



Adsorption and thermal decomposition of ethylbenzene and styrene on Pt(111) studied by UPS and XPS

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[†]We must sadly report that Werner Weiss passed away before the completion of this work.

Abstract

The interaction of ethylbenzene (EB) and styrene with Pt(111) was studied by UPS and XPS for adsorption temperatures between 135 K and 870 K. Below 350 K, styrene chemisorbs strongly and the work function decreases by more than 2 eV indicating strong polarization or charge transfer. This is accompanied by different bonding shifts of the p and s orbitals towards smaller binding energy. After saturation of the chemisorbed layer, physisorption and finally condensation in form of clusters is observed. The isosteric heats of adsorption for physisorbed and condensed styrene are 61 kJ/mol and 58.5 kJ/mol, respectively. The first EB layer dissociates into chemisorbed styrene and hydrogen atoms. The following physisorbed and condensed layers consist of undissociated EB. Upon annealing in EB or styrene atmosphere, chemisorbed g-styrene polymerizes at about 400 K with a saturation coverage slightly above one monolayer. Upon further annealing the layer starts to decompose and beyond 700 K it forms a graphitic coke layer. Annealing of a g-styrene layer without further gas admission yields the same species but with lower coverages.

Keywords: Adsorption isotherms; ultraviolet photoelectron spectroscopy; X-ray photoelectron spectroscopy; adsorption kinetics; surface chemical reaction; platinum; aromatics.

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1. Introduction

The interaction of organic molecules with transition metal surfaces is of general interest in the study of catalytic conversion reactions. Among unsaturated molecules, the adsorption of ethylene has probably been studied most widely. As reviewed in [1], it adsorbs molecularly at low temperatures both on Rh(111) and Pt(111). Upon annealing it converts in a series of dehydrogenation steps. At 310 K ethylidyne has formed which begins to decompose further at 450 K into CH_x fragments. They eventually form polymeric carbon chains terminated by hydrogen and beyond 750 K a chemically completely inert graphitic layer. Concerning nonpolar aromatics, the adsorption of benzene onto Pt(111) surfaces is studied most widely. NEXAFS measurements have shown that the first benzene layer binds with the p ring parallel to the surface [2, 3]. From a LEED analysis it was concluded that the C-C bond length is expanded when coadsorbed with CO [4]. When adsorbed alone, it was found to be deformed with different expanded C-C bonds and a buckling distortion of the ring [5]. The interaction of benzene and toluene with Pt(111) have been compared using thermal desorption spectroscopy (TDS) [6]. The first half monolayer of benzene decomposes by dehydrogenation whereas the second half monolayer desorbs intact. In contrast, toluene decomposes almost totally. At least on Rh(111), the decomposition products of benzene are C₂H and CH as in the case of ethylene. However, no ethylidyne intermediate is observed [1]. As we have reported recently [7], exposing the Pt(111) surface at 300 K to EB leads immediately to dehydrogenation into chemisorbed styrene and hydrogen. However, the styrene does not desorb molecularly upon annealing [8]. Therefore Pt is not suitable as dehydrogenation catalyst for EB. In the present paper we will show that this is due to the strong bonding of styrene to Pt(111). Different to benzene, toluene and ethylbenzene, the styrene molecule is capable to polymerize and we will demonstrate that a polymerized intermediate species appears at elevated temperatures before further decomposition starts and finally the graphitic layer is formed.

We use photoelectron spectroscopy as analytical tool. It probes the species residing on the surface and is complementary to TDS which probes molecules coming off the surface. UPS is a spectroscopic method and similar to the frequently applied vibrational spectroscopies it yields information on the nature of the adsorbed species and on its chemical interaction with the substrate. In their early UPS study on benzene adsorbed on Ni(111) [9], Demuth and Eastman have assigned spectral features to benzene π-orbitals in a way to yield increased binding energies (positive bonding shift) due to specific interaction and the formation of adsorbate-substrate hybrid orbitals. Other authors followed this assignment for benzene adsorbed on different transition metals, also for benzene on Pt(111) [10] and on Pt(110) [11]. For chemisorbed styrene we will present evidence for a decrease of binding energies of π relative to σ orbitals which we assign to a weakening of intramolecular bonding. Such considerations imply that there is no specific adsorbate-substrate interaction leading to hybrid orbitals. When the interaction is specific, a separation into substrate and adsorbate orbitals is no longer a good approximation as has been demonstrated e.g. for ethylene and acetylene ad-

sorption on Ni(110) by Weinelt et al. [12-14]. UPS further yields absolute values of the work function and of its change upon adsorption. Finally, the coverage can be deduced quantitatively, at least as long as the adsorbate molecules are not decomposed or severely destructed.

The paper is organized as follows. After a short experimental section, we present results on styrene and EB adsorption in the low temperature range ($T \leq 300$ K) where sequential adsorption of chemisorbed, physisorbed and condensed species is observed. From measurements of isobars in adsorption-desorption (AD) equilibrium, isosteric heats of adsorption and kinetic information on the adsorption and desorption process are deduced. After that, the behaviour at elevated temperature ($T > 300$ K) is analysed. We show that chemisorbed styrene polymerizes in the range up to about 400 K, followed by decomposition and finally dehydrogenation and formation of a graphitic layer between 600 and 800 K.

2. Experimental

The experimental setup and procedures were described before [7]. The vacuum chamber (base pressure 5×10^{-11} mbar) was equipped with a double-pass cylindrical mirror analyser (CMA, Physical Electronics), a resonance lamp (He I line 21.2 eV, He II line 40.8 eV) for UPS and a Mg K α source for XPS. The spectra are averaged over a large range of escape angles. The chamber was further equipped with a high resolution LEED system suitable for spot profile analysis (SPA-LEED), an Ar $^{+}$ -sputter gun and a gas inlet system. The Pt(111) sample was mounted by tungsten wires and molybdenum screws onto a sapphire sample holder which could be cooled with liquid N $_2$. Heating occurred from behind by electron bombardment through a hole in the sapphire holder.

The Pt(111) substrate was cleaned by repeated sputter-annealing (1 keV Ar $^{+}$, annealing at 1300 K) as well as oxidation-annealing cycles until a (1x1) LEED pattern with sharp spots was obtained and no contaminations were detectable by XPS. Ethylbenzene and styrene were filled into small glass bulbs and degassed by several freezing-melting cycles under vacuum. Before each inlet, the vapor from the gas line was pumped off to remove possible accumulated contaminants. The pressure indication of the ionization gauge was corrected for the ionization probability of EB which we have determined to be 6.1 times higher than for N $_2$, in good agreement with values for benzene and toluene [15].

