THERMAL EVOLUTION OF BENZENE ADSORBATE PHASES ON A Os(0001) SURFACE

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The molecular structure and orientation of adsorbed benzene (C_6H_6) on Os(0001) has been investigated by angle resolved UV photoemission spectroscopy (ARUPS), low energy electron diffraction (LEED) and thermal desorption spectroscopy (TDS) in the temperature range 200 < T< 1000 K. A well ordered ($\sqrt{7} \times \sqrt{7}$)R19.1° structure of intact benzene molecules was observed for 200 < T < 290 K. Dissociative desorption associated with successive dehydrogenation in five steps was recorded for T > 290 K at saturation coverages. Dehydrogenation occurs via C_6H_5 and C_6H_4 species which are expected to have an intact carbon ring system up to a temperature of $T \approx 500$ K. Cracking of the carbon ring occurs at T > 500 K where C–H fragments are formed at the substrate surface. Increasing the temperature leads to a successive loss of H atoms. For T > 830 K H₂ desorption ends and an ordered (9×9) graphitic carbon structure was detected. The characterisation of the different adsorption phases was performed by calculating ARUPS spectra. A reaction and decomposition path for the system $C_6H_6 + Os(0001)$ is proposed.

1. Introduction

In the process of practical heterogeneous catalysis Os is of particular relevance because it exhibits one of the highest activities for hydrogenolysis of hydrocarbon molecules [1]. In the 5d transition metal group Os shows boundary element characteristics between molecular and dissociative chemisorption of benzene. Investigations of adsorbed benzene on transition metal surfaces have been performed in the last few years which generally agreed in a model of the

0039-6028/89/\$03.50 © Elsevier Science Publishers B.V. (North-Holland Physics Publishing Division) adsorbate complex in which essentially parallel orientation of the molecular plane relative to the substrate surface is postulated.

For benzene adsorption on the 3d and 4d transition metals Pd, Rh and Ru even an undistorted carbon ring system was deduced from several angle resolved UV photoemission spectroscopy (ARUPS) and high resolution electron energy loss spectroscopy (HREELS) measurements [2–12]. A C_{6v} symmetry was found for the adsorbate complex of these elements. The bonding occurs via the π orbitals le_{1g} and la_{2u} . Ni(111) seems to be an exceptional case because a C_{3v} symmetry of the adsorbed benzene is determined [11]. For Rh(111) adsorption in an on-top adsorption site has been reported [3,4].

In contrast the 5d transition metals show different adsorption characteristics. On W(100) and Re(0001) benzene reportedly dissociates at room temperature and low adsorbate coverages [13,14]. ARUPS data for Pt(111), Ir(111) and Os(0001) indicate a lowering of symmetry for the adsorbed benzene molecule from D_{6h} in the gas phase to C_{3v} in the adsorbed phase [15–18]. Applying selection rules for photoemission in high symmetry directions these data have been interpreted in terms of a trigonal Kekulé distortion of the adsorbate complex with alternating C–C bond lengths [18]. Comparison of C₆H₆ + Os(0001) and C₆H₆ + Re(0001) [43] indicates a high distortion of the carbon ring system at room temperature for Os(0001).

In this paper we report ARUPS and thermal desorption spectroscopy (TDS) measurements of adsorbed benzene on Os(0001) in a temperature range of 200 < T < 1000 K. The experimental data indicate the following reaction path of the system: dissociative desorption (only H_2) is observed for 290 < T< 830 K, where successive dehydrogenation occurs in five steps. Investigations in the temperature range 200 < T < 290 K show a small amount of molecular desorption from an ordered $(\sqrt{7} \times \sqrt{7})$ R19.1° layer of chemisorbed benzene [18]. Successive losses of a single H atom per molecule by increasing the temperature indicate that dehydrogenation occurs through intermediates like C_6H_5 and C_6H_4 as also revealed by ARUPS. Both species still have an intact carbon ring system and especially C_6H_4 is a well known and very reactive intermediate in complex chemistry [32-35]. Model calculations using a many body approach support the proposed model of the C_6H_5 and ortho- C_6H_4 benzyne species at the Os(0001) surface. As in the case of C₆H₄-Os₃ complexes [32], where the molecular plane is inclined by approximately 60° with respect to the plane of the Os triangle, the C₆H₄ molecule assumes a corresponding geometry on the Os single crystal surface. The angular distribution of this ion state is very sensitive to the orientation of the adsorbate complex.

Further increasing of the temperature T > 500 K probably leads to a cracking of the carbon ring system. A comparison of H₂ TD spectra for the systems H₂/C₆H₆ + Os(0001) and H₂/C₂H₂ + Os(0001) shows similar data for temperatures T > 575 K indicating equal reaction products at the substrate

surface for high coverages. The notation $H_2/C_6H_6 + Os(0001)$ which will be used in the following, stands for the detection of H_2 from a benzene covered Os(0001) surface. For low coverages a cracking of the C_6H_6 molecules into C_2H_2 at the Os(0001) surface is proposed as a first step without loosing any hydrogen. Similar to the high coverage case, we assume successive dehydrogenation reactions of C_2H_2 on Os(0001) as well as for other transition metals. H_2 desorption ends at 830 K where an ordered (9 × 9) graphitic carbon structure is formed.

