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The multi-structure of oxidized–reduced tungsten carbide surface(s)

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The XPS of bulk tungsten carbide, partially oxidized WC surfaces at 373 and 573 K as well as tungsten trioxide have been reported. Bulk WC has been prepared from WO_3 as a starting material in a mixture of CH_4 (20%) and H_2 (80%) at 1150 K for 4 h, while partially oxidized WC surfaces were prepared by oxygen chemisorption on a clean WC surface at 200 K, then the temperatures were raised to 373 and 573 K respectively. The XPS of a freshly prepared WC reveals the presence of a small amount of WO_3 on the surface and a slightly higher concentration in the bulk. The oxygen-exposed fresh WC surfaces and surfaces treated at temperatures higher than 373 K show the presence of WO_3 in a considerable quantity depending on the length and the treatment temperature. Ar^+ bombardment of this partially oxidized surface reduces WO_3 to WO_2 and W(0), while WC is partially reduced to W(0). Isomerization reactions of alkanes on oxygen-exposed WC surface occurs in reality on a composite surface structure containing WC, WO_3, WO_2 and elemental W(0).

Keywords: tungsten carbide; surface composition; XPS; argon ion bombardment

1. Introduction

Recent interest in some transition metal carbide(s) such as W and Mo as possible substitute of noble metals known for its bifunctional catalytic activity in hydrogenolysis and isomerization reactions of alkanes, has led to several publications [1–7] from different research laboratories. In the case of bulk tungsten carbide(s), it has been observed that alkane hydrogenolysis reactions are predominant where light hydrocarbon species constitute the major reaction products for *n*-hexane at 623 K [5–7]. The presence of a relatively small amount of WO_3 on a freshly prepared tungsten carbide WC has no apparent effect on the catalytic properties and performances of this surface. However, the introduction of oxygen at temperatures higher than 373 K on a freshly prepared WC surface alters significantly these properties where isomerization reactions are observed associated with a net decrease in relative concentrations of hydrogenolysis reaction products [5–7]. The drastic modification of the catalytic properties of this oxygen-exposed WC surface has been attributed mainly to the chemisorbed oxygen species on the surface [6,7] and/or WO [6]. The nature and abundance of the isomerization products were found to depend on the oxygen-exposure time and temperature [5,6]. In order to define the nature of the different species present on the surface of a freshly prepared and oxidized WC, we have used the XPS as a surface technique by considering the W 4f, C 1s, O 1s and the valence band energy regions. Since catalytic reactions occur under reducing conditions due to the use of hydrogen at a relatively high temperature, we have used argon ion bombardment in situ, as reducing agent in a similar way to hydrogen [8] in addition to its sputtering effect. Such Ar^+ bombardment would enable to obtain further information concerning the possible presence of different tungsten oxide(s) and other species on the surface of an active catalyst [9]. For this reason, we have studied in this work the XPS and Ar^+ bombardment of WO_3 as a reference sample.

The XPS and catalytic properties of relatively clean WC and oxygen-exposed WC surfaces at different temperatures using different reactants will be published separately [10].

2. Experimental

Tungsten carbide WC was prepared in the laboratory by subjecting tungsten trioxide to a mixture of CH_4 (20%) and H_2 (80%) at 1150 K for 4 h. Excess deposited carbon has been removed from the surface by H_2 at 1150 K. In order to protect the sample surface from contamination upon its transfer from the reaction preparation chamber to the XPS instrument, we usually passivate the surface by either carbon or chemisorbed oxygen. X-ray diffraction analysis of a freshly prepared sample shows that it is completely composed of WC. On the other hand, elemental analysis of this sample (CNRS Analysis Laboratory Vernaison) does not show any oxygen within an experimental error of 0.2%. The bulk WC surface area was determined at 15 m^2/g.

The oxidation of the two freshly prepared tungsten carbide samples A and B studied in this work was carried out by exposing each to a flux of He gas containing oxygen in increasing quantities from 1 to 10% at 200 K first, then 298 K in order to avoid the oxidation of the bulk WC. This process is followed by increasing the temperature by an increment of 20 K/min up to 373 K for 10 min in the case of sample A and to 573 K for 5 min in the case of sample B.

The XPS spectra were obtained using an ESCA III, VG instrument with Al Kα radiation. All the spectral lines binding energies were reported within an experimental error of ±0.15 eV taking into consideration the differences in the W 4f binding energies of the different tungsten oxides, carbide, and the C 1s as well as O 1s in different states [5,8,11,12]. Argon ion bombardment (3 kV, 30 μA) was employed as a sputtering and reducing agent.