3. Results and discussion

3.1 Coverage determination and uptake

Fig. 1 shows a selection of He I photoelectron spectra taken before and during continuous styrene admission at a constant pressure of 5×10^{-5} mbar at 295 K until saturation is reached. Adsorption induced attenuation of the substrate emission dominates between 0 and -4 eV with respect to E_F whereas adsorbate induced emission features dominate below -5 eV. Only the region around the Fermi level cutoff is free of adsorbate features. Therefore, difference spectra were formed by adjusting the substrate attenuation factor AF at the indicated position at -0.3eV. Shown is the resulting difference spectrum for saturation coverage from which the empirical background curve (crosses) may be subtracted as has been done with all further spectra discussed in this paper. Apart from adsorbate features it may contain adsorbate-induced changes of the substrate emission. As will be discussed below, they are weak in the present case. The difference spectrum in fig. 1 represents chemisorbed g-styrene as will be discussed in more detail below. The attenuation factor is related to the electron mean free path λ_e in the adlayer and to the escape angle θ :

$$AF = I / I_0 = e^{-(d/l_e)} \quad \text{with} \quad l_e = l_e \cos \theta. \quad (1)$$

From this, the adlayer thickness d in terms of the electron escape depth l_e can easily be deduced:

$$d/l_e = -\ln(AF). \quad (2)$$

As long as we compare adlayers of similar composition, this is a good measure for the coverage. In previous measurements for the related molecule ethylbenzene adsorbed on FeO(111) films [7, 16] we have shown that a physisorbed layer consisting of densely packed flat lying molecules with a Van-der-Waals area of 50 \AA^2 ($\Theta_{sat} = 2 \times 10^{14} \text{ cm}^{-2}$) saturates at $d/l_e = 0.7$. It will be shown, that this calibration also applies for ethylbenzene and styrene on Pt(111).

Another measure for the coverage is the adsorbate induced intensity. We have determined the total areas between the difference spectra and the background curve (crosses in the upper part of fig. 1). It turned out that these areas were exactly proportional to the corresponding d/l_e values as long as the adsorbate is not decomposed (see paragraph 3.4). All this proves that d/l_e is a reliable measure for the coverage in the investigated system.

The increase of d/l_e with exposure time deduced from spectra as in fig. 1 is plotted in the uptake curve shown in fig. 2a. The coverage increases completely linearly with a sharp break at saturation. This indicates that adsorption occurs via a mobile precursor state [17]. Also the work function Dj (fig. 2b) decreases linearly at the beginning but the transition to saturation is smoother. This is due to depolarization effects when the density of adsorbate dipoles increases. This suggests repulsive dipole-dipole interaction. Indeed, saturation is reached for $d/l_e = 0.58$ which corresponds to only 83% of the density of a physisorbed monolayer ($\Theta = 1.66 \times 10^{14} \text{ cm}^{-2}$). Different to the quantity d/l_e , Dj is thus no longer useful as a measure for the coverage when it exceeds about $1/2$ ML.

From the saturation coverage, the time for reaching it and the applied pressure, we can calculate the sticking coefficient. Assuming a relative sensitivity of the ionization gauge compared to N $_2$ between 5.18 (as for benzene) and 6.81 (as for toluene)[15], the sticking coefficient formally turns out to be between 0.84 and 1.11, i.e. near unity. If we assume that it is 1, the sensitivity factor for our ionization gauge was 6.14.

Using the Helmholtz equation $Dj = nm/e_p$ [18], we can determine the electrical dipole moment m of chemisorbed styrene from the adsorbate density n and the work function change Dj . The initial dipole is 4.4 debye units which is quite large (the dipole of the free water molecule is 1.84 D). A more meaningful quantity is the dipole moment per C atom which is 0.55 D and thus in the usual range of dipole moments of small molecules.

3.2 Adsorption isobars and isosteric heats of adsorption

He I spectra were measured in adsorption-desorption equilibrium at constant styrene pressures upon stepwise cooling the sample in the same way as described before [7] for EB adsorption on Pt(111), FeO(111) and Fe $_3$ O $_4$ (111). The coverages in terms of d/l_e

were determined and plotted versus T . The resulting isobars for two pressures are plotted in fig. 3. For comparison, also the corresponding EB isobars from ref. [7] are shown. The isobar for $p_{sty}=5 \times 10^{-9}$ mbar was measured first, starting at 295 K and decreasing the temperature stepwise. Between 295 and 205 K, the coverage remains almost constant ($d/l_e=0.58-0.62$), increases then and forms a plateau at 178 - 162 K ($d/l_e=1.35-1.55$), before it increases further below 160 K. This is due to sequential adsorption of chemisorbed (g), physisorbed (b) and condensed (a) styrene as concluded from the UP spectra presented below. Surprisingly, d/l_e drops upon further cooling to a value of 1.98-2.18.

The sample was then heated to 250 K, the pressure was increased to 5×10^{-7} mbar and another isobar measured. Again, the coverage of g-styrene is constant beyond 275K, although slightly higher ($d/l_e=0.68$) than upon initial adsorption. This is not connected with a further decrease of the work function. Possibly, some more molecules are squeezed into the chemisorbed layer upon deposition of a thick layer and they remain there. The physisorbed layer saturates at the same coverage as for the lower pressure.

Again, the condensed layer seems to stop growing at $d/l_e=2.1$, however, without swing-over as in the low pressure isobar. We ascribe this apparent saturation to the formation of thick styrene clusters on top of the layer consisting of altogether three styrene layers. These clusters occupy only a small portion of the surface and thus do not contribute significantly to the adsorbate signal and the attenuation of the substrate emission. The swing-over of the low pressure isobar suggests that initially a thicker metastable film is formed which suddenly tears up. This implies that the molecules are quite mobile even at $T < 150$ K. The d/l_e values are 0.6-0.68, 1.35-1.55 and 2.1, respectively, for saturation of g-, b- and a-styrene. This corresponds quite accurately to 1, 2 and 3 ML according to the calibration of $d/l_e=0.7$ for a physisorbed layer of the related molecule EB on a FeO(111) film deduced before [7, 16] and confirms it at the same time. Styrene grows thus in a Stranski-Krastanov mode. The 1st layer is strongly chemisorbed. Although the 2nd and 3rd layer are much more weakly bound, they are stabilized sufficiently by the substrate to grow layer-by-layer. Only from the 4th layer on, condensation as solid styrene is more favourable and further growth occurs in the form of clusters.

After completion of the chemisorbed layer, the work function (fig. 4b) is almost constant ($D_j = -2.08$ eV). Only upon saturation of the second layer a slight further decrease to $D_j = -2.14$ eV occurs.

The adsorption of EB was discussed before [7]. Also here, a chemisorbed layer is formed first. It has been shown that it consists of EB dissociated into styrene and hydrogen. The lower saturation coverage (between 300 and 200 K in fig. 3) is caused by the blocking of adsorption sites by the coadsorbed hydrogen atoms. Since hydrogen begins to desorb between 300 and 400 K both when adsorbed alone [19] or when produced by decomposition of benzene [11], the saturation coverage depends on the temperature where initial adsorption was performed. The UP spectra show that the second layer consists of physisorbed molecular EB [7]. Incidentally it begins to form at the same temperature as the physisorbed second styrene layer. Final condensation of EB starts at lower temperature than styrene condensation. This agrees with the lower freezing temperature and smaller heat of evaporation of EB compared to styrene [21]. Also upon EB exposure, the work function decreases strongly in the range of chemisorption (fig. 4b). The initial slope is equal to that of styrene as expected since EB dissociates to styrene and the expected contribution of the coadsorbed hydrogen to D_j is small [7, 19]. The saturation value of D_j is smaller than upon exposure to styrene because of the smaller saturation coverage. Also for EB, D_j remains constant over the ranges of physisorption (b) and condensation (a) with only a small drop when the physisorbed layer is completed.