2. Experimental

The investigations of the system $C_6H_6 + Os(0001)$ were performed in a VG ADES 400 electron spectrometer system containing facilities for low energy electron diffraction (LEED), Auger electron spectroscopy (AES) and angle resolved UV photoelectron spectroscopy (ARUPS). The electron analyser was rotatable in two orthogonal planes and electrons were collected within an acceptance angle of $\pm 1.5^{\circ}$. The energy resolution was typically 0.05–0.2 eV. The spectra were recorded with HeI (21.2 eV) resonance radiation in the laboratory and several photon energies at the electron storage ring BESSY under similar experimental conditions. The experiments were performed with p- and s-polarized light. By varying the photon angle of incidence α from 15° to 72.5° the (x + y) and z polarization components of the photon vector potential [27,28] could be emphasized. This change in polarization composition of the ultraviolet radiation will be used to apply photoemission selection rules to the recorded spectra to determine the symmetry and orientation of the adsorbate complex.

TDS measurements were performed in a Varian vacuum chamber containing facilities for LEED, AES and a quadrupole mass spectrometer (Balzers QMG 112) for recording the TD spectra. The mass analyser was covered by a "Feulner cup" around the ionisation region of the detector [21]. The crystal is spaced via a small hole (3.7 mm in diameter) in front of the cup. Advantages of this arrangement are increasing signal heights and a very small background. For good reproducibility the distance between crystal and entrance aperture of the cup was held constant. Only a transfer of the crystal in z direction of the manipulator was necessary for dosing C_6H_6 and C_2H_2 . The Os(0001) surface was cleaned in situ by heating in oxygen at a pressure of 10^{-7} mbar and $T \approx 1000$ K and by subsequent high-temperature treatment in vacuum at $T \approx 2000$ K. Cleanliness of the Os(0001) surface was also reached by high temperature treatment at T > 2000 K for some hours without using an oxygen atmosphere. Surface order and cleanliness were checked by LEED and AES. Benzene was introduced into the vacuum chamber via a dosing system and surface exposures were obtained in dosing units (du = pressure in the dosing

system (Pa) \times time in seconds). The measurements of the pressure in the doser system occurred via a spinning rotor vacuum gauge (SRV) providing conservation of the gas molecules. Ionisation gauge readings for pressure measurements in the main chamber were not corrected for ionisation probabilities.

3. Experimental results

In the temperature range 200 < T < 290 K a chemisorbed ordered ($\sqrt{7} \times \sqrt{7}$)R19.1° monolayer, the low T phase, exists as monitored by LEED and ARUPS experiments [18]. Very small amounts of molecular C₆H₆ desorption is observed up to a temperature of 320 K. Increasing the temperature to T > 290 K leads to dissociative chemisorption. Fig. 1 shows a series of H₂ TD spectra from C₆H₆ + Os(0001) with variation of the initial coverage and a constant heating rate β ($\beta = dT/dt = 3.5$ K/s). Five desorption states are detected in the range of 300 < T < 830 K for high coverages. The first H₂ desorption peak α is observed at 326 K followed by a second more intense feature β at 372 K. The combined areas of the structures α and β take about 1/3 of the whole area covered by the spectrum at saturation coverage. This indicates the loss of two H atoms per benzene molecule at 400 K. Further



Fig. 1. Hydrogen desorption spectra after adsorption of benzene on an Os(0001) surface at T = 180 K for various exposures: (1) 0.065, (2) 0.13, (3) 0.26, (4) 0.52, (5) 0.63, (6) 0.78, (7) 0.94, (8) 1.25, (9) 3.12, (10) 12.6 du. Dosing units, du, are explained in the text. Heating rate $\beta = 3.5$ K/s. Inset: Hydrogen desorption spectra after adsorption of hydrogen on an Os(0001) surface at T = 180 K for various exposures: (1) 1.58, (2) 3.15, (3) 6.3, (4) 12.6, (5) 25.2, (6) 50.4, (7) 106.0, (8) 211.0, (9) 660.0 du. Heating rate $\beta = 3.5$ K/s.

heating leads subsequently to three desorption peaks γ , δ and ϵ at 460, 675 and 750 K, respectively. H₂ desorption ends at 830 K and an ordered (9 × 9) graphitic structure is formed as indicated by LEED and AES.

The number of dehydrogenation steps is dependent on the coverage. Lower coverages lead to a broad dehydrogenation feature in the TD spectrum with only two peaks whereas high coverages cause five clearly distinguishable dehydrogenation steps.

No shift of the α -peak maxima at various exposures is observed. This indicates a first order desorption reaction, perhaps related to C-H bond breaking. In contrast to that the β -peak maximum shifts towards lower temperatures with increasing coverages. A superposition of a low coverage



Fig. 2. (a) Hydrogen desorption spectra after adsorption of acetylene (C_2H_2) on an Os(0001) surface at T = 180 K for various exposures: (1) 46.1, (2) 13.7, (3) 5.28, (4) 3.76, (5) 2.04, (6) 0.57 du. Dosing units are explained in the text. Heating rate $\beta = 12$ K/s. (b) Comparison of hydrogen desorption spectra after adsorption of acetylene (46.1 du) and benzene (15 du) on Os(0001), at T = 180 K. Heating rate $\beta = 12$ K/s.



