Electron spectroscopic study of the interaction of WC(0001) with different adsorbates (C₆H₆, CO and NO)

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Abstract

We report ARUPS, TDS and AES data for a clean and adsorbate covered (CO, NO, C₆H₆) WC(0001) surface. All studied molecules interact strongly with this carbide surface. NO and CO adsorb in an upright adsorption geometry and dissociate even below room temperature. For CO it could be shown that it bonds via its carbon end to the surface. The interaction of benzene with WC(0001) depends strongly on oxygen precoverage. With no oxygen precoverage, decomposition at about 200 K is observed. When the surface is covered by an oxidic phase, benzene interacts only weakly with the substrate and no dissociation is observed. Benzene on WC(0001) precovered with an oxycarbide represents an intermediate case. © 1998 Elsevier Science B.V.

1. Introduction

Tungsten carbide exhibits physical properties that make it an interesting material for technical applications. This concerns especially its hardness which is exploited in applications such as coating material, for instance for drills. Due to its small thermal expansion coefficient it was used for the fabrication of pointers in the past. But it is also catalytically active. It has been shown to catalyze isomerization, hydrogenation and dehydrogenation reactions [1–5]. Its catalytic properties are similar to those of some noble metals like Pt, Pd, Rh and Ru [6–9], so the idea arose of replacing these expensive metals with the cheaper tungsten carbide. This triggered a number of studies dealing with the catalytic properties of the carbide [1–14]. One of the questions tackled in these investigations concerned the influence of the surface

composition on the catalytic properties of the carbide. Some authors have shown that the activity of the surface is strongly dependent on oxygen contamination [4,11,12]. There is still a discussion as to whether the activity of the carbide is related to carbide, oxycarbide or even tungsten oxide [4,11–13].

Some studies have also been performed on single crystalline tungsten carbide. Stefan *et al.* [15] have reported studies on the electronic structure and some data have been published on the adsorption of CO, NO and O₂ [16–19].

2. Experimental

The experiments were performed in a UHV system which is equipped with facilities for sample preparation, angular resolved photoemission spectroscopy (ARUPS), Auger electron spectroscopy (AES) and thermal desorption spectroscopy (TDS) using a
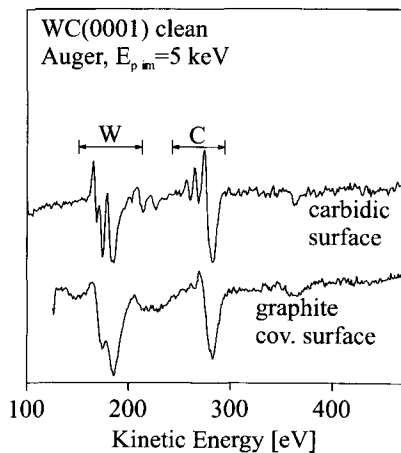
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Fig. 1. Auger spectra of WC(0001) with carbidic and graphitic carbon on the surface.

Fig. 2. Experimental geometry of the ARUPS experiments.

differentially pumped quadrupole mass spectrometer equipped with a so called Feulner cup [20]. For the ARUPS experiments, light from the TGM3 monochromator at the BESSY synchrotron radiation center in Berlin was used. The sample was attached to two tantalum wires (0.25 mm thickness) which were spot-welded to two tungsten rods (1 mm thickness). These were plugged into a sapphire block connected to a liquid nitrogen reservoir so that the sample could be cooled down to $T \approx 90$ K. Heating was possible either by electron impact or by heat radiation from a filament mounted behind the backside of the crystal. With this set-up temperatures of more than 2000 K could be reached. The sample temperature was determined with a W–Re 26%/W–Re 95% thermocouple spot-welded to one of the tantalum wires at a point where the latter was in direct contact with the crystal.

The tungsten carbide single crystal has been cut from a single crystal block after orientation with Laue backscattering. It contained a large amount of iron which was removed by annealing at $T \geq 2000$ K prior to polishing.