From isobars taken at different pressures, the isosteric heats of adsorption q_{st} can be determined [7]. They are plotted in fig. 4a for EB (from [7]) and styrene (determined from the isobars in fig. 3) for the range of the b- and a-species. The chemisorbed species (which is g-styrene in both cases) is bound so tightly that adsorption-desorption-equilibrium cannot be established. For b-EB, q_{st} starts at relatively high values (85 kJ/mol) and decreases almost continuously until it reaches the value of condensed a-EB (52 kJ/mol). In contrast, q_{st} is almost constant for physisorbed b-styrene with an average value of 62 kJ/mol. Concerning physisorption we would have expected that EB and styrene behave similarly. The different behaviour may be due to the different composition of the underlying chemisorbed layer which consists of styrene coadsorbed with hydrogen in the case of exposure to EB and of styrene alone in the case of exposure to styrene. However, it must also be checked whether the isobars in fig. 3 really represent AD-equilibrium.

The position and shape of the isobars is given by the condition that the adsorption rate r_a and the desorption rate r_d are equal [18,22]:

$$r_a = \frac{P}{\sqrt{2\pi} mkT} \exp(-E_{ad}/kT) s_0 f(\Theta_r) \quad (3)$$

$$r_d = n \exp(-E_{des}/kT) N_A \Theta_r^n \quad (4)$$

E_{ad} and E_{des} are the activation energies for adsorption and desorption, respectively, s_0 is the initial sticking coefficient, N_A is the density of adsorption sites and $\Theta_r = \Theta/\Theta_{sat}$ the relative coverage ($0 < \Theta_r < 1$) of the species under consideration. The function $f(\Theta_r)$ describes the dependence of the sticking coefficient s on the coverage, $s = s_0 f(\Theta_r)$. The desorption order n is one in case of molecular desorption of undissociated species and two in case of recombinative desorption of dissociated species. If s is proportional to the unoccupied part of the surface, we arrive at the Langmuir isobar

$$\Theta_r(T, p) = \frac{b_1(T) p}{1 + b_1(T) p} \quad \text{with } n = 1, \quad f(\Theta_r) = 1 - \Theta_r \quad (5)$$

The function $b_1(T)$ is given by

$$b_1(T) = \frac{s_0 \exp(q_{st}/kT)}{n_1 \sqrt{2\pi} mkT N_A} \quad q_{st} = E_d - E_a \quad (6)$$

If a mobile precursor is involved in the adsorption process, the sticking coefficient decreases more slowly with coverage when compared to the Langmuir model. According to Kisliuk [17], the function $f(\Theta_r)$ for nondissociative adsorption ($n=1$) is then given by

$$f(\Theta_r) = \frac{1 - \Theta_r}{1 + \Theta_r(K - 1)} \quad \text{with } K > 0. \quad (7)$$

For $K=1$ this reduces to the simple Langmuir case and eq. (5) is obtained. In case of a mobile precursor kinetics, K is smaller than 1 and may even assume values near zero. For the isotherm or isobar we obtain

$$\Theta_r(T, P) = \frac{1 + b_1(T) p - \sqrt{[1 - b_1(T) p]^2 + 4 K b_1(T) p}}{2(1 - K)} \quad (8).$$

Further possibilities including dissociative adsorption are discussed in [22].

From the time needed for the establishment of the equilibrium coverage, the sticking coefficient can be estimated. It turned out that s_0 was always high. We have fitted the isobars for EB and Sty in the physisorption region (b-species) assuming $s_0=1$ and the results are presented in fig. 3 (thick solid and dashed lines). The isobar for b-styrene can be fitted perfectly assuming molecular (1st order) adsorption with mobile precursor kinetics ($K=0.13$). The isosteric heat of adsorption $q_{st}=62$ kJ/mol agrees with the value from the CC analysis. Like the frequency factor $\eta_I=1.4 \times 10^{15} \text{ s}^{-1}$ it is independent of the coverage.

In contrast, the fit of the isobars of b-EB yields no satisfying parameters. It can be seen in fig. 3 that the isobars are closer together at low coverage than at high coverage of b-EB. This results in the high initial values of q_{st} and its decrease with coverage (fig. 4a). Using these values of q_{st} , strongly coverage dependent values of the frequency factor are obtained. For low Θ_b , it exceeds 10^{21} s^{-1} which does not make sense. Therefore the dashed fit curve in fig. 3 is plotted only in the range where $\eta_I < 10^{19} \text{ s}^{-1}$. With increasing Θ_b it decreases further and reaches $10^{15} - 10^{14} \text{ s}^{-1}$ when approaching saturation.

These findings suggest that the measured isobars do possibly not represent AD-equilibrium, at least not in the low Θ_b -range which would imply that also the values of q_{st} in that range are incorrect. Anyway it appears surprising that q_{st} of b-EB on a chemisorbed g-Sty (+H) layer should be so much higher than that of b-Sty on g-Sty. It should be mentioned in this context that also for EB adsorption on Fe_3O_4 , the CC analysis did not yield meaningful values of q_{st} for b-EB adsorbed on top of a chemisorbed g-EB layer. In that case this could be attributed to nonequilibrium related to a structural rearrangement of the whole g+b-layer when the coverage increased [7]. In contrast, b-EB adsorbed on an FeO film where no chemisorbed 1st layer is formed, yields reasonable values for q_{st} [7] and can be fitted well.

The values of q_{st} for condensed EB and styrene are 52 and 58.5 kJ/mol. Comparison with heats of evaporation in the 1-10 Torr range from literature [21] which are 56.6 and 61.3 kJ/mol, shows that their difference comes out reasonably but that the absolute values are too low. The likely reason is that the 5×10^{-9} mbar isobars in fig. 3 are not steep enough in the condensation regime. At this low pressure the impact rate is so low that the coverage had possibly not yet reached its new equilibrium value after the constant waiting period of about 3 min. A comparable effect was not observed in the physisorption regime.

With average values of 62 kJ/mol for b- and at least 58.5 kJ/mol for a-styrene, the isosteric heats of adsorption for physisorbed and condensed styrene are quite similar. However, the onset temperatures for physisorption and condensation are quite different and separated by a plateau in fig. 3 thus indicating different driving forces. The driving force is determined by the Gibbs energy for adsorption $Dg_a = Dh_a - T Ds_a$ with $Dh_a = q_{st}$ being the isosteric heat of adsorption and Ds_a the entropy of adsorption. Since q_{st} is almost equal, we conclude that the adsorption entropy for physisorption and condensation must be clearly different. A possible reason could be disorder in the physisorbed b-layer due to the mobility of the molecules which is quenched upon its completion so that the plateau observed in the isobars marks a two-dimensional disorder-order transition. A similar behaviour was observed for NH_3 on Ge(001) [20].

