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Electron Spectroscopic Studies of the Reduction of WO_3

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Five different doublets corresponding to W 4*f* electrons were observed in the course of reduction of WO_3. On contact of WO_3 with hydrogen, W^{5+} ions are formed. Reduction results at first in formation of isolated W^{4+} ions. Clusters of edge-sharing octahedra on shear planes are then formed, in which pairing of W^{4+} ions occurs due to metal–metal bonding, corresponding to an apparent 2+ oxidation state.

Introduction

In our recent study (*1*) we showed using X-ray photoelectron spectroscopy that on reduction of MoO_3 formation of isolated Mo^{4+} ions is at first observed, followed by the formation of metal–metal bonds between pairs of two adjacent Mo^{4+} ions, which in photoelectron spectra appear as having an apparent oxidation state of 2+. This phenomenon of pairing was interpreted as being due to the formation of shear planes composed of clusters of edge-linked octahedra with pairs of Mo^{4+} ions forming metal–metal bonds. The W–O system is also known to form shear structures on reduction by transformation of initially corner-linked octahedra into the arrangement of edge-linked octahedra along the shear plane. Thus, it can be expected that this phenomenon will be accompanied by formation of metal–metal bonds, manifested in the X-ray photoelectron spectra.

Experimental

The photoelectron spectra were obtained with an ESCA-3 Vacuum Generator spectrometer, using the $K\alpha$ line of Al as the source of X-ray excitation. The spectra were calibrated using the Au $4f_{7/2}$ line assumed to have a B.E. value of 84.0 eV. The samples were prepared from W-foil and Analar grade WO_3 powder and were outgassed in the spectrometer for 12 hr at 230°C. Test experiments showed that even outgassing WO_3 for 12 hr at 500°C does not provoke any changes in the spectrum of the sample. WO_3 was then reduced *in situ* in the preparation chamber of the spectrometer with the electron gun running in hydrogen at low pressure. Characteristic changes of the spectra of W 4*f* levels appeared to be quite similar to those of Mo 3*d* levels (*1*).

Results

The W 4*f* region of the spectrum at different degrees of reduction is shown in Fig. 1. Spectrum a represents the spectrum of the initial WO_3 sample and shows the B.E. value of W $4f_{7/2}$ level to be 36.1 eV. Spectrum b was obtained after exposing WO_3 to hydrogen for a short time, when only a very small degree of reduction of the sample was attained. Spectrum c was registered after longer exposition to hydrogen, and spectrum d was taken in still later stages of the reduction. Spectrum e represents that of metallic W-foil. Deconvolution of spectrum b showed the presence of two doublets (Fig. 2): that of the initial W^{6+} ions with a B.E. value at the W $4f_{7/2}$ level of 36.0 eV and a second one with a B.E. value of 35.4 eV. Deconvolution of spectrum c revealed that in

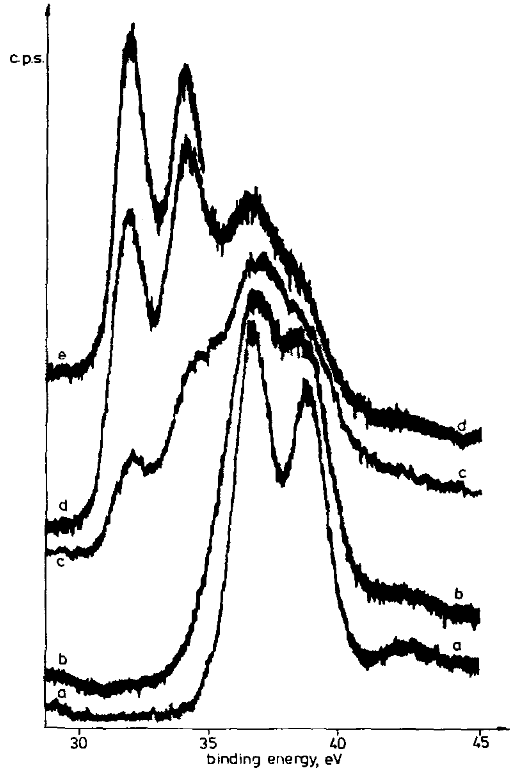

FIG. 1. Changes of XPS spectra of W 4f level in WO_3 in the course of reduction in hydrogen. (a) Fresh sample, outgassed at 270°C for 12 hr; (b) exposed to 5×10^{-5} Torr of hydrogen for 1 min; (c) exposed to 5×10^{-5} Torr of hydrogen for the next 5 min; (d) exposed to 1×10^{-4} Torr of hydrogen for the next 15 min; (e) metallic W-foil. All experiments were carried out with an electron gun running at $J_e \sim 5$ mA.