Fig. 3. HeI photoelectron spectra ($\alpha = 72.5^{\circ}$) of a saturated benzene adlayer on Os(0001) at selected temperatures to demonstrate the existence of different reaction intermediates. Adsorbate bands are labeled A-D. Binding energies are referenced to the Fermi level.

effect and a high coverage effect has to be considered which may be responsible for the observed shift. In the temperature range 290 < T < 340 K the observed ($\sqrt{7} \times \sqrt{7}$)R19.1° benzene structure develops broad LEED spots with increasing background intensity and vanishes subsequently.

To get more information about the system in the higher temperature range we investigated $C_2H_2 + Os(0001)$ with TDS (fig. 2a). Increasing the initial coverage leads to the development of four H_2 desorption states β' at 375 K, γ' at 500 K, δ' at 675 K and ϵ' at 775 K. Hydrogen desorption ends at $T \approx 830$ K similar to the system $C_6H_6 + Os(0001)$. A direct comparison of both systems (fig. 2b) shows that for T > 575 K the shapes of the two spectra look very similar. A similar reaction path for T > 575 K can therefore be expected with differently populated reaction channels.

ARUPS data were recorded in the temperature range of 200 < T < 1000 K. Fig. 3 shows a series of normal emission spectra at different temperatures and saturation coverage with a photon energy of $h\nu = 21.21$ eV and the angle of incidence $\alpha = 72.5^{\circ}$, i.e. dominant z polarization [18,27,28]. The experiments were performed by heating the sample up to the temperature T noted on the left hand side of the diagram and then cooling it down to ~ 200 K. This procedure was applicable because the observed transition processes turned out to be irreversible.

The lowest spectrum in fig. 3 is typical for the low temperature phase (low T phase) observed after adsorption of benzene at temperatures below 290 K. Structures close to the Fermi edge up to 4 eV binding energy can be attributed to emission from the osmium 5d bands. Adsorbate induced features are observed in the binding energy range 4–14 eV, with a prominent peak at 11 eV, a double peak around 8 eV and weaker structures around 6 and 4 eV. After heating the sample, the shapes of the spectra vary significantly indicating several adsorption phases. The first variation is observed at $T \approx 330$ K, when hydrogen desorption starts (cf. figs. 1 and 3). At T = 340 K desorption of the α -peak is complete and the photoemission spectrum changes. The former intense peak at 11 eV weakens and eventually disappears, and the spectrum is now dominated by a peak at 8.5 eV. The work function shows no significant variation during this phase transition.

Further heating of the sample to 380 K leads to further desorption of hydrogen (β -peak in fig. 1) and to the formation of another adsorbate phase. The absence of the peak at 11 eV and the appearance of a new feature at 10.5 eV (fig. 3) are characteristic for this phase. The work function increases from 3.7 to 3.92 eV. Heating to temperatures above 380 K leads to less structured spectra. Finally the clean surface was obtained by flashing the sample up to very high temperatures above 2000 K for a longer time. The work function of the clean surface was determined to be 5.6 eV and could also be used as a monitor of the cleanliness of the Os(0001) surface.

In order to characterize the different adsorption phases in more detail, angle resolved photoemission spectra are presented as a function of the electron emission angle θ . These spectra are used in the next section to identify the nature of the involved chemical species and to estimate their relative orientation with respect to the Os surface. Comparing binding energies of the adsorbate induced bands with theoretical calculations (see next section) the molecular ring structure can be deduced.

In fig. 4 photoemission spectra of benzene on Os(0001) are shown as a function of the electron emission angle θ for the low T phase. Photoelectron spectra of this phase have already been investigated using synchrotron radiation [18]. From this study, it has been concluded that benzene is adsorbed molecularly with a trigonally distorted ring system (C_{3v} symmetry) oriented parallel to the surface. The data presented in fig. 4 are in full agreement with this interpretation. The reason to show the He I data of the low T phase here is to lay a basis for the different dehydrogenation phases which will be presented in the following. The peak at 4.5 eV binding energy (A band of



Fig. 4. He I photoelectron spectra ($\alpha = 72.5^{\circ}$) of benzene on Os(0001) at T = 260 K as a function of the emission angle θ . The bar diagram denotes the relation of adsorbate and gas phase spectra for C₆H₆, aligned at band D.

benzene) induced by the $1e_{1g}$ orbital shows very high intensity at an emission angle $\theta = 15^{\circ}-20^{\circ}$. This is caused by a superposition of very intense substrate induced effects to the adsorbate features. An analogous effect can be observed in figs. 5 and 6 at the same emission angle.