3.3 Adsorbate characterization, negative bonding shifts

We will discuss the characteristics of the adsorbate in terms of photoelectron difference spectra formed as described along with fig. 1. A crucial problem is always the distinction between adsorbate derived features and adsorbate-induced changes in the substrate emission which may occur especially in the range of the strongly structured substrate d -bands and for adsorbates which interact specifically with certain substrate orbitals by formation of hybrid orbitals. One way to estimate the importance of adsorbate-induced changes of the substrate emission is to compare spectra taken with different $h\nu$ of the exciting radiation. Upon varying $h\nu$, valence band features of the substrate display dispersions and variations in intensity due to changes of the excitation matrix elements. Dispersions of adsorbate peaks are expected only when the adsorbate layer is ordered and when the adsorbate-adsorbate interaction is strong. Otherwise their spectra can readily be interpreted in the density of states picture. We will present difference spectra after excitation with He I and He II radiation. It will be shown that although the relative intensities vary, the position of features is equal almost everywhere for both excitation energies. From this we conclude that they correspond to adsorbate orbitals whereas adsorbate-induced changes of the substrate emission are weak. For the molecules EB and styrene discussed here this is reasonable since they do probably not adsorb in an ordered way, do not interact specifically but mainly via their extended p orbitals and since their lateral interaction is weak and possibly only indirect via their adsorption-induced dipoles. Fig. 5 presents incremental photoelectron difference spectra excited by He I and He II radiation. Incremental means that the saturation spectrum of the respective preceding species is subtracted and not the clean surface spectrum. The He II spectra of condensed (a) and physisorbed (b) styrene are very similar and agree well with the gas phase spectrum (from [23] shifted by a relaxation shift $E_R=1.5$ eV towards smaller binding energies). Also the He I spectra show all features of the gas phase spectrum. However, a- and b-styrene display different relative intensities of some of them, especially in the mainly phenyl derived [23] p_p double peak structure between -7 and -8 eV. This may be due to a changed molecular orientation in the thick layer. In all spectra, the peak at -9 eV labeled p_V is clearly visible. It is derived predominantly from the vinyl group [23].

Because of the stronger interaction with the substrate, the spectrum of chemisorbed g-styrene is not so sharp. Nevertheless it contains all expected molecular features. Compared to the spectra of a- and b-styrene, however, the spectrum is shifted and „expanded“. The peaks below -16 eV are derived from C 2s orbitals which are essentially localized at the C atoms. Their shift is 0.4-

0.6 eV which may be explained by an additional relaxation shift of first layer molecules because of a more effective screening of the photohole by the metallic substrate which exceeds a possibly also existing bonding shift. However, the shift increases to 1.4 eV for the uppermost p_p orbitals which is hardly explainable by relaxation effects. Due to insufficient resolution and to the overlap of p and s orbitals in the range around -10 eV, we are not able to determine whether this shift increases continuously or whether the p orbitals are generally shifted by a larger amount than the s orbitals. Usually, a strong interaction of adsorbate orbitals with a substrate is considered to cause an *increase* of their BE (bonding shift). Also in spectra of benzene adsorbed on Ni(111) [9] and Pt(111) [10], the assignment of spectral features to benzene π orbitals was performed in a way to yield *increased* BEs. This was even taken as proof for a configuration with the aromatic ring parallel to the surface. Our results suggest another interpretation for chemisorbed styrene. Generally, a bonding interaction between the substrate and the adsorbate is expected to weaken the intramolecular bond strength in the adsorbate. (In the case of benzene on Pt(111), even a substantial increase of bond lengths has been concluded from LEED calculations [5]). In the molecular orbital picture, this would cause a reduction of the split between bonding and antibonding orbitals. The occupied orbitals visible in UPS have preferentially bonding character and their BEs should *decrease* as we have observed. We thus do not interpret the extra shift of the high-lying orbitals of chemisorbed styrene as differential relaxation shift but as bonding shift due to weakening of intramolecular bonds. The reason may be the strong polarization of the molecules evidenced by the decrease of D_j which indicates removal of charge preferentially from the extended and strongly polarizable π -orbitals.

The p_V orbital is also visible in the spectra of g -styrene, especially intense in the He I spectrum. It is shifted by a similar amount as the π_p orbital which suggests that the styrene molecules lie flat on the surface with both the phenyl- and the vinyl-group, a configuration which corresponds to the most stable gas-phase configuration [23,24].

According to [5], benzene adsorbs on a bridge site on Pt(111) with two carbon atoms almost on top of Pt atoms interacting strongly and specifically with short Pt-C distances of 2.02 Å. The other C atoms are bent away from the surface and have considerably longer Pt-C distances. The Pt-benzene interaction is thus specific and strongly related with this special site geometry. This may be the reason why hybrid orbitals with the observed positive bonding shifts are formed. The ground state geometry of styrene is planar with the vinyl group bent by an angle of about 53° with respect to the axis of the phenyl group [24]. The phenyl and the vinyl group form a common conjugated p system. Due to the size and the low symmetry of styrene, however, an adsorption geometry with specific substrate-adsorbate interaction is less probable. Instead we suggest that the chemisorbed styrene molecules are essentially planar and interact via their extended p electron system which is strongly polarized as the large D_j indicates but without marked tendency for hybrid orbital formation. This difference may explain why it exhibits negative bonding shifts. Substantiation of these speculations would need further experiments as well as calculations. We are aware that this interpretation is qualitative and intuitive. Experiments using vibration spectroscopy or angle resolved photoemission with a tunable light source as well as theoretical treatments would be highly desirable.

The total width of the p_p peak of chemisorbed g -styrene agrees in the He I and the He II spectra but its shape is slightly different. The He I spectrum seems to have a weak dip so that it looks as if it consisted of a shifted main peak and a shoulder. If this structure were true, we should have been able to resolve it also in the He II spectrum. Therefore we believe that it represents the only visible adsorbate-induced change of the substrate emission. Such influences seem to be generally weaker in the He II spectrum. The spectra of EB adsorbed between 300 and 200 K have the same shape as those of g -styrene and were therefore assigned to EB dissociated into styrene and hydrogen [7]. The spectra of a - and b -EB are equal. Fig. 5 shows the He II spectrum of condensed EB as example. The most significant differences when comparing it to the spectrum of condensed a -styrene are that the split of the topmost mainly phenyl derived p_p orbitals is much smaller and not resolved, that the structure corresponding to the mainly vinyl-derived p_V orbital in styrene is missing in EB, and that the positions and shapes of the mainly C $2s$ related peaks between -15 and -22 eV differ.

