0 eV and are compared in Figure 4. Note that no

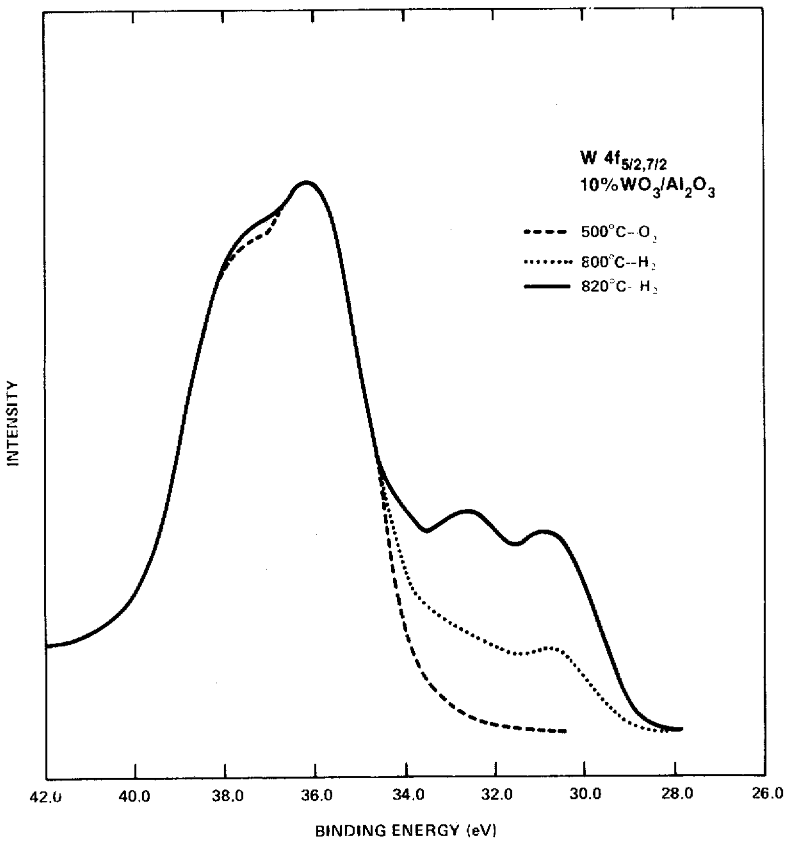

Figure 4 Comparison of ESCA W $4f_{5/2,7/2}$ spectra for oxidized and partially reduced 10% WO_3/Al_2O_3 samples.

broadening of the W^{+6} doublet occurs upon partial reduction of the 10% WO_3/Al_2O_3 sample. This is in contrast to the extensive broadening of the ESCA W 4f spectra during the reduction of bulk WO_3. Furthermore, deconvolution of the ESCA W 4f spectra of the 10% WO_3/Al_2O_3 samples reduced at 800 and 820°C shows only the presence of W^0 and W^{+6}. The deconvolution procedure involved substraction of the W^0/Al_2O_3 signal, Figure 3f (900°C reduction), from the partially reduced 10% WO_3/Al_2O_3 samples. The resultant spectra were then compared to the normalized ESCA spectra of the unreduced 10% WO_3/Al_2O_3 sample, see Figures 5 and 6. The rather good agreement between the deconvoluted signals from the 800 and 820° reduction treatments and the unreduced 10% WO_3/Al_2O_3 suggests that either intermediate oxidation states of tungsten (W^{+5}, W^{+4}, and W^{+2}) are not present in the partially reduced WO_3/Al_2O_3 sample or are present in very small concentrations that cannot be resolved with ESCA. Thus, the high temperature reduction of the tungsten oxide (W^{+6}) monolayer on the alumina support to metallic tungsten (W^0) does not proceed through ESCA observable intermediate tungsten oxidation states of W^{+5}, W^{+4}, and W^{+2}.