Heating of the sample from the saturated low T phase (T < 290 K) to 330 K leads to some H₂ desorption and a transformation into the first dehydrogenation phase. In fig. 5 angle resolved photoemission spectra are presented at various electron emission angles for this temperature. First, we note that all the adsorbate induced bands A-D known from the benzene gas phase and the low T phase are also detected here, but with different relative intensities. The maximum intensity of the 11 eV feature is now found at $\theta = 15^{\circ}$, compared to $\theta = 0^{\circ}$ in the low T phase. An additional weak peak is observed at about 10 eV binding energy for higher detection angles θ . Second, the feature around 8-9 eV has now a different shape and different angular variation. The formation of a second dehydrogenation phase occurs at $T \approx 380$ K after



Fig. 5. HeI photoelectron spectra ($\alpha = 72.5^{\circ}$) of benzene on Os(0001) heated to T = 340 K as a function of the emission angle θ . The bar diagram denotes the relation of adsorbate C₆H₅ and gas phase C₆H₆ spectra aligned as in fig. 4.

desorption of some more hydrogen (β -peak). Fig. 6 shows a series of ARUPS spectra of the new phase analogous to figs. 4 and 5. The observable adsorbate peaks are very weak and in normal emission the features in the range 10–12 eV seem to be almost absent. At higher emission angles θ the intensity in this region increases and at about $\theta = 45^{\circ} - 50^{\circ}$ a relative intensity maximum is found. Increasing the emission angle to $\theta > 50^{\circ}$ the spectra become less well defined but the feature at 10.5 eV is undoubtedly detectable. Normal emission data recorded with polarized light and the application of the selection rules for photoemission indicate a symmetry lower than C_{3v} for the adsorbate complex of this phase. This may imply an orientation of the adsorbate molecule with an inclination angle as a structure model, assuming no other distortions. Comparison of the first and second dehydrogenation phase at $T \approx 340$ K and $T \approx 380$ K, shows a significant quenching of the formerly dominant peak at 8 eV. The group of three orbitals (2a₁, 1a₂ and 10a₁) in the calculated gas phase



Fig. 6. He I photoelectron spectra ($\alpha = 72.5^{\circ}$) of benzene on Os(0001) heated to T = 380 K as a function of the emission angle θ . The bar diagram denotes the relation of adsorbate C₆H₄ and gas phase C₆H₆ spectra aligned as in fig. 4.

spectrum for C_6H_4 molecules (see fig. 10 below), which are expected to be seen also in fig. 6, are partly covered by the d band features of the substrate in the adsorbed phase.

In addition to the He I spectra fig. 7 shows a normal emission photoelectron spectrum recorded from a benzene covered Os(0001) surface at T = 380 K, with photon energy of $h\nu = 45.5$ eV and angle of incidence $\alpha = 27.5^{\circ}$. The adsorbate induced features are observed in the energy range of 4–15 eV. Fig. 7 shows an electron distribution curve (EDC) with a smooth background. All features known from the He I spectra of this phase are also recognized here. Different intensities are caused by different cross sections. An additional band E, however, is detected in the energy range of 11–13 eV. Two components of this band at 11.5 and 13 eV are identifiable. Secondary electron final state effects can be excluded here as implied from several energy series of the clean surface.



Fig. 7. Photoelectron spectrum ($h\nu = 45.5 \text{ eV}$; $\alpha = 27.5^{\circ}$) in normal emission of benzene on Os(0001) heated to T = 380 K. Spectrum with a smooth calculated background (full line).

At temperatures above T = 420 K the spectra exhibit very weak features, so that an identification of the different phases detected in TD measurements is not possible.

4. Discussion

The dissociation of chemisorbed C_6H_6 , ordered in a $(\sqrt{7} \times \sqrt{7})R19.1^\circ$ structure, is proposed to proceed mainly via three steps:

(i) dissociation of two C-H bonds per benzene molecule under conservation of the carbon ring structure;

(ii) dissociation of C-H and C-C bonds under destruction of the carbon ring structure;

(iii) subsequent dehydrogenation of the resulting hydrocarbon fragments under formation of new hydrocarbon compounds.

To identify the opening reaction of the carbon ring system ARUPS data are important.

In the following sections TDS and ARUPS data are discussed first in detail for high coverages and increasing temperatures. Subsequently the low coverage case will be treated in a more tentative way. A reaction path dependent on the temperature will be developed where ARUPS data are compared to theoretical calculations of gas phase molecules and used to identify the intermediate species during the dehydrogenation reaction. The TD data in fig. 1 compared to the ARUPS results presented in fig. 3 show a stepwise dehydrogenation of chemisorbed benzene on Os(0001). For T < 290 K we find the low T phase characterised by an ordered ($\sqrt{7} \times \sqrt{7}$)R19.1° structure at saturation coverage. For comparison see fig. 3 where a group of UP spectra selected from a temperature series is presented. The bottom spectrum of this figure at 260 K corresponds to the low T phase. No H_2 desorption occurs in this temperature range. When increasing the temperature above T = 290 K dissociation of the chemisorbed layer is observed in five steps (fig. 1). Parallel to this result the UP spectra (fig. 3) show significant changes in lineshapes at $T \approx 340$ K where the D band at ~11 eV decreases drastically and the 8.5 eV peak (C band) develops. When passing the second H₂ desorption maximum at $T \approx 380$ K corresponding observations can be made in UPS (fig. 3) i.e. the D band feature shows only small intensity and the low energy part of band C at 7.9 eV vanishes in normal emission. This means we detect the first and second dehydrogenation phase in the temperature series of UP spectra. Increasing the temperature to T > 420 K the spectra reveal weaker structures containing only little information.