Two major problems arose during the preparation of the sample. Firstly the surface stoichiometry had to be adjusted. This was done by growing in methane or ethane in case the surface was carbon deficient or by annealing in an oxygen atmosphere at $T \geq 1300$ K when the carbon concentration was too high. The second problem was that the carbon on the surface was often not in a carbidic state. Prolonged annealing at T
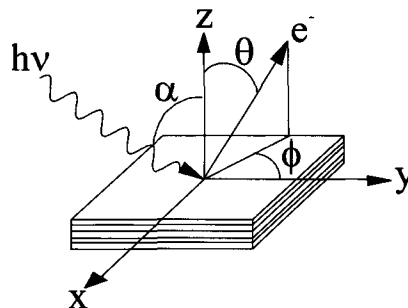
≈ 1600 K usually solved this problem. Carbidic carbon exhibits characteristic states at energies below that of the main line in the AES spectrum. These states are missing for the graphitic phase of carbon (see Fig. 1).

The meaning of the angles given in some of the following figures exhibiting ARUPS data is explained in Fig. 2.

3. Results and discussion

3.1. Interaction with CO and NO

Figs 3 and 4 exhibit ARUPS taken in normal emission as a function of temperature for WC(0001) dosed with CO and NO, respectively. The spectra indicate that both NO and CO dissociate on the surface. CO is stable until about 270 K whereas NO is already partly dissociated at $T = 105$ K. At $T = 170$ K all NO is decomposed. After dissociation in both cases clear signals of atomic oxygen show up in the spectra at binding energies of about 6 eV (see spectra of oxygen dosed surfaces at the top for comparison). As has been shown previously [18], the atomic fragments desorb at temperatures between 600 and 1200 K.

Both molecules adsorb with their molecular axes parallel to the surface normal. This is concluded from spectra taken in the so-called allowed and forbidden geometry (Figs 5 and 6). According to the dipole selection rules the intensities of the 4σ and 5σ ionizations should vanish in the plane containing the surface normal and being perpendicular to the electrical field vector of the incident light when the molecular axes of the CO molecules are oriented parallel to the surface normal and the
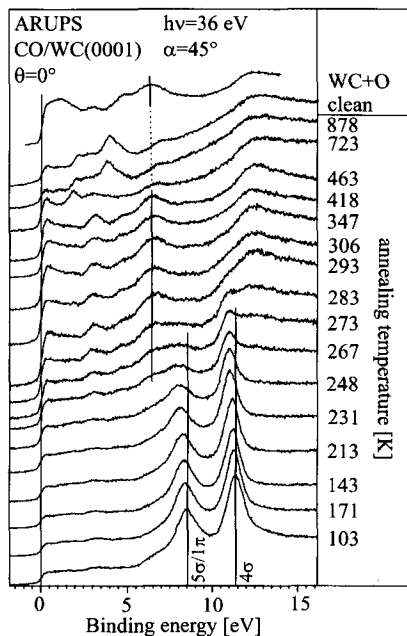
Fig. 3. Valence band spectra of CO/WC(0001) taken after annealing the sample at different temperatures.
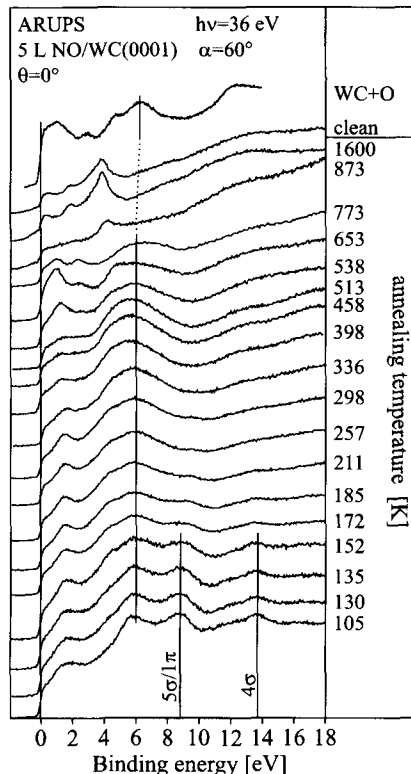

Fig. 4. ARUPS spectra of NO on WC(0001) taken as a function of the annealing temperature.

light is incident perpendicular to the surface plane ($\alpha = 0°$, $\phi = 90$, see Fig. 2) [21,22]. This is called the 'forbidden geometry'. Detection in 'allowed geometry', i.e. $\alpha = 0$ and $\phi = 0$, should lead to strong σ intensities. Figs 5 and 6 clearly show that according to these rules both types of molecules adsorb with their molecular axes parallel to the surface normal.