3.4 Adsorbate transformation upon heating

Spectra were measured upon heating during EB or styrene admission at constant pressure (EB-on, Sty-on) as well as with the gas inlet closed after saturation exposure around 300 K (EB-off, Sty-off). The former corresponds to the situation of measurements in AD-equilibrium, the latter to the situation when TDS spectra are measured. Since EB dissociates into styrene and hydrogen at 300 K, the starting points are always chemisorbed styrene. Only the initial coverages are smaller after exposure to EB because of coadsorption with hydrogen. Fig. 6 shows the development of the coverages in terms of d/l_e (a) and the work function changes (b). Each data point was deduced from a spectrum after heating shortly to the respective temperature.

Upon heating with EB or styrene on (EB-on, Sty-on), d/l_e (fig. 6a) increases, passes a maximum around 500 - 550 K and decreases again. Also shown are C $1s$ intensities for styrene measured under the same conditions by XPS (see fig. 9 below) and adjusted to the d/l_e curve at 315 K. Until 550 K both increase by exactly the same amount which proves that d/l_e reliably is proportional to the carbon coverage. At 800 K, however, XPS gives a much higher value for the carbon concentration. It will be shown, that the adsorbate layer has transformed to graphite there. The corresponding work function change for EB-on or Sty-on conditions (fig. 6b) is characterized by two plateaus at 400-600 K and beyond 780 K. Further exposure at $T < 350$ K (last data point) leaves both d/l_e and j almost unchanged which shows that the surface is almost completely passivated by a closed graphitic coke layer.

Heating of the adsorbate layer with EB or styrene off yields a continuous decrease of d/l_e to about half the initial value. The work function changes display a similar plateau structure which indicates that the same surface species are formed as with gas exposure. This is confirmed by inspecting the UP spectra (not shown). Additional exposure at $T < 350$ K leads to appreciable readorption of g -styrene. Comparison of the readorption intensity with the amount adsorbed initially yields that between 60% (styrene) and 70% (EB) of the Pt surface must have become free of adsorbate by the heating cycle. TDS measurements show no desorption of molecular EB or styrene but only of hydrogen [8]. Whether also other C_xH_y fragments desorb was not checked. At least most of the carbon remains on the surface and forms coke clusters.

The temperature induced changes are analysed in figs. 7 and 8. Fig 7 presents background corrected He I difference spectra for a selection of temperatures, measured under Sty-on conditions. The spectral shapes are the same when heating in EB or styrene or when heating with the gases turned off, only the intensities are different. The 315 K spectrum is the same as the He I spectrum of g -styrene displayed in fig. 5. Upon heating, the first change is the reduction of the predominantly vinyl-derived p_V peak labeled (a). Also the mainly phenyl-derived p_p peak (b) is slightly reduced in intensity, probably because of the removal of the vinyl-

derived minority contribution to this peak. Instead, the spectral intensity in the -6.5 to -9 eV region has increased and forms a shoulder at (c). The spectrum as a whole has remained well-structured suggesting that a defined molecular structure persists. From the reduction or even disappearance of the vinyl-derived p -contribution we conclude therefore that the styrene has polymerized or at least formed oligomers. The Sty-on curve in fig. 6a shows that the coverage increases steeply in this range. In polystyrene, the aliphatic backbone requires a denser packing with the phenyl groups no longer adsorbed flat because of steric reasons. This allows adsorption of further styrene from the gas phase which also is incorporated into the polymer islands. Further annealing results in a gradual decrease of the structural sharpness of the spectra. At about 600 K, the minimum at (d) is smoothed out and at 785 K all fine structure has disappeared with the exception of the minimum at -3.5 eV which is typical for graphitic species and separates the p - and s -band regions. Whereas the Sty-on curve in fig. 6a increases up to 550 K, the degradation of the spectra beyond 600 K is related with a decrease of d/l_e . The simultaneous increase of the C 1s intensity in XPS indicates that more carbon is incorporated. We conclude that beyond about 400 K the adlayer consists of a mixture of cracking products of the polystyrene adlayer. However, dehydrogenation and coke formation starts only beyond 550 K resulting in a graphitic layer beyond about 750 K. Due to further adsorption from the gas phase, this layer grows in thickness. The weak readorption at 350 K shows that no free Pt is left and that the graphitic layer is closed.

The temperature ranges for decomposition and coking are quite similar to those found for benzene and toluene [6]. The preceding polymerization has, of course, not been observed for these gases.

The corresponding changes are also observed in the He II spectra a few of which are compared in fig. 8 to He I spectra and to condensed phase reference spectra. The 315 K spectra (A) are the same as in fig. 5 and represent chemisorbed g -styrene. Upon heating to 400 K (B), the feature attributed to the p_V orbital has become very small also in the He II spectrum and the double peak at -16, -17.2 eV has merged into a single peak at about -16.5 eV. Comparison of the He II spectrum of condensed styrene with that of spin-coated polystyrene [25] yields exactly corresponding changes as the He II spectra of g -styrene and g -styrene heated to 400 K supporting our interpretation of polymerization. The 400 K spectra display the same extra relaxation shift and a similar negative bonding shift of the p -derived orbitals as the g spectra. Also the work function change D_j in fig. 6b is still large (although the coverage has increased simultaneously so that the dipole moment per styrene unit has decreased, see below) and we conclude that the oligomers interact with the surface mainly via their phenyl rings. This probably prevents threedimensional growth and limits the coverage at 400 K in fig. 6 to a d/l_e value of 0.65 (EB) to 0.75 (Sty) which corresponds to not much more than one ML.

After heating beyond 750 K, any fine structure in the spectra has disappeared and they look like poorly ordered graphite with the p band maximum at -7.1 eV and a broad s maximum between -8.5 and -14 eV. Also the reduction of d/l_e at this temperature (fig. 6a) with simultaneous increase of the C 1s intensity shows that the nature of the adsorbate has changed considerably. Thermodesorption experiments [8] yield no further hydrogen desorption beyond about 780 K and also the position of the C 1s peak in XPS at a binding energy of 284.4 eV (see below) suggests a hydrogen free graphitic species.

Mg K α excited C 1s spectra are shown in fig. 9. The peak areas are included in fig. 6a. Polymerization and beginning decomposition at 550 K is associated with a shift by 0.5 eV towards lower BE and graphitizing at 810 K with a slight backward shift by about 0.15 eV. Whereas all C atoms within the chemisorbed styrene monomers are unsaturated, we expect that those which are incorporated in the backbone of polystyrene have become aliphatic. The C 1s spectra of unfunctionalized hydrocarbons are very similar [26]. High resolution measurements indicate, however, that the BE of aliphatic carbon in polystyrene is 0.25 eV higher than for the aromatic carbon [27] which is opposite to the observed shift direction. Also a final state effect, i.e. a change of the relaxation shift between chemisorbed styrene and polystyrene seems unlikely. However, the work function under „Sty-on“ conditions has increased by 0.2 eV during polymerization (cf. fig. 6b) and the coverage has increased by a factor of about 1.6 at 500 K. This means that the dipole moment per styrene unit has decreased considerably from 4.4 D (or 0.55 D per C atom) for chemisorbed monomers to 2.4 D (or 0.3 D per C atom) at 500 K which corresponds to a transfer of electronic charge from the substrate back to the adlayer. The observed BE decrease can therefore be explained by an increase of the charge density at the location of the carbon atoms, i.e. a chemical shift. Graphitizing is connected with a further increase of the work function and of the carbon coverage. The dipole moment per C atom is reduced further to only about 0.11 D. This means that the Pt-graphite interaction is almost nonpolar. In fact, the absolute value of the BE is 284.4 eV which agrees well with values reported for graphite (284.2 - 284.7 eV [28, 29]). Also the decrease of the binding energy when going from chemisorbed styrene (curve A in fig. 9) to graphite (curve C) agrees with the generally observed trend [29].