Next, we will attempt a more detailed characterisation of the observed dehydrogenation phases. Within the spirit of the oriented free molecule approach (OFM) the assignment of adsorbate derived spectral features in the UP spectra at different temperatures in terms of their free molecular orbital origin can be attempted by comparing binding energies and relative intensities of the adsorbate spectra with corresponding gas phase spectra. In order to account for different reference levels and for extra molecular relaxation effects, the deeper lying σ levels of the molecules, which are not expected to be greatly influenced by the surface bonding, are aligned in each case. As reported in [18] the bands D and E in the photoemission spectra are associated with the $2a_{1g}$ and the $1e_{2g}$ ion states of the gas phase benzene. The band E ($1e_{2g}$ ion state) is expected at $E_B = 13$ eV, where the He I spectra (figs. 3 and 4) show a broad secondary electron tail.

Application of the OFM method to the data in figs. 3-6 offers the possibility to identify the various ion states in the different dehydrogenation phases. In the chemisorbed phase, in particular, the π ion states $1e_{1g}$ and $1a_{2u}$ of the benzene molecule are observed to shift towards higher binding energies as compared to the gas phase. This may be a consequence of the strong interaction of the surface d bands and the π electron system of the adsorbate molecules. The observed shift for the low T phase is ~ 1.5 eV. Using the photoemission selection rules a symmetry lower than C_{6v} is deduced for $C_6H_6 + Os(0001)$ at T < 290 K from normal emission spectra recorded with polarized light [18]. This has been interpreted in terms of a trigonally distorted benzene molecule. A Kekulé distortion with alternating single and double



D- Band Intensity of Os(0001) / C6H6

Fig. 8. Polar plot of the integrated intensities of the D band ion states (C-H bond) of adsorbed benzene molecules on an Os(0001) surface at various temperatures: (a) T = 260 K, (b) T = 340 K, (c) T = 380 K.

bonds in the carbon ring system is a likely candidate for such a species. The molecules appear to lie flat on the substrate surface, bonded via electron donation involving the occupied π states and the d bands of the substrate. Inspection of the angle resolved data in fig. 4 shows that band D is very intense in normal emission, which is characteristic for the low T phase. With increasing θ a decrease in intensity of the $2a_{1g}$ emission is observed. For $\theta = 45^{\circ}$ the band is no longer observable whereas other features are still visible (see figs. 4 and 8a). For flat lying benzene in a $(\sqrt{7} \times \sqrt{7})$ R19.1° mesh emission from the $2a_{1g}$ derived band shows the highest intensity in normal emission (fig. 4). This means the emission characteristic is symmetrical to the normal of the carbon ring plane. Flat orientation of the molecule at this temperature deduced from symmetry investigations is in line with the observed emission characteristic [18].

Increasing the temperature above $T \approx 300$ K leads to dissociation reactions of the adsorbate complex. Passing the first H₂ desorption maximum α at

 $T \approx 330$ K (fig. 1) a sharp irreversible phase transition connected with the loss of hydrogen at the surface occurs indicated by a drastic variation in the shape of photoemission spectra (fig. 3). We can now try to deduce the nature of the possible intermediates from the combined experimental information. Two observations in the spectra are significant: firstly, an attenuation of the D band and secondly, a drastic intensity redistribution within band C as a function of temperature. Bands A and B are still observed and the B band develops towards a broad feature centered at about 6.5 eV binding energy. The ARUPS spectra still show the presence of the ion states known from the gas phase benzene, thus indicating an intact carbon ring of the intermediate bound to the substrate surface. The shift of the π orbitals relative to the gas phase implies a bonding of the adsorbate via the π electron system. A possible candidate for an intermediate at this temperature is a C₆H₅-type species, which is essentially a benzene molecule with one H atom missing. For an adsorbate complex like C_6H_5 a delocalized π electron system is expected very similar to that of the benzene except that in addition to the π system the nonhydrogen coordinated carbon atom tries to establish a bonding interaction with the substrate, leading to a slight inclination of the molecular ring plane. The above mentioned redistribution of the C band intensity may be caused by this inclination of the ring plane and the different bonding mode in this phase.

As the D band in benzene originates from C-H-type orbitals, we expect an influence of this band by the loss of a H atom in going from a C_6H_6 to a C_6H_5 molecule. We can now use the above mentioned experimental observation to tentatively propose a geometry of the adsorbate complex: the D band, attenuated in normal emission, is now detected with maximum intensity at $\theta = 15^{\circ}$ (figs. 5 and 8b). This could be either due to a tilting of the benzene carbon ring with respect to the surface plane or due to a changed emission characteristic because of the missing H atom. In a forthcoming paper [44] we will demonstrate via HREELS data, that C-H stretching vibrations, lying in the carbon ring plane of the molecule, are observable for temperatures above 290 K where dehydrogenation of the adsorbed benzene starts. In contrast HREELS data for the ordered and intact chemisorbed phase below 290 K show no C-H induced loss peaks. This clearly supports the model of an inclined carbon ring plane of the intermediate C₆H₅ species at the osmium surface. Under the assumption of only small changes in emission symmetry the change in the intensity behaviour of the D band may reflect an inclination of the molecular plane by $\sim 15^{\circ}$. The transformation from a sharp to a diffuse $(\sqrt{7} \times \sqrt{7})$ R19.1° LEED structure found for this phase can be explained easily by the proposed inclination of the C_6H_5 species along six possible directions. In addition work function measurements show only a small variation from 3.6 to 3.8 eV in going from the C_6H_6 to the C_6H_5 phase, which is in line with a small inclination angle. In our model the C₆H₅ molecules are oriented in a slightly inclined geometry. A random tilting leads to a symmetry reduction and a diffuse LEED pattern as observed at this temperature.