In order to find out whether the CO molecules bond to the surface via the C- or the O-ends we have taken ARUPS spectra in normal emission as a function of the photon energy which are displayed in Fig. 7. Molecules coordinated to the surface via their carbon ends should exhibit an intensity resonance of the 4σ level at a photon energy of about 35 eV due to the σ shape resonance whereas the opposite bonding geometry should induce a resonance of the 5σ level [23]. These rules are somewhat relaxed due to the adsorbate–substrate interaction. Nevertheless, the data exhibit a strong resonance of the 4σ level whereas that of the 5σ level is somewhat weaker (see inset to Fig. 7), so that we conclude that the molecules bond to the surface via their carbon ends.
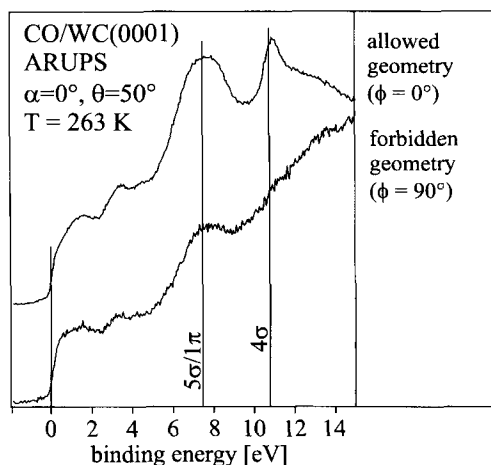

Fig. 5. ARUPS spectra of CO on WC(0001) taken in the so-called allowed and forbidden geometries.
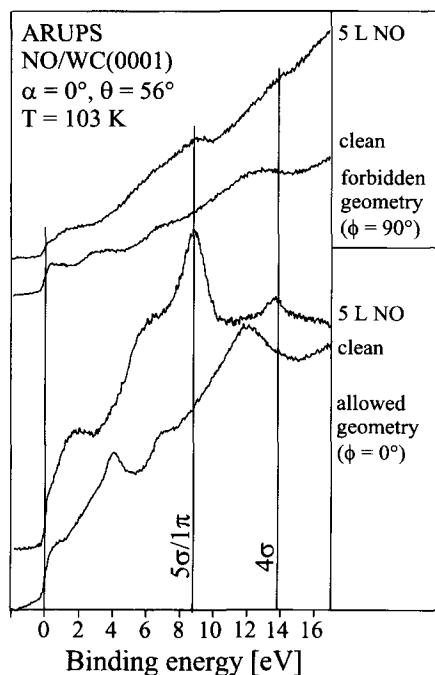
Fig. 6. ARUPS spectra of NO on WC(0001) taken in the allowed and forbidden geometries in comparison with spectra of uncovered surfaces.

3.2. Interaction with C_6H_6

ARUPS spectra taken as a function of temperature are displayed in Fig. 8 for C_6H_6 on WC(0001), WC_xO_y/WC(0001), and WO/WC(0001). The oxygen covered surfaces have been prepared by O_2 dosage onto clean WC(0001). A discussion of the interaction of O_2 with WC(0001) may be found in Ref. [19]. From Fig. 8(a)–(c) a decreasing interaction strength is observed. In all three cases multilayer adsorption is found up to temperatures of about 200 K. After desorption of the multilayer some features show up in the spectra of C_6H_6/WC(0001) and C_6H_6/WC_xO_y/WC(0001) which are visible up to $T \approx 300$ K and $T \approx 340$ K, respectively, whereas no adsorbate induced structures remain on WO/WC(0001). The spectra taken from benzene on WC(0001) after annealing at temperatures above 300 K are different from those of the clean tungsten carbide surface, indicating that the adlayer remaining after multilayer desorption decomposes on the surface. This seems not to be the case for the oxygen treated carbide, since in this case the spectra recorded at temperatures above
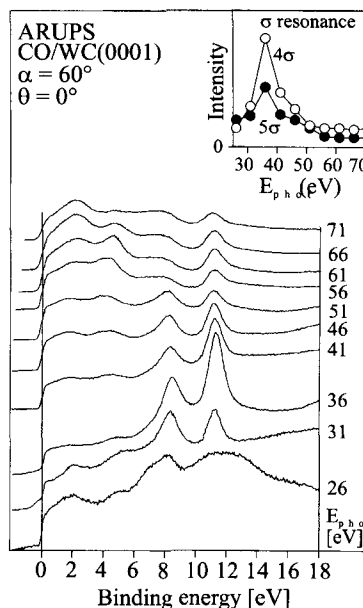

Fig. 7. ARUPS spectra of CO/WC(0001) taken as a function of the photon energy.