3. Results and discussion

In the following, the XPS and Ar^+ bombardment of four different samples, freshly prepared tungsten carbide WC, tungsten trioxide, oxygen-exposed tungsten carbide at 373 and 573 K will be discussed separately.

3.1. TUNGSTEN CARBIDE WC

The XPS of a freshly prepared tungsten carbide, shows the presence of two well-defined spectral lines at 31.8 and 33.9 eV characteristic of the W 4f spin–orbit components in the WC sample of fig. 1a. Deconvolution of this spectrum reveals

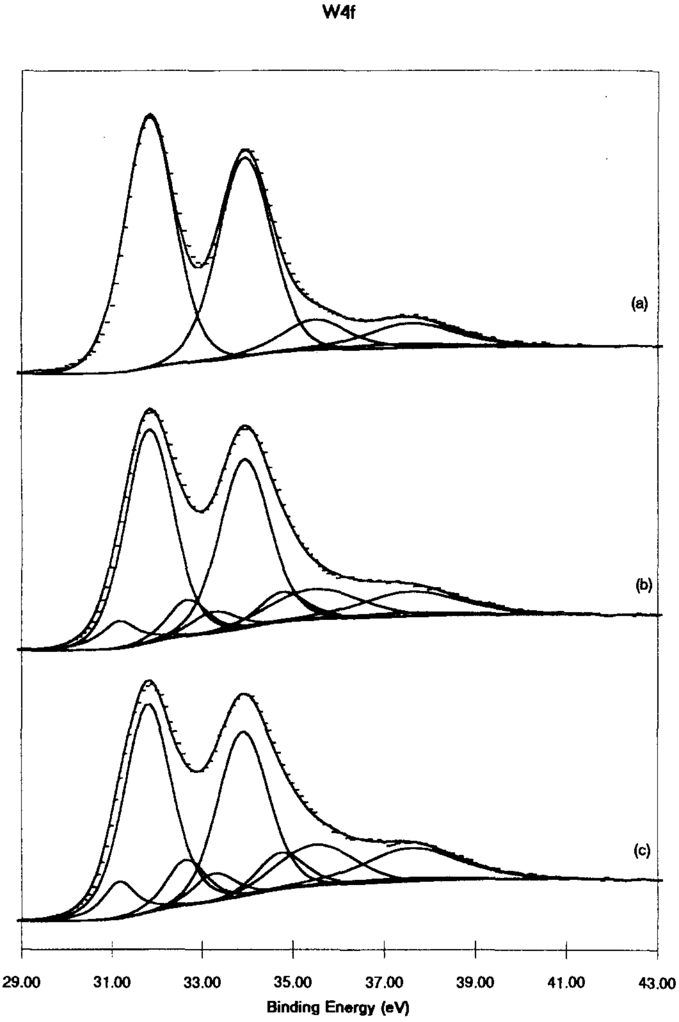

Fig. 1. The XPS of the W 4f energy region of tungsten carbide WC. (a) Fresh sample, (b) after 5 min of Ar^+ bombardment, (c) after 25 min of Ar^+ bombardment.

the presence of a relatively small amount of WO_3 at 35.5 and 37.7 eV. The oxygen 1s energy region shows the presence of the oxide oxygen at 530.5 eV as well as a amount of chemisorbed oxygen at 532 eV (fig. 2a). The carbide carbon can be observed in fig. 2a as a relatively intense line at 282.7 eV as compared to the amorphous deposited carbon on the surface at 284.6 eV. The valence band energy region between E_f and 14 eV consists mainly of: the W 5d derived states between E_f and 3.5 eV, the C 2p and O 2p, if any, between 3.5 to 8 eV and the C 2s band at ~ 12.5 eV (fig. 3a).