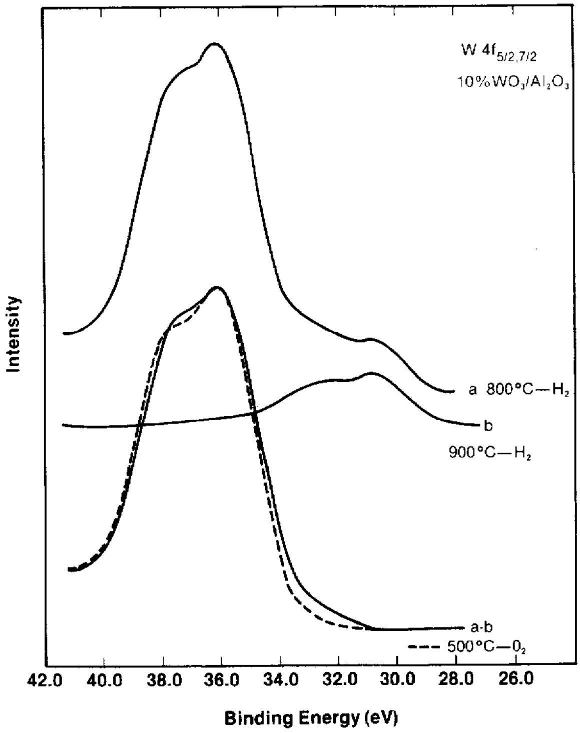

Figure 5 Deconvolution of ESCA W $4f_{5/2,7/2}$ spectrum for 10% WO_3/Al_2O_3 reduced at 800°C for 5 minutes.

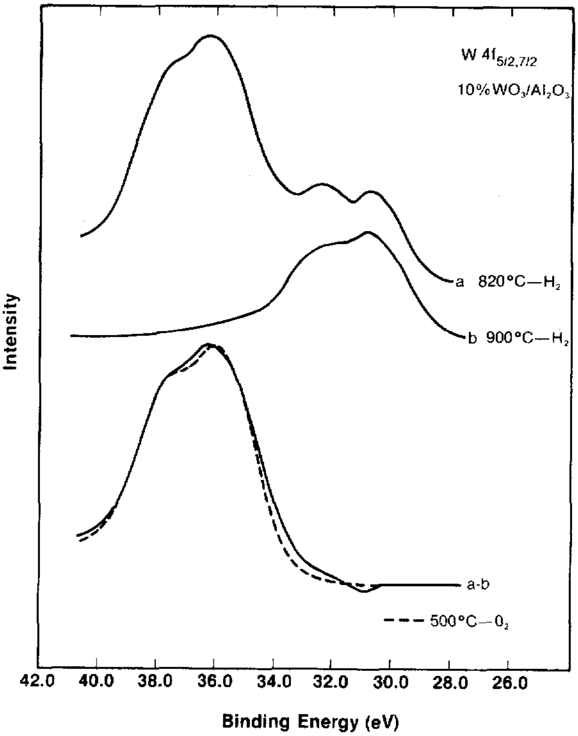

Figure 6 Deconvolution of ESCA W $4f_{5/2,7/2}$ spectrum for 10% WO_3/Al_2O_3 reduced at 820°C for 5 minutes.

The reduction behavior of the 60% WO_3/Al_2O_3 sample was also examined with ESCA to determine the reduction characteristics of WO_3/Al_2O_3 when more than a monolayer of tungsten oxide is present on the alumina support. X-ray diffraction confirmed the presence of crystalline WO_3. The ESCA W 4f spectra for the 60% WO_3/Al_2O_3 sample are presented in Figure 7 as a function of reduction temperature. Note the much lower reduction temperatures required to initiate reduction of 60% WO_3/Al_2O_3 than 10% WO_3/Al_2O_3. The W $4f_{7/2}$ binding energy for the unreduced sample occurs at ~36 eV and reveals that tungsten is present as W^{+6}. Reduction of 60% WO_3/Al_2O_3 between 250 and 480°C markedly changes the appearance of the ESCA W $4f_{5/2,7/2}$ signal. The shape of the ESCA W $4f_{5/2,7/2}$ signal is altered and the signal becomes very broad. This broadening reveals that tungsten oxidation states besides W^{+6} and W^{0} are present on the partially reduced 60% WO_3/Al_2O_3. At a reduction temperature of 580°C the two