Increasing the temperature up to $T \approx 380$ K, where the second H₂ desorption maximum β is passed (fig. 1), an irreversible phase transition into the next dehydrogenation phase is reflected in the photoemission spectra (figs. 3 and 6). After this second desorption step no LEED patterns are observable. A C_6H_4 -type intermediate is expected to be the most probable species at the substrate surface. Comparison of the UP spectra (figs. 3-6) to the gas phase spectrum of benzene (bottom of figs. 3-6) suggests that the carbon ring is still intact. The C band is further attenuated in intensity but the shape of the spectrum is still comparable to that of the C_6H_5 phase. The shift of the D band towards lower binding energy (cf. fig. 3) and its change in intensity (cf. fig. 8c) is characteristic for this adsorbate species. HREELS spectra [44] show a more pronounced C-H stretching loss indicating a stronger inclination of the C_6H_4 species compared to the C_6H_5 species. Clear differences in the photoemission characteristic of the D band are visible in the polar plots (fig. 8). Maximum intensity is observed at 15° for the C_6H_5 species and at 45° for the C_6H_4 species supporting the idea of a larger inclination angle. At T = 380K a minor part of C_6H_5 species coexists with the C_6H_4 species. Assuming similar electron emission characteristics for this ion state of the ortho- C_6H_4 species at the Os surface as for benzene (see discussion before) a tilt angle of 45° is indicated by the experimental data (fig. 8c). This behaviour is in line with the structural model of ortho-C₆H₄ bound as a ligand in the $Os_3(CO)_9(PEt)(C_6H_4)$ complex [32]. There, an inclination angle of ~ 60° has been determined compatible with inclination angles in the range from 50° to 75° reported for other $Os_3-C_6H_4$ clusters [45]. Several domains are possible for the C_6H_4 molecules at the Os(0001) surface. The intact C_6 ring system is invariably inclined to the metal surface forming σ bonds to two osmium atoms and having a π interaction with the third osmium i.e. one C atom is linked to one Os atom forming an sp² hybrid, the second C atom is bound to two additional Os atoms forming an sp³ hybrid (fig. 9).

Summarizing these results so far, UPS and TDS data show a stepwise loss of H atoms from chemisorbed benzene on Os(0001). Up to $T \approx 420$ K an intact carbon ring system of the adsorbate complex is observed. This temperature is reached after passing the second H₂ desorption peak β . As only H₂ desorption is detected above 300 K, one can associate the total area in the H₂ desorption spectra with six H atoms per molecule. This leads to the conclusion that two H atoms are lost from benzene by elevating the temperature of the system to this point.

For a better understanding of the electronic structure and more detailed characterization of adsorbed C_6H_4 molecules we refer to some calculations [29–31,36,37]. To see the trend in going from C_6H_6 to an ortho- C_6H_4 type molecule during dehydrogenation, ab initio SCF many-body calculations with



Fig. 9. Top: structure formula for possible adsorbate substrate bondings of C_6H_4 on a Os₃ cluster reported in ref. [32]. Bottom: schematic (not site specific) 3D plot of the proposed ortho- C_6H_4 type intermediates at the Os(0001) surface at $T \approx 380$ K for different domains. The molecules are inclined by 45°.

equivalent basis sets have been reported by v. Niessen et al. for C_6H_6 and C_6H_4 molecules in the gas phase [36,37]. Lorentzian convoluted plots of these many-body calculations are presented in fig. 10 together with one particle states from refs. [36,37] which have been used as a basis. The two main results of the single particle calculations are firstly, the splitting of all e orbitals of benzene when going to an ortho- C_6H_4 type molecule. Apart from the $2e_{2g}$ splitting, which is not directly observable because one of the resulting states, the $3b_1$ component is covered by the substrate d bands, the most prominent splitting is associated with the $1e_{2g}$ ion state, the E band (b_2 and a_1 components). Secondly, a 0.5 eV shift of the D band ($2a_{1g}$ in benzene) towards lower binding energy ($7a_1$) in benzyne (C_6H_4) is calculated (fig. 10). The spectroscopic states of the Lorentzian convoluted many-body results are connected by dashed lines with those single particle states from which they borrow most of



Fig. 10. Calculations of photoemission intensities for benzene and ortho- C_6H_4 type molecules (benzyne) in the gas phase considering a many body approach. Results are presented as Lorentzian convolutes. The spectroscopic states of the many-body results are connected by dashed lines with those single particle states from which they borrow most of the intensity.

the intensity. We note the strong orbital specific relaxation shift of the various levels upon inclusion of many-body interaction in the molecular ion. In addition, some single particle states distribute their intensities over several ion states so that – not so much in benzene, but more pronounced in benzyne – the one-to-one correspondence of the one-particle levels and ion states is lost. In the region of the $5b_2$ and $6a_1$ levels this effect is rather notable and leads to a less pronounced splitting of the two states in the spectrum due to the redistribution of intensities. The presented experimental results are fully compatible with the theoretical predictions: (i) the D band, corresponding to the $7a_1$ single particle state shifts to lower binding energies; (ii) the two predicted components of the $1e_{2g}$ level in benzene are split in benzyne as observed and shown in fig. 7, where a splitting of ~ 1.0 eV between the components and nearly the predicted intensity distribution due to many-body effects is observable.