Argon ion bombardment of this surface for 5 min results in apparent broadening of the W 4f energy region, where relatively small amounts of WO_2 at 32.7, 34.9 eV and elemental W(0) at 31.2, 33.4 eV could be observed after deconvolution

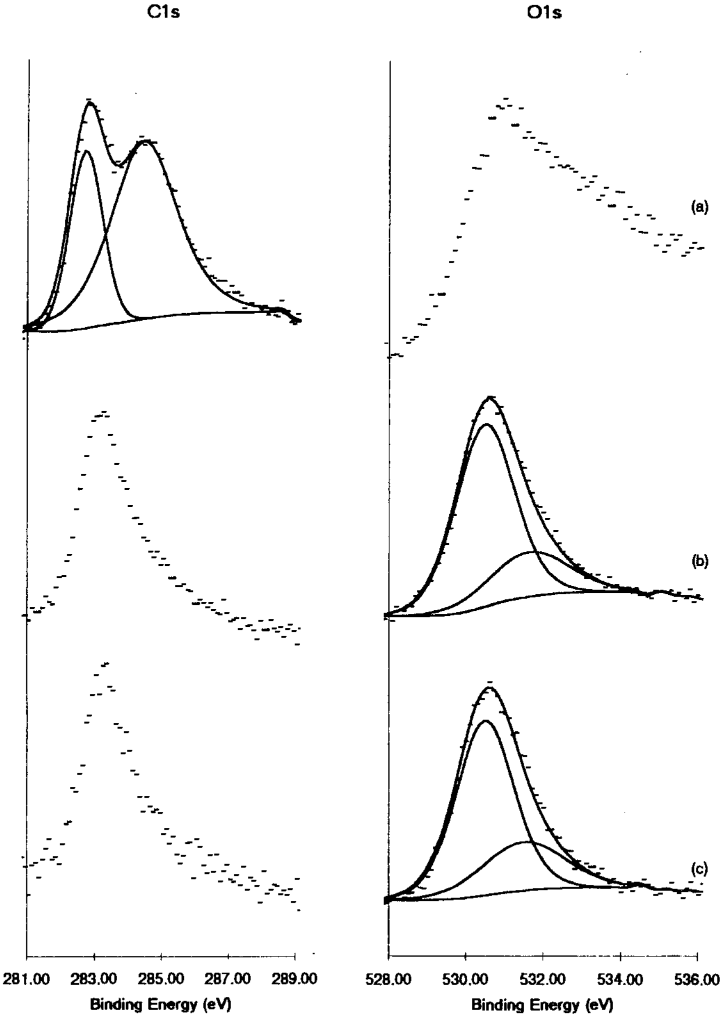

Fig. 2. The XPS of the C 1s and O 1s energy region of WC. (a) Fresh sample, (b) after 5 min of Ar^+ bombardment, (c) after 25 min of Ar^+ bombardment.

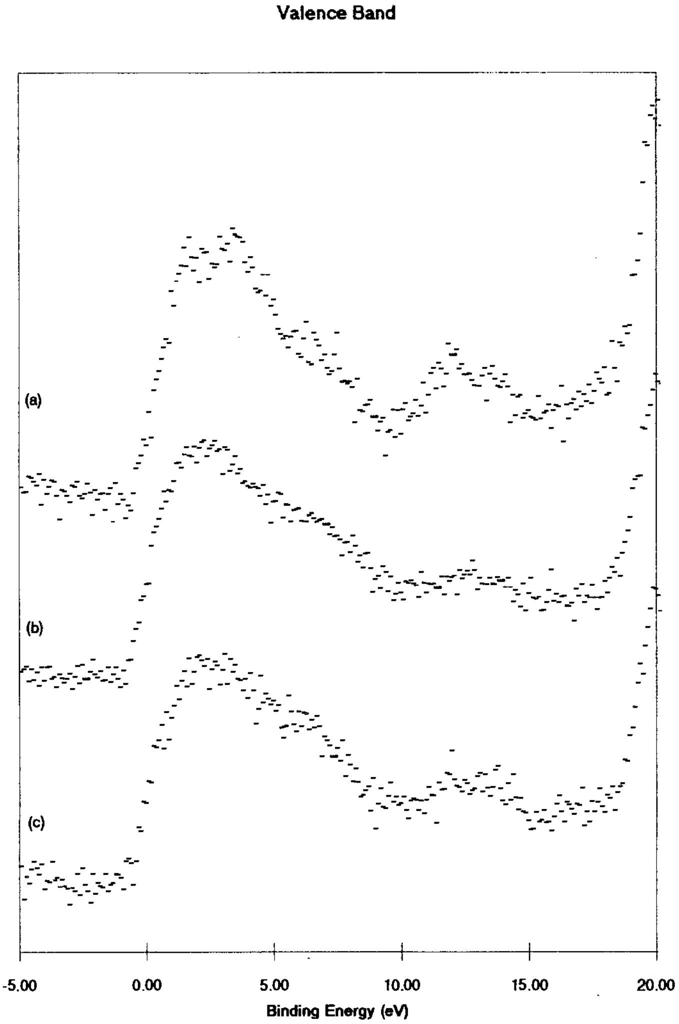

Fig. 3. The XPS of the valence band energy region of WC. (a) Fresh sample, (b) after 5 min of Ar^+ bombardment, (c) after 25 min of Ar^+ bombardment.