Summary and conclusions

Styrene interacts strongly with Pt(111). At room temperature it forms a chemisorbed first layer (g -species). Negative bonding shifts (towards lower BE), especially of its p orbitals, indicate that intramolecular bonding is weakened. This is in contrast to the spectra of benzene adsorbed on Ni(111) or Pt(111) where positive bonding shifts for the p orbitals were observed and suggests that adsorbate-substrate hybrid orbitals are not formed between styrene and Pt. On top of the g -layer, a physisorbed (b) and finally a condensed (a) layer is formed. The condensate tends to form 3D clusters on top of altogether 3 layers. From measurements in adsorption-desorption-equilibrium, the isosteric heat of adsorption $q_{st}=62$ kJ/mol and a 1st order frequency factor $\eta_f=1.4 \times 10^{15} \text{ s}^{-1}$ for desorption were deduced for b styrene.

Ethylbenzene dissociates upon chemisorption to form g -styrene coadsorbed with hydrogen. The physisorbed and condensed layers, however, consist of undissociated molecules. Different to styrene, the condensed layer does not form clusters. At low b-EB coverage, q_{st} and η_f turn out very high so that non-equilibrium in the adlayer cannot be ruled out.

When a chemisorbed g -styrene layer is annealed in presence of ethylbenzene or styrene at constant pressure, a transformation with two distinct stages is observed. First, the adsorbate intensity increases and near 400 K a film with a thickness of slightly more than one monolayer has formed. Changes in the UPS spectra indicate that it consists of polystyrene. The observed saturation thickness suggests that interaction with the substrate is essential, probably via the phenyl groups interacting with their p orbitals. Upon further annealing, the layer transforms to graphite. This process is completed around 780 K. When the chemisorbed g -styrene layer is annealed without constant gas admission, the same transformations are observed. However, the apparent adsorbate coverage decreases slightly, mainly by dehydrogenation and hydrogen desorption, and the final graphite film covers only about 1/3 of the surface.

UPS has emerged as an ideal method even for measurements during gas admission. It is nondestructive, gives information about the nature of adsorbed species, allows quantitative coverage determination and from the work function changes informations related to adsorbate polarization and orientation can be obtained.

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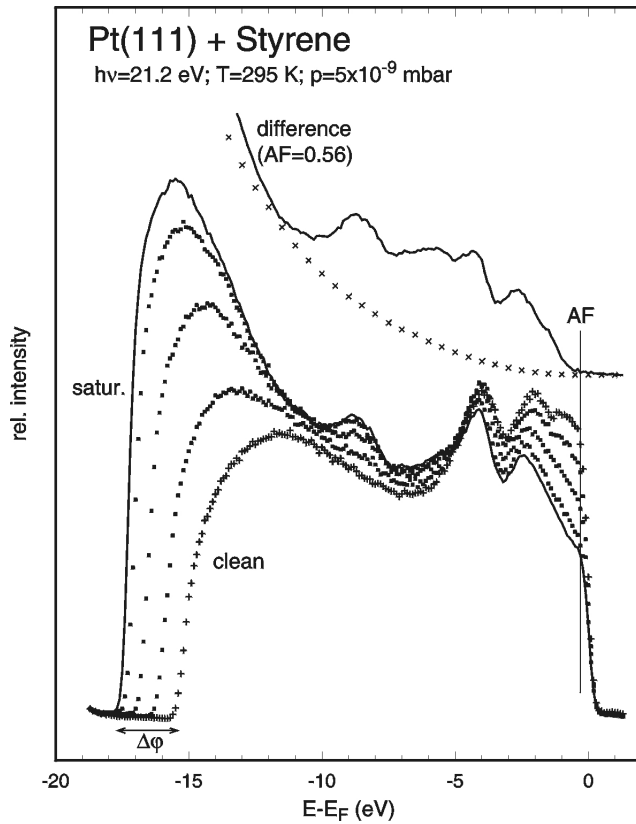


Fig. 1: He I spectra of clean Pt(111) and during admission of styrene at a pressure of 5×10^{-9} mbar at 295 K until saturation is reached. Adsorption causes an attenuation of the substrate emission, the appearance of adsorbate-induced features and a reduction of the work function Dj . Difference spectra are formed by subtraction of the properly attenuated clean surface spectrum. The attenuation factor is adjusted at the position marked AF. In order to remove the inelastic background from the difference spectrum, an empirical curve (crosses) is usually subtracted.

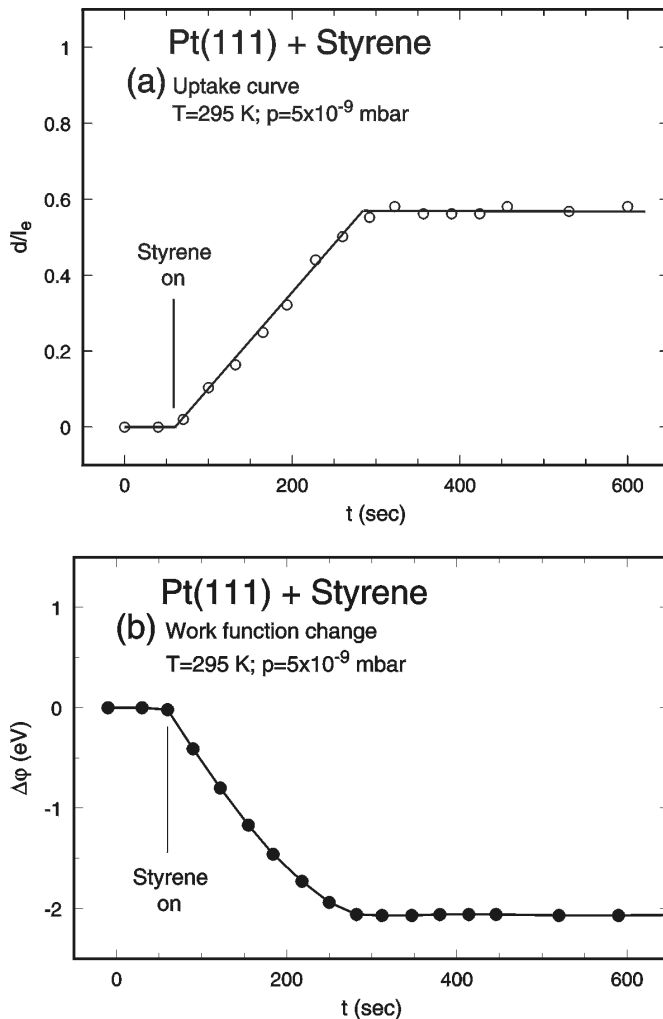


Fig. 2: (a) Adsorbate coverage in terms of d/I_0 determined from the attenuation of the substrate emission and (b) work function change Dj determined from the shift of the low energy onset of the spectra in fig. 1. At the position marked „Styrene on“, styrene was admitted at a constant pressure of 5×10^{-9} mbar.