340 K are rather similar to that of the surface before C_6H_6 dosage.

One hint towards an identification of the adsorbate remaining on WC(0001) after desorption of the multilayer may be found in Fig. 9 which compares spectra of benzene and ethene taken after annealing the surface at 210 and 230 K, respectively (see Fig. 9). Ethene dissociates at this temperature as indicated by a comparison with the spectrum of C_2H_4 taken at $T = 80$ K. The spectra of benzene and ethene on the annealed surfaces are virtually the same, showing that the species remaining on the surface after desorption of the benzene multilayer are identical with the decomposition product of ethene, proving that benzene is dissociated at $T \approx 210$ K. The dissociation process must be accompanied by a cracking of the benzene ring. At $T \approx 300$ K the fragments may dehydrate, leaving carbon behind which would give rise to the modification of the spectra at $T \geq 300$ K with respect to that of the clean surface.

The decreasing interaction strength with increasing oxygen precoverage is in line with observations made for CO adsorption on clean and oxygen precovered WC(0001) [18]. Comparison of Fig. 8(a) and (b) shows that the adsorption properties of WC(0001) are strongly different from those of
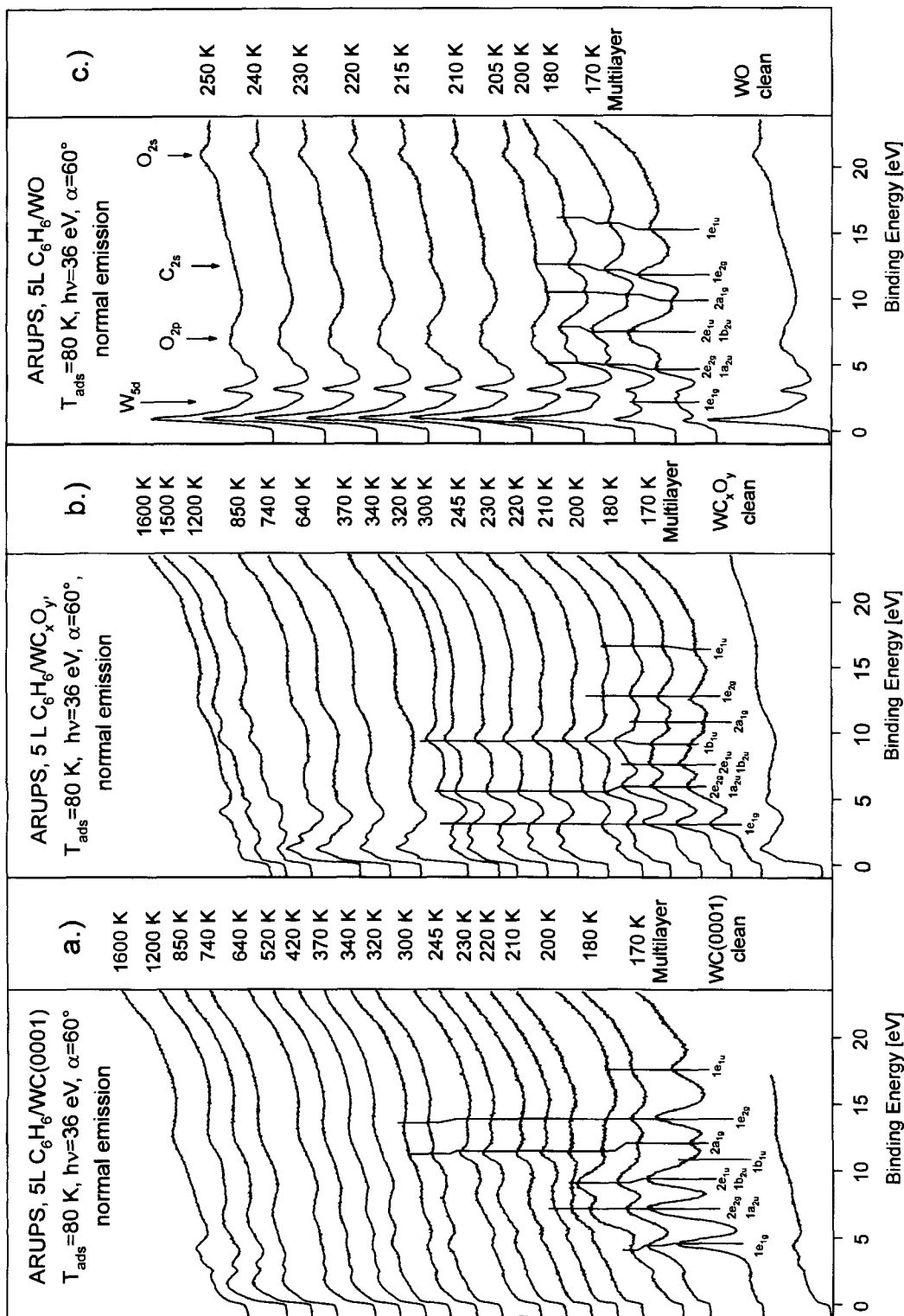
Fig. 8. ARUPS spectra of C_6H_6 on WC(0001) (a), WC_xO_y/WC(0001) (b), and WO/WC(0001) (c) taken as a function of temperature.
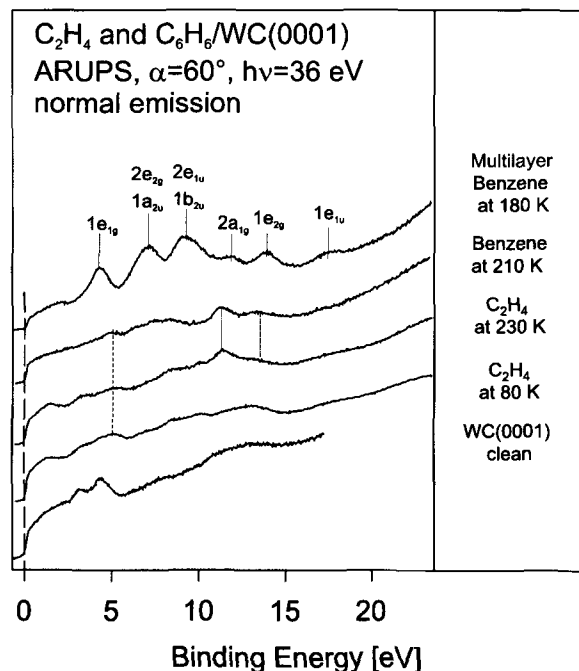
Fig. 9. Comparison of ARUPS spectra of C_6H_6 and C_2H_4 on WC(0001).