of this spectrum (fig. 1b). On the basis of the relative intensities of WO_3 spectral lines before and after Ar^+ bombardment, where no change has been observed, it is apparent that WO_3 is present in higher concentration in the bulk as compared to the surface. Consequently, some of this oxide has been partly reduced to WO_2 and W(0) by Ar^+ bombardment. The possible reduction of some of WC to W(0) by this ion bombardment is not excluded. It is interesting to note that most of the chemisorbed oxygen and deposited amorphous carbon have been removed after the Ar^+ bombardment for 5 min, as can be observed from the symmetrical spectral lines of C 1s and O 1s (fig. 2b). A slight decrease in the relative intensities of the bands at ~ 3.5 eV and ~ 12.5 eV characteristics of the C 2p and 2s, and the appearance of a shoulder at ~ 0.2 eV could be observed in the VB energy region (fig. 3b).

Continuous exposure of this surface to Ar^+ for 25 min results in further increase in the relative concentrations of WO_3, WO_2 and W(0) and a slight decrease of WC as can be observed from the W 4f energy region (fig. 1c), while in the valence band (fig. 3c) we observe a relative decrease in the C 2p (~ 3.5 eV) and C 2s (~ 12.5 eV) and an increase in the 0.2 eV shoulder attributed to the W(0) metal and the O 2p at 6 eV. Further Ar^+ bombardment of this surface for 40 and 55 min did not produce any significant changes, neither in the relative concentrations nor in the structures of the different species present on this surface. It is important to note at this point that different experiments were carried out in order to verify that the relative increase in the WO_3 concentration upon Ar^+ bombardment of the fresh WC surface is not due to the residual oxygen in the vacuum chamber of the XPS instrument or other source(s), but the sample structure itself.

On the basis of the above results, it seems that carburization of WO_3 as a starting material in order to obtain WC is not complete. The relative concentration of WO_3 seems to be higher in the bulk as compared to the surface. Chemisorbed oxygen and deposited amorphous carbon can be easily removed by Ar^+ bombardment.

3.2. TUNGSTEN TRIOXIDE WO_3

The binding energies of the W 4f in WO_3 powder at 35.5 and 37.6 eV (fig. 4a) are similar to those reported in the literature [12]. Deconvolution of this energy region reveals the presence of a relatively small amount of W(V) oxide at 34.3 and 36.4 eV. Argon ion bombardment of the sample for 30 s results in increased reduction of WO_3 to W(V) oxide, fig. 4b, in a similar way to what has been observed by using H_2 as a reducing agent [9]. Further reduction to W(0) and WO_2, where elemental W(0) is relatively high, could be observed after 5 min of Ar^+ bombardment (fig. 4e). A considerable change could also be observed in the appearance of new structure in the valence band due to these oxide species. A stable surface structure composed of WO_3, WO_2 and elemental W(0) with almost equal concentrations has been obtained after long periods (45 min) of Ar^+ bombardment (fig. 4d). These results indicate that bulk WO_3 could be reduced by Ar^+ to elemental W(0) after its initial reduction to W(V) then W(IV) oxides. Such reduction mechanism is completely different from what we observed in the case of $Al_2(WO_4)_3$, where W(VI) oxide is directly reduced in an apparent one single step to W(0) [8]. It is interesting to note the absence of W(II) oxide in the reduction process of WO_3 by Ar^+ bombardment.