Increasing the temperature above T = 500 K leads to the cracking of the carbon ring system of the adsorbate complex. The H₂ dehydrogenation steps

labeled as γ , δ and ϵ are observed in the temperature range 500 < T < 830 K where different kinds of C-H species probably C-CH₂, C-CH₃ and CH₂ fragments are expected [5,6,19,20,23-26,42]. ARUPS data recorded at T > 500 K show only weak structures. All ion states indicating an intact carbon ring system are missing now. Therefore a cracking reaction of the C₆H₄ intermediate must be proposed (cf. fig. 3). A reaction like C₆H₄ \rightarrow 2C₂H₂ + 2C at the Os(0001) surface may be a possible decomposition path.

TD measurements of $H_2/C_2H_2 + Os(0001)$ for comparison show desorption features labeled as δ' at 675 K and ϵ' at 750 K (fig. 2a). The ARUPS spectra recorded in the high temperature range are nearly identical with very ill-defined structure which is representative for different C-H like species. The nature of these high temperature products has been discussed by several groups [6,13,14,19,20,23-26,42]. It is expected that similar surface species may be formed from several unsaturated hydrocarbons on Os(0001) for T > 575 K, but the relative amounts can be different. A common reaction path for unsaturated hydrocarbon species on different transition metal surfaces in the high temperature region may therefore be likely. Finally the formation of a (9×9) graphitic carbon structure after termination of H desorption at 830 K is observed.

The recorded TD data for low coverage (fig. 1) show a broad H₂ desorption peak in the temperature range 370 < T < 500 K containing probably two features at $T \approx 410$ K and $T \approx 455$ K. A "tail" is observed up to $T \approx 600$ K where H₂ desorption ends. From the thermodynamical point of view a dissociation reaction with a simultaneous loss of all H atoms seems to be unlikely because the activation energy for such a reaction has to be much higher than the energy which is needed for a stepwise dissociation of the single C-H bonds. Therefore a step by step dissociation reaction involving C-H and C-C bond breaking is proposed for low benzene coverage on Os(0001). H₂ desorption shows the first maximum at $T \approx 410$ K where ARUPS data for saturation coverage indicate the beginning of C-C bond breaking. In consideration of the strong trigonal distortion of the carbon ring system a dissociation of the benzene molecules into C₂H₂ fragments seems to be likely. This speculation presumably supported by weak lateral interaction cannot be deduced directly from the presented data.

Cyclotrimerisation reaction of C_2H_2 to C_6H_6 as reported for Pd(111) [38-41] leads to the idea of an inverse reaction like a retro-cyclotrimerisation of C_6H_6 into C_2H_2 compounds in the case of low benzene coverage because of the highly distorted C ring system.

Hydrogen desorption spectra of an acetylene (H–C=C–H) and a benzene covered Os(0001) surface (fig. 2) show the α and β structure only in connection with benzene, whereas γ , δ and ϵ are observable for both hydrocarbons on Os. H₂ desorption data of an acetylene and benzene covered Ru(0001) surface show comparable results [19,26]. However, there are some differences

observed in the H₂ desorption spectra of $C_2H_2 + Ru(0001)$: firstly, a shift of about 100 K to lower T for all desorption features compared with Os, beginning with a prominent peak at 385 K. Secondly, the absence of the desorption feature β' in fig. 2 for a Ru substrate; thirdly, termination of H₂ desorption at $T \approx 750$ K for Ru in contrast to Os where H₂ desorption is terminated at about 830 K.

Assuming similar reaction mechanisms for C_2H_2 adsorbed on Ru and Os surfaces we would propose a model for C_6H_6 decomposition for low coverages. Although on the basis of the presented data this model may have a speculative character, the prominent desorption peak γ' in fig. 2, which is only observable for $H_2/C_2H_2 + Os(0001)$ is explained by differences of hydrogen adsorption on Os and Ru surfaces. Weaker bonding of hydrogen to the Os substrate is deduced from lower desorption temperatures (see inset of fig. 1 and ref. [22]). The hydrogen desorption behaviour and the decomposition of C_2H_2 via the above mentioned disproportionation reaction leads to the idea that some separated H_{ad} must be present at the substrate surface during the decomposition of the adsorbed C_2H_2 . In the case of Os part of H_{ad} desorbs leading to the desorption feature β' in fig. 2. Another part is used for hydrogenation of the remaining C-H compounds. In the case of Ru the H_{ad} species are not able to leave the surface because of the stronger bonding. The difference in peak height relation of γ' at 500 K (see fig. 2) and the desorption feature at 385 K in the $H_2/C_2H_2 + Ru(0001)$ spectra [19] leads to the idea, that β' and γ' belong to competing reaction channels. The sum of β' and γ' peak areas in fig. 2 should then be comparable to the strong single desorption peak area at 385 K in $H_2/C_2H_2 + Ru(0001)$ [19].