WC_xO_y/WC(0001), since the emission intensities of the benzene levels differ considerably.

4. Summary and conclusions

WC(0001) is a very sensitive surface. It may easily be modified by adsorbates like CO, NO, or that dissociate on the surface. This may lead to a reduction of the surface or to the formation of graphite. It also means that the catalytic properties of tungsten carbide will depend strongly on the environment.

NO and CO both dissociate on the surface with CO being stable up to $T \approx 270$ K whereas dissociation of NO starts already at the lowest temperature accessed in our experiments (105 K). Both molecules adsorb with their molecular axes parallel to the surface normal. For the case of CO it could be shown that it bonds via its C-end to the surface. The NO–surface bond may be similar, although this was not tested. As far as it concerns these two molecules, the WC(0001) surface behaves like a typical transition metal: the bond is strong, the molecular axis is parallel to the

surface plane and the valence level binding energies are similar to those observed for CO on typical transition metals like Pt, Ni, Pd, etc. It is likely that the bond may be described by the Blyholder model which has been developed for the transition metal nickel since the band structure of tungsten carbide is similar to that of a transition metal [6].

Benzene also interacts strongly with tungsten carbide. C_6H_6 on clean tungsten carbide seems to fragment already at temperatures above 200 K. The fragments likely dehydrate at temperatures above 300 K, leaving pure carbon behind. This is not observed for benzene on oxide covered WC(0001) where no adlayer induced signal is found in the spectra after desorption of the multilayer. C_6H_6 on WC_xO_y/WC(0001) is an intermediate case in that the final dehydration step does not seem to take place. The properties of the species remaining on the surface after multilayer desorption are different from those of the species formed on WC(0001) not predosed with oxygen. It seems to be the case that the interaction strength of benzene with the surface decreases with increasing oxygen precoverage.

Studies dealing with the surface structure (LEED I/ V) and the decomposition of C_6H_6 (IRAS) are respectively planned for the near future.

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