3.3. OXIDIZED WC AT 373 K FOR 10 MIN

Deconvolution of the W 4f energy region spectrum of the partially oxidized WC sample by its exposure to oxygen and its treatment at 373 K for 10 min as explained in the experimental part reveals the presence beside WC as the major surface constituent, of WO_3, WO_2 and WO (fig. 5a). The carbon 1s energy region shows the presence of a predominant carbidic carbon at 282.7 eV and a relatively

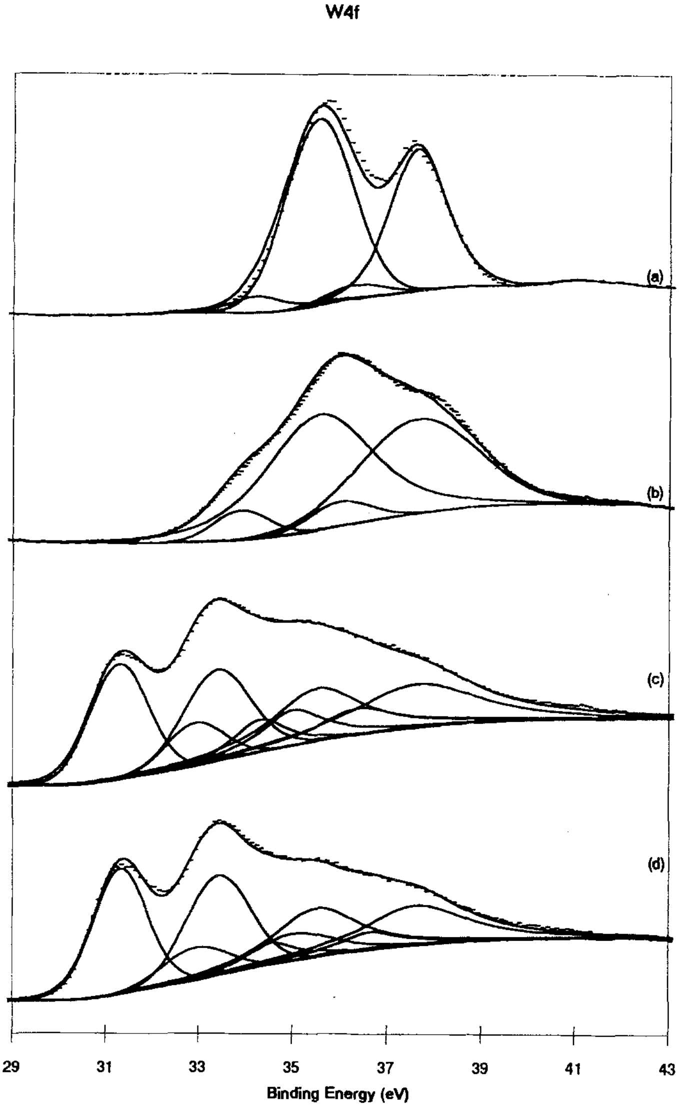

Fig. 4. The XPS of the W4f energy region of tungsten trioxide WO_3. (a) Fresh sample, (b) after 30 s of Ar^+ bombardment, (c) after 5 min of Ar^+ bombardment, (d) after 45 min of Ar^+ bombardment.

small amount of deposited amorphous carbon at 284.7 eV which results from the initial carburization process (fig. 6a). On the other hand, the O 1s energy region shows the presence of a strong line at 530.5 eV characteristic of oxidic oxygen and a relatively small amount of chemisorbed oxygen at ~ 531.8 eV (fig. 5a). Also, it can be observed that the relative intensity of the band at ~ 6.5 eV attributed to O 2p has been increased as compared to the same VB structure of a clean WC surface (fig. 7a).