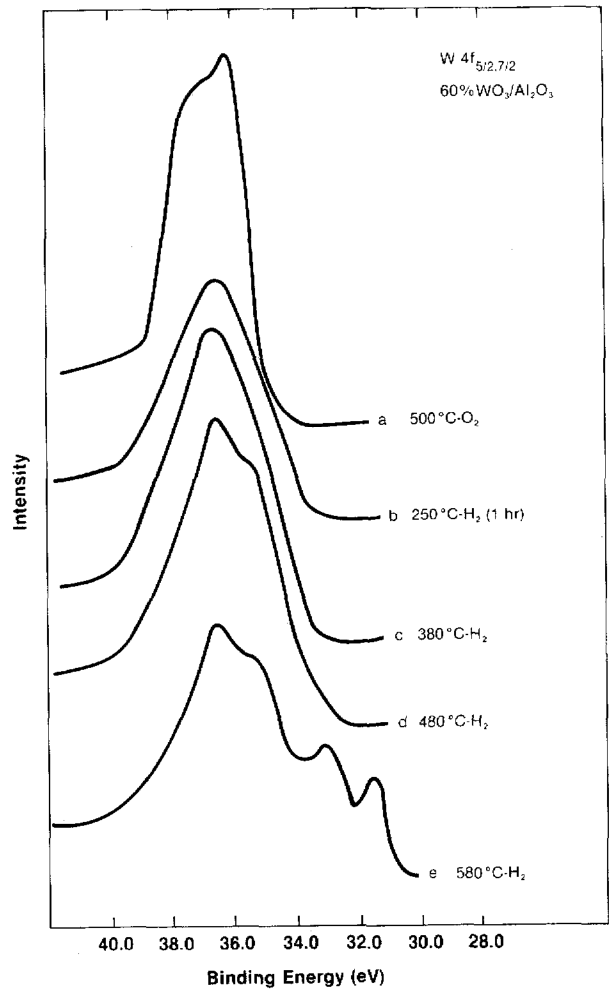

Figure 7 ESCA W $4f_{5/2,7/2}$ spectra for reduction of 60% WO_3/Al_2O_3. Sample b was reduced for 1 hour, and samples d-e were reduced for 5 minutes.

metallic tungsten ESCA peaks appear. Much higher reduction temperatures and reduction times are required to completely reduce the 60% WO_3/Al_2O_3 sample.

DISCUSSION

The present ESCA findings for the in situ reduction of bulk WO_3 are in excellent agreement with previous reports in the literature on this oxide system.[4,9-11] De Angelis et al. examined the surface of several nonstoichiometric tungsten oxides ($WO_{2.96}$, $WO_{2.90}$, $WO_{2.72}$, and WO_2) with ESCA.[10] $WO_{2.96}$ and $WO_{2.90}$

were found to contain W^{+5} in addition to W^{+6} and in fair agreement with that expected from the stoichiometry of these oxides. The crystallographic shear planes were suggested to be the location of the W^{+5} cations. $WO_{2.72}$ showed the presence of W^{+4} and W^{+5} as well as W^{+6}. The surface of the WO_2 sample was extensively oxidized and significant amounts of W^{+6} and W^{+5} were present in addition to the expected W^{+4}. The W^{+4} cations were thought to be related to the shorter W-W distances present in the more reduced oxides. The intermediate tungsten oxidation states were also observed with ESCA by Biloen et al.,[4] Haber et al.[9] and Salje et al.[11] upon partial reduction of bulk WO_3. All of these studies conclusively establish that during the reduction of bulk WO_3 the intermediate tungsten oxidation states of W^{+5}, W^{+4}, and W^{+2} are observable with ESCA.