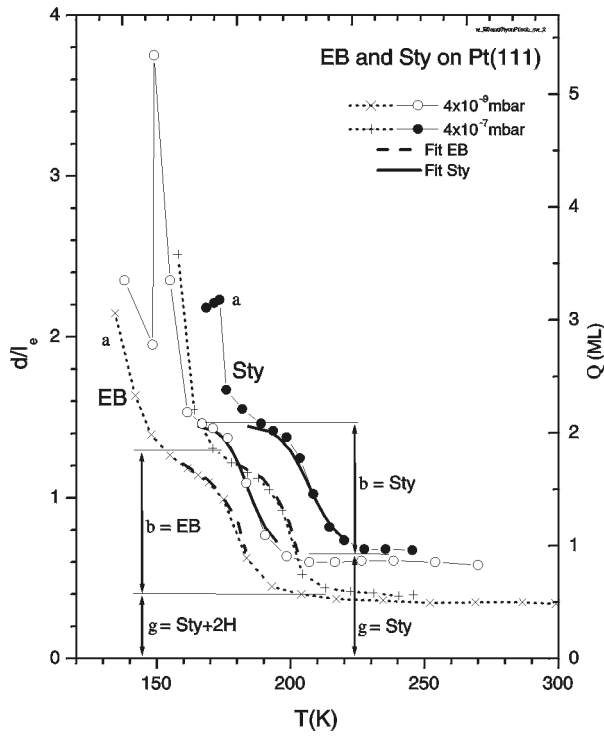


Fig. 3:

Adsorption isobars (saturation coverages in terms of d/I_e versus temperature) for styrene (solid and open circles, thin solid lines) and ethylbenzene (crosses and thin dotted lines) at a pressure of 5×10^{-9} mbar and 5×10^{-7} mbar. The kind of adsorbed species is indicated: a=condensed, b=physisorbed, g=chemisorbed. The chemisorbed species is styrene also after ethylbenzene adsorption. The thick lines (solid for Sty, dashed for EB) are the result of a kinetic fit of the isobars in the b-region, see text.

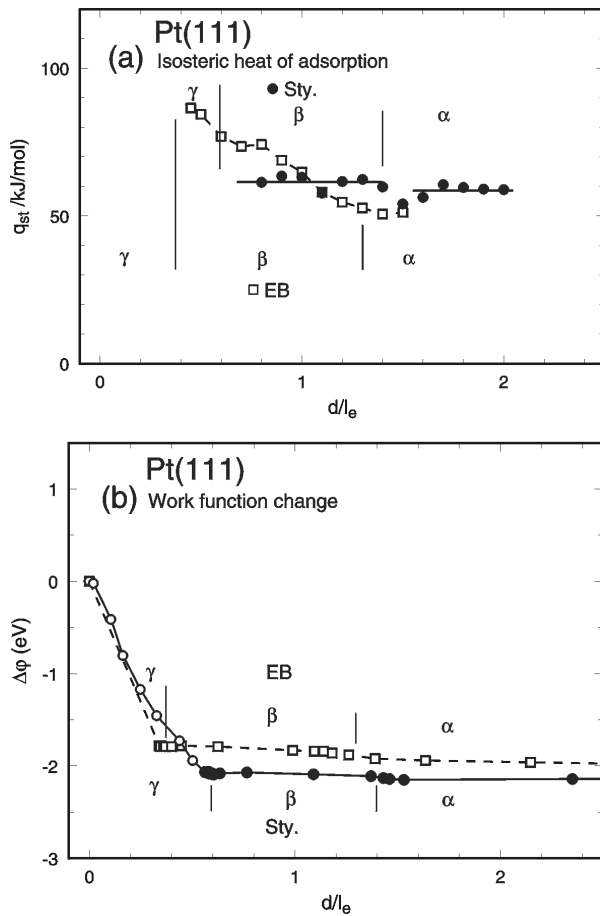


Fig. 4:

(a) Isosteric heat of adsorption for ethylbenzene and styrene in the range of physisorption and condensation on top of the chemisorbed g-styrene layer. (b) Coverage dependence of the work function change for styrene during initial adsorption of the g-species (open circles) as well as for ethylbenzene and styrene during further adsorption of the respective physisorbed and condensed species.

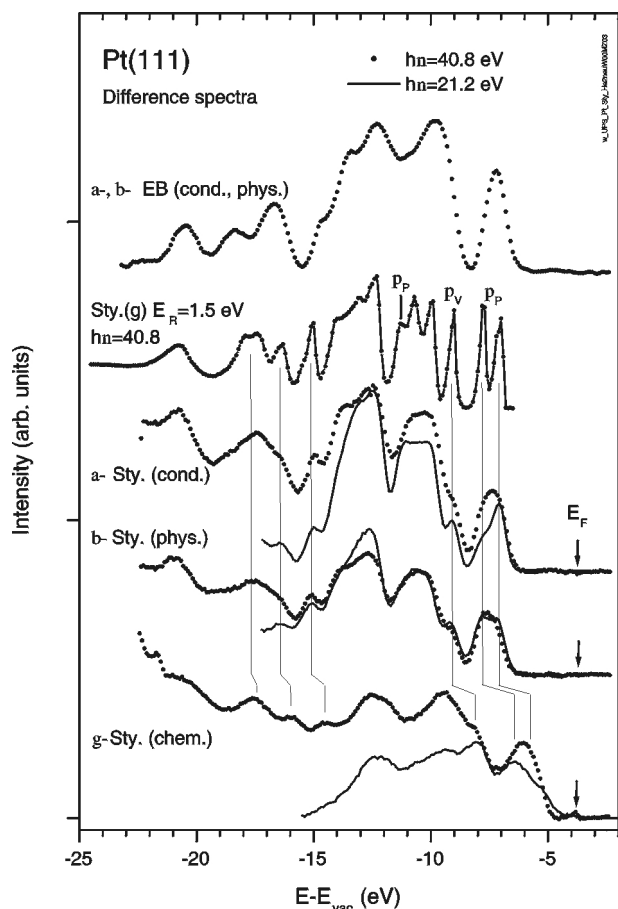


Fig. 5: He I (solid lines) and He II (dotted) spectra of chemisorbed, physisorbed and condensed styrene as well as of condensed ethylbenzene. The energies are given with respect to the vacuum level. The positions of the Fermi level are indicated. The gas phase spectrum of styrene (from [23]) is shifted by a relaxation shift $E_R=1.5$ eV with respect to the adsorbate spectra.