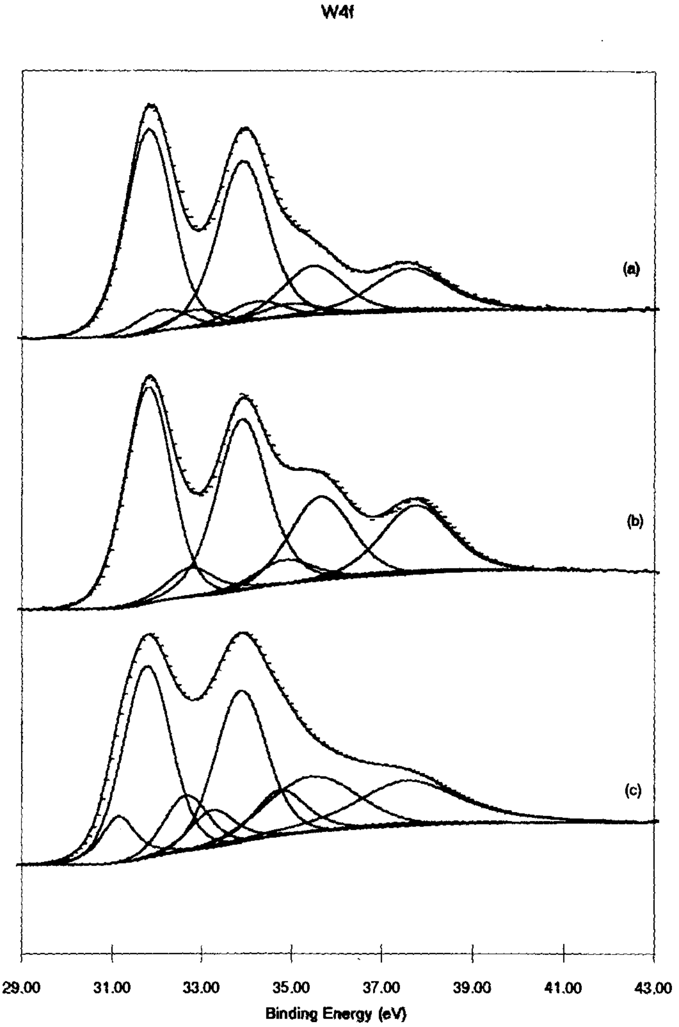

Fig. 5. The XPS of the W 4f energy region of WC + O_2 at (a) 373 K, (b) 573 K, (c) after 5 min of Ar^+ bombardment of (b).

The above results indicate that the treatment of the oxygen chemisorbed WC surface at 373 K for 10 min results in the partial oxidation of WC to WO_3 and WO_2 as well as WO in minor quantity. In this process most, if not all of the chemisorbed oxygen has been converted to the oxidic form.

3.4. OXIDIZED WC AT 573 K FOR 5 MIN

The relative intensity of WO_3 seems to increase considerably upon the treatment of the oxygen chemisorbed WC surface at 573 K for 5 min as compared to 373 K in the previous experiment (fig. 5b). Also, we notice the absence of WO species while the WO_2 relative intensity has been slightly increased. It can also be observed

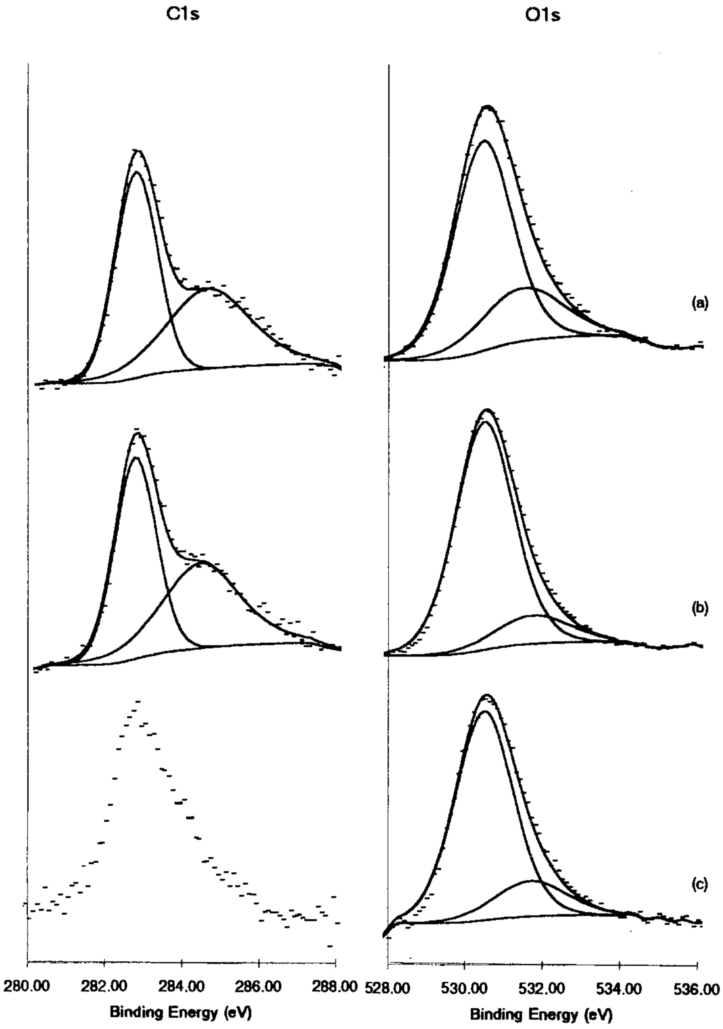

Fig. 6. The XPS of the C 1s and O 1s energy regions of WC + O_2 at (a) 373 K, (b) 573 K, (c) after 5 min of Ar^+ bombardment of (b).

that the O 1s energy region (fig. 6b) consists mainly of the oxidic form with negligible amount of chemisorbed oxygen. The C 1s energy region shows a similar structure (fig. 6b) as the previous sample at 373 K. In both samples A and B, amorphous carbon seems to be present in a certain amount on the WC surface as part of the carburization procedure.