For low coverages a cracking reaction from adsorbed C_6H_6 into $3C_2H_2$ is proposed whereas a cracking from adsorbed C_6H_6 via C_6H_5 and C_6H_4 intermediates into $2C_2H_2 + 2C_{ad}$ is a possible reaction for medium and high coverages. The absence of the α -labeled desorption feature (fig. 1) for medium coverages at $T \approx 330$ K is possibly caused by the appearance of the C_6H_5 as a stable intermediate with an increasing barrier for $C_6H_5 \rightarrow C_6H_4 + H_{ad}$ than from a reduced barrier for $C_6H_6 \rightarrow C_6H_5 + H_{ad}$ reaction. C_6H_4 formed at the Os(0001) surface must still go through a C_6H_5 intermediate because the latter is simply not stable in this coverage regime. The hydrogen recombines and desorbs forming the α -labeled desorption feature. Increasing the lateral interaction by increasing the benzene coverage results in the appearance of the α -peak at 330 K without any shift of the peak maximum. Higher repulsive interaction between the H atoms of the molecules might open a second reaction channel via $C_6H_6 \rightarrow C_6H_5 + H$.

The shift of the β desorption peak towards lower temperatures by increasing the initial coverages can be interpreted as a continuous transition from the low coverage reaction path with a cracking of the carbon ring system into $3C_2H_2$ and the medium and high coverage mechanism with successive



Decomposition of $C_6 H_6 + Os(0001)$

Temperature .

Fig. 11. Schematic model of the proposed decomposition path of the system $C_6H_6 + Os(0001)$ for temperatures of 200 < T < 830 K. Intermediates like C_6H_5 and ortho- C_6H_4 are proposed for dehydrogenation steps at high coverages and a retro-cyclotrimerisation is suggested for low coverages. Cracking of the aromatic ring system occurs at T > 500 K where C-H fragments are formed at the Os(0001) surface.

dehydrogenation via C_6H_5 and C_6H_4 intermediates as briefly illustrated in fig. 11.

In concluding we note that additional techniques would be highly desirable to support and refine the presently proposed reaction model in particular for the medium and the low coverage case. Both HREELS and NEXAFS would yield complementary information on the structure of the various intermediates.

5. Conclusions

Thermal evolution of benzene adsorbate phases on an Os(0001) surface has been investigated by TDS and ARUPS in the temperature range 200 < T <1000 K. For 200 < T < 290 K chemisorbed C₆H₆ in the low T phase with a well ordered ($\sqrt{7} \times \sqrt{7}$)R19.1° structure is observed. The adsorbate complex shows C_{3v,od} symmetry indicating a flat lying distorted, intact C₆H₆ molecule oriented with its carbon ring parallel to the surface [18].

The dissociation of the adsorbate layer begins at T > 290 K and proceeds mainly via the following three steps: firstly, a dissociation of C-H bonds under conservation of the carbon ring structure for 290 < T < 500 K, secondly, a dissociation of C-H and C-C bonds under destruction of the carbon ring system for T > 500 K, and thirdly, a subsequent dehydrogenation of the residual hydrocarbon fragments accompanied by formation of smaller hydrocarbon compounds; at $T \approx 830$ K hydrogen desorption ends and a graphitic (9×9) carbon layer is observed.

For high coverages a successive dehydrogenation occurs via C_6H_5 ($T \approx 340$ K) and C_6H_4 ($T \approx 380$ K) intermediates. From ARUPS data an inclined orientation for both species is deduced. Intensity measurements of the $2a_{1g}$ derived band indicate an inclination angle of $\theta = 15^{\circ}$ for C_6H_5 and of $\theta = 45^{\circ}$ for the ortho- C_6H_4 intermediate with respect to the Os(0001) surface. The identification of the intermediate dehydrogenation phases has been carried out by comparing calculated molecular spectra of C_6H_6 and ortho- C_6H_4 to the experimental data. Destruction of the carbon ring system is indicated for temperatures of $T \approx 500$ K where probably several hydrocarbon fragments are formed which dehydrogenate subsequently at higher temperature. The comparison of $C_2H_2 + Os(0001)$ and $C_6H_6 + Os(0001)$ shows similar reaction paths of both systems for T > 575 K, compatible with expectations from the literature [6,19,20,23-26,42].

For medium coverage the absence of the α -labeled desorption feature is possibly caused by an increased barrier for a $C_6H_5 \rightarrow C_6H_4 + H_{ad}$ reaction. The formation of C_6H_4 at the Os(0001) surface must still go through a C_6H_5 intermediate because the lateral interaction at this coverage regime is not able to stabilise the latter. Increasing the lateral interaction by increasing the C_6H_6 exposures the high coverage reaction channel opens continuously.

For low coverages a different reaction mechanism is suggested by proposing a cracking of the carbon ring system of chemisorbed benzene into $3C_2H_2$ and subsequent decomposition into smaller C-H fragments via different hydrocarbon residues. The proposed reaction sequence is illustrated in fig. 11.

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