The interaction between tungsten oxide and alumina has a pronounced effect on the reduction kinetics of the supported tungsten oxide monolayer. The alumina surface stabilizes the tungsten oxide monolayer as W^{+6} and substantially suppresses its reduction. This dramatic suppression of the tungsten oxide monolayer reduction rate relative to the reduction rate of bulk WO_3 reflects the very strong interaction between tungsten oxide and the alumina surface. The high temperatures required to significantly reduce the tungsten oxide monolayer on the alumina support also results in the agglomeration of the metallic tungsten on the alumina support, and suggests that these high temperatures metallic tungsten is mobile on the alumina surface.

The absence of ESCA observable intermediate tungsten oxidation states during the reduction of the tungsten oxide monolayer on alumina suggests that the reduction of the tungsten oxide monolayer may proceed through a different reduction mechanism than bulk WO_3. The reduction of bulk WO_3 is accompanied by bulk structural rearrangements of the oxide which results in nonstoichiometric WO_{3-x} phases. These partially reduced tungsten oxide phases accommodate the oxygen defects and preserve the octahedral coordination of the tungsten cations. ESCA analysis of these nonstoichiometric tungsten oxide surfaces, as was already discussed, reveals the presence of W^{+5}, W^{+4}, and W^{+2} cations. The tungsten oxide monolayer on the alumina support consists of individual surface tungsten oxide species coordinated to the alumina surface.[12,13] The highly dispersed state of the tungsten oxide monolayer on the alumina surface precludes the formation of the bulk nonstoichiometric tungsten oxide structures present during the reduction of unsupported WO_3. Thus, it appears that the strong interaction between tungsten oxide and the alumina surface is also reflected in the tungsten oxide reduction mechanism.

For WO_3/Al_2O_3 samples containing more than a monolayer of tungsten oxide the extra tungsten oxide is present as WO_3 crystallites on top of the tungsten oxide monolayer.[5-7,12] These WO_3 crystallites are not in direct contact with the alumina support and are indistinguishable from bulk WO_3 in their reduction behavior. The WO_3 crystallites reduce at mild temperatures and exhibit ESCA observable intermediate tungsten oxidation states. The different reduction kinetics of the WO_3 crystallites and the tungsten oxide monolayer can be used to distinguish between these two forms of tungsten oxide on alumina. Salvati et al. used this approach to distinguish between the tungsten oxide monolayer and the WO_3 crystallites.[12] Below monolayer coverage of tungsten oxide on alumina no reduction of W^{+6}, 550°C for 12 hours, was observed with ESCA, but above monolayer coverage partial reduction of W^{+6} to W^0 was observed with ESCA. The fraction of the tungsten oxide that was reduced to metallic tungsten was associated with the crystallites of WO_3 on alumina.

CONCLUSIONS

The interaction between tungsten oxide and alumina has a pronounced effect on the properties of the supported tungsten oxide monolayer. This strong interaction is reflected in the reduction behavior of the tungsten oxide monolayer on alumina. The alumina surface stabilizes the tungsten oxide monolayer as W^{+6} and substantially suppresses its reduction. Furthermore, the tungsten oxide monolayer supported on alumina, unlike bulk WO_3, does not exhibit ESCA observable intermediate tungsten oxidation states (W^{+5}, W^{+4}, and W^{+2}) upon reduction. This is thought to be a consequence of the different reduction mechanism of the highly dispersed tungsten oxide monolayer on the alumina surface which precludes the formation of bulk nonstoichiometric tungsten oxide structures present during the reduction of unsupported WO_3. However, tungsten oxide in excess of monolayer coverage on alumina is present as WO_3 crystallites on top of the tungsten oxide monolayer, and exhibits reduction kinetics and mechanism indistinguishable from bulk WO_3.

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