Argon ion bombardment for 5 min of this partially oxidized surface enables to reduce some of the WO_3 to WO_2 and W(0), while a small amount of WC is reduced to W(0) as can be observed from the relative concentrations of these species in the W 4f energy region (fig. 5c). A considerable change in the valence band energy region (fig. 7a), as compared to one prior to Ar^+ bombardment, shows the appearance of a shoulder at ~ 0.2 eV attributed to the W(0) state, while the O 2p intensity

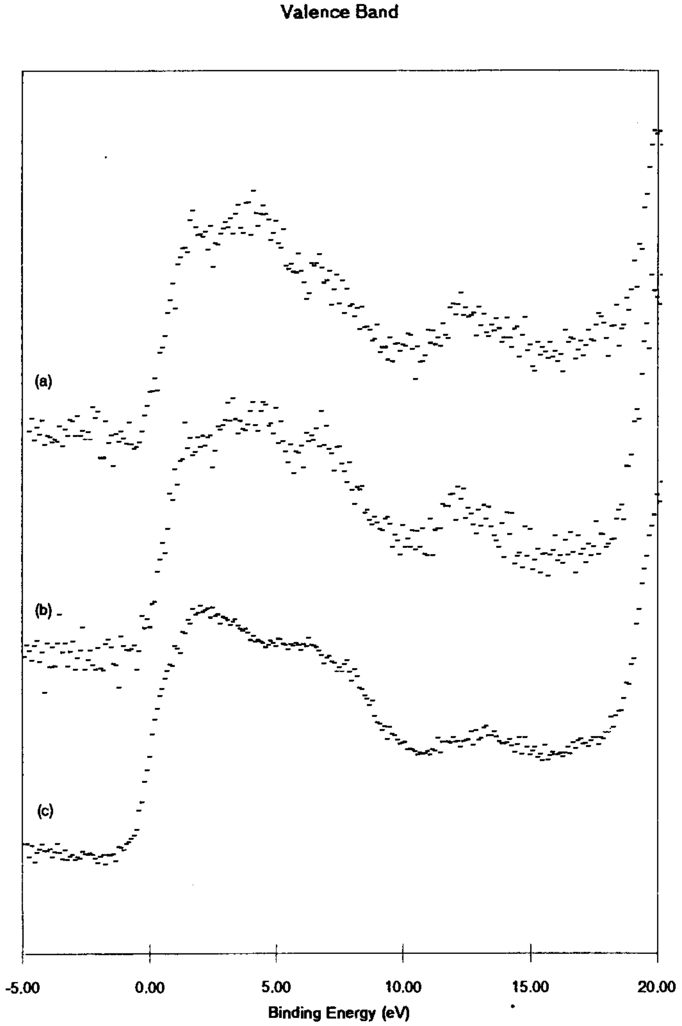

Fig. 7. The XPS of the valence band energy region of WC + O_2 at (a) 373 K, (b) 573 K, (c) after 5 min of Ar^+ bombardment of (b).

remains relatively high as compared to a clean WC surface (fig. 3a). Moreover, we notice that 5 min of Ar^+ bombardment of this surface is sufficient to remove all the deposited amorphous carbon from the surface (fig. 6c). Similarly, no chemisorbed oxygen could be observed in the O 1s energy region (fig. 6c) after this Ar^+ bombardment.