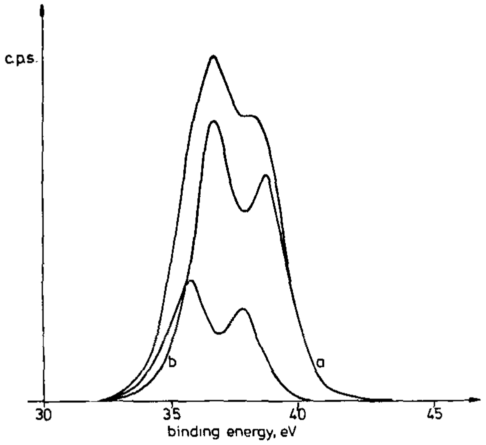

FIG. 2. Deconvolution of spectrum b from Fig. 1.

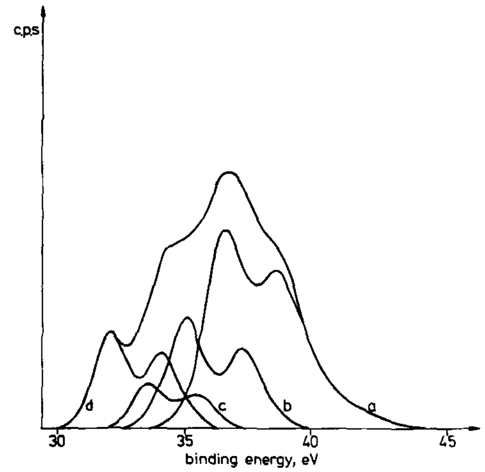

FIG. 3. Deconvolution of spectrum c from Fig. 1.

addition to the doublet of initial W^{6+} ions, the spectrum is composed of three other doublets (Fig. 3) different from that observed in spectrum b after a very short-term reduction; the B.E. values of the W $4f_{7/2}$ levels amounted to 34.6, 33.1, and 31.5 eV, respectively.

Discussion

For a series of simple compounds which consist of similar coordination polyhedra of a given cation and differ only in the valence state of the cation, i.e., in the way in which the coordination polyhedra are linked together, it may be assumed that a linear dependence exists between the B.E. value of core electrons and the valence state. This dependence was thus used for the assignment of the five different W 4f doublets observed in the course of the reduction of WO_3, two points being fixed: the positions of the W^{6+} ions and the position of metallic tungsten. The results shown in Fig. 4 indicate that tungsten ions of apparent oxidation numbers 5+, 4+, and 2+ appear as intermediates.

Detailed studies of the reduction of WO_3 in hydrogen have shown (*2*, *3*) that it reduces through $W_{20}O_{58}$ directly to metallic tungsten, no intermediate oxide formation being ob-

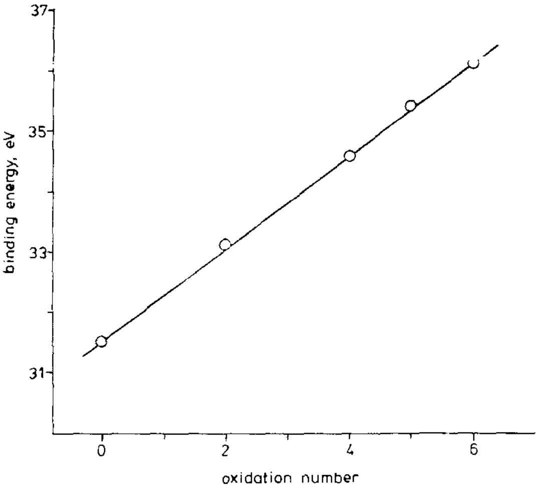

FIG. 4. Binding energy value of W $4f_{7/2}$ level as function of the apparent oxidation number.

served. Thus, in order to explain the appearance of five different tungsten species, similar to those observed by us earlier (*1*) in the case of the reduction of Mo–O system, we may propose the following mechanism of the phenomena taking place on reduction of WO_3. On contact of WO_3 with hydrogen, W^{5+} ions are at first formed at the surface, probably due to chemisorption of hydrogen resulting in the formation of OH groups. In the stronger reduction conditions, isolated oxygen vacancies are generated with the two electrons localized at the adjacent cation appearing as W^{4+}. On further reduction, transformation of the corner-linked WO_6 octahedra takes place along the shear planes into the arrangement of edge-sharing octahedra (*4*). The W–W distance in the shear plane is considerably smaller then in the normal WO_3 matrix (*4*), indicating that a metal–metal bond has been formed between the two paired W^{4+} cations, the four *d* electrons being localized on the molecular orbitals of the two cations, each of them thus showing an apparent oxidation number of 2+.

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