4. Catalytic results

In order to show the catalytic behaviour of a relatively pure WC (10 m^2/g) surface with and without oxygen addition at different temperatures, we have studied 2-methylpentane as reactant (fig. 8). It could be observed in this figure that a total

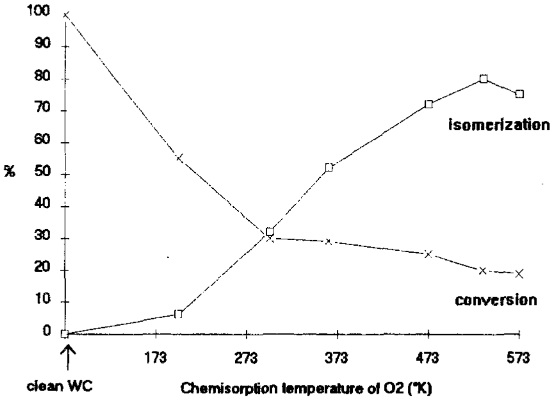

Fig. 8. Catalytic reactions of 2-methylpentane at 623 K on pure and partially oxidized WC surfaces.

conversion of 2-methylpentane to methane has been obtained in the case of a relatively pure WC surface. However, the addition of oxygen at 200 K in the order of a monolayer results in a considerable decrease in the conversion reaction associated with the appearance of 3-methylpentane as a result of the isomerization reaction. The addition of more oxygen (2 monolayers) at higher temperature results in isomerization reactions with 3-methylpentane as the major product and *n*-hexane and 2,3-dimethylpentane in relatively small amount.

Since the catalytic reaction takes place under hydrogen at 623 K, we expect that some of WO_3 formed upon the oxidation of WC will be reduced to lower oxidation states of tungsten.

An extensive work covering the characterization as well as the catalytic results of these systems using different reactants will be published shortly [10].

5. Conclusion

Carburization of tungsten trioxide following the procedure mentioned in this work results almost in its complete conversion to the carbidic WC form. The presence of a very small amount of WO_3 on the WC surface and slightly higher in the bulk apparently has no pronounced effect on the extensive hydrogenolysis catalytic reactions of hexanes, on this WC surface.

Argon ion bombardment used as reducing agent results in the reduction of WO_3 incorporated in the WC structure to WO_2 and elemental W(0). The relative concentration of W(0) was found to depend on the time of the sample exposure to argon ions.

Chemisorbed oxygen at 200 K on a freshly prepared WC followed by treatment of this surface at temperatures higher than 373 K for 10 min resulted in the partial formation of WO_3 and small amounts of WO_2 and WO. The relative concentrations of WO_3 and WO_2 have been increased upon the treatment of a different chemisorbed oxygen on a clean WC surface at 573 K for 5 min. No W(II) oxide has been observed in this case. Argon ion bombardment of this surface results in partial reduction of WO_3 and WO_2 as well as of WC to W(0). It is interesting to note that almost all the chemisorbed oxygen in both samples A and B has been either converted to the W oxide form or left the surface in an carbon oxide form. These results suggest that the isomerization products of hexanes observed on oxygen-exposed tungsten carbides can be attributed to a multi-site surface composed of WC, WO_3, WO_2 and W(0) species.

References

[1] J.M. Muller and F. Gault, Bull. Soc. Chim. (1970) 416.
[2] R.B. Levy and M. Boudart, Science 181 (1973) 547.
[3] A. Frennet, G. Leclercq, L. Leclercq, G. Maire et al., in: *Proc. 10th Int. Congr. on Catalysis*, Budapest, 19–24 July 1992, eds. L. Guczi, F. Solymosi and P. Tétényi (Elsevier, Amsterdam, 1993) p. 927.
[4] V. Keller, M. Cheval, M. Vayer, R. Ducros and G. Maire, Catal. Lett. 10 (1991) 137.
[5] A. Katrib, F. Hemming, P. Wehrer, L. Hilaire and G. Maire, Topics in Catalysis 1 (1994) 75.
[6] V. Keller, Thesis ULP Strasbourg, France (1993).
[7] F.H. Ribeiro, M. Boudart, R.A. Dalla Betta and E. Iglesia, J. Catal. 130 (1991) 498.
[8] A. Katrib, F. Hemming, P. Wehrer, L. Hilaire and G. Maire, J. Electron Spectry. Rel. Phenom. 68 (1994) 589.
[9] I.E. Wachs, C.C. Chersich and J.H. Hardenbergh, Appl. Catal. 13 (1985) 335.
[10] A. Katrib, F. Hemming, P. Wehrer, L. Hilaire and G. Maire, to be published.
[11] L. Salvati, L.E. Makovsky, J.M. Stencel, F.R. Brown and D.M. Hercules, J. Phys. Chem. 85 (1981) 3700.
[12] G. Gu, C.G. Olson and D.W. Lynch, Phys. Rev. B 48 (1993) 12178.