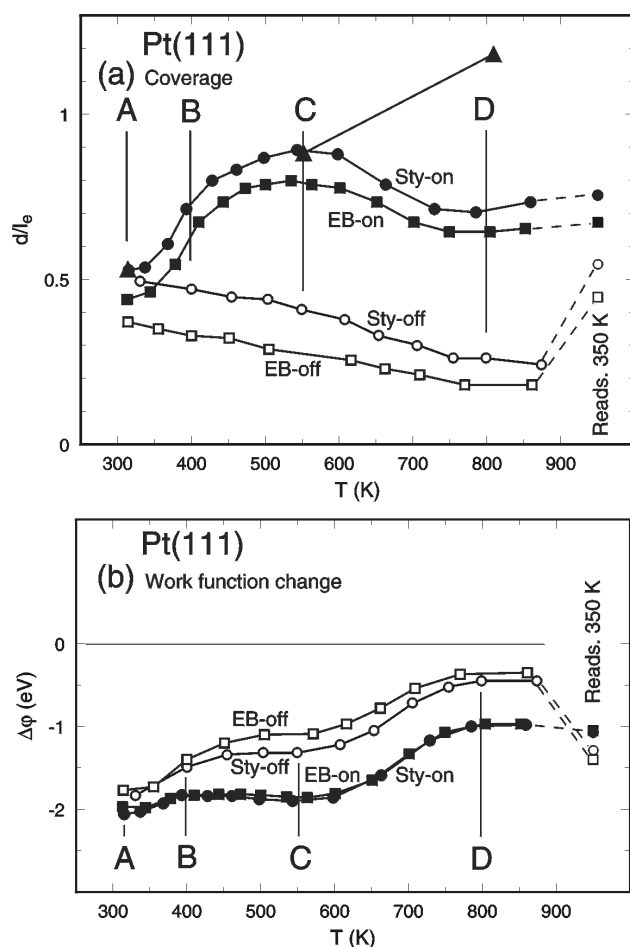


Fig. 6: Development of the adsorbate coverage in terms of d/I_e (a) and of the work function change $\Delta\phi$ (b) upon stepwise annealing of a chemisorbed styrene layer. This layer was produced by exposure to ethylbenzene (EB) or styrene (Sty). Open symbols: without gas admission during the annealing process (EB-off, Sty-off); full symbols: gas admission at 5×10^{-9} mbar during the annealing process (EB-on, Sty-on). Large full triangles: C 1s intensity in XPS taken under the same conditions as for the „Sty-on“ curve and scaled to it at 315 K. The last data points labeled „readsorption“ are taken after exposure to the respective gases at $T < 350$ K.

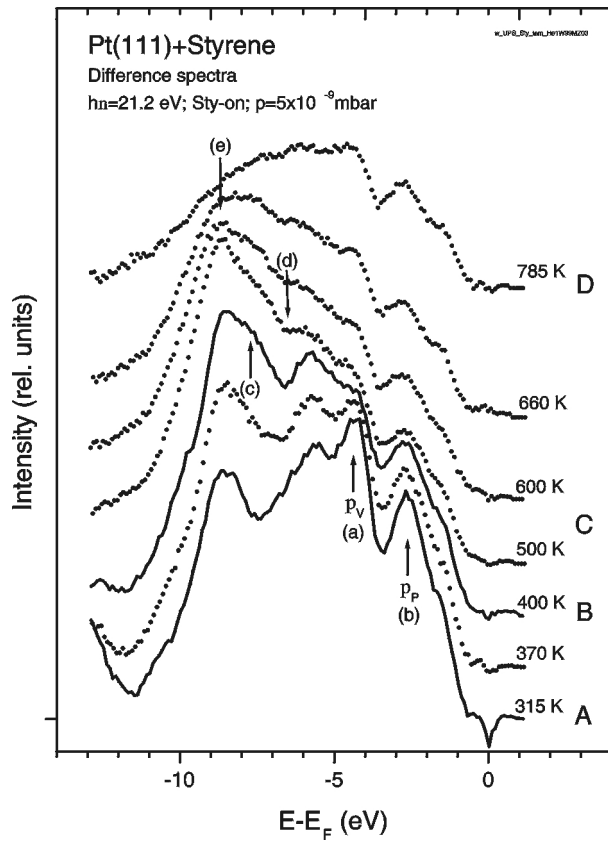


Fig. 7: Background corrected He I difference spectra of styrene chemisorbed at 315 K and annealed to the indicated temperatures. The spectra labeled A to D correspond to the temperatures marked in fig. 6.

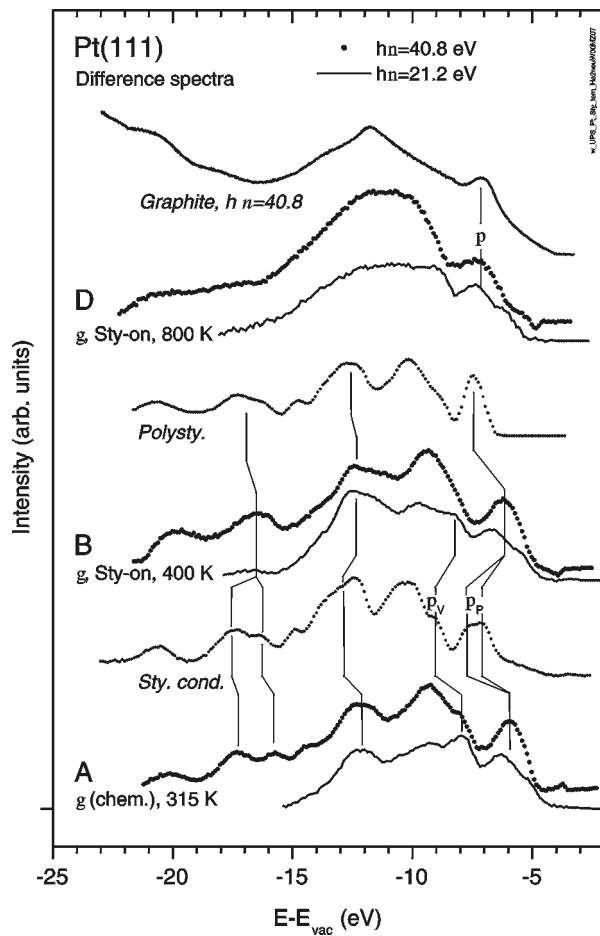


Fig. 8: He I (solid lines) and He II (dotted) adsorbate spectra of chemisorbed styrene, annealed under „Sty-on“ conditions to the indicated temperatures marked in fig. 6. A: chemisorbed (g) at 315 K, compared to the spectrum of condensed styrene. B: g-styrene, annealed at 400 K, compared to the spectrum of spin coated polystyrene (from [25]). D: g-styrene, annealed at 750 K, compared to the spectrum of natural graphite (graphite flakes, from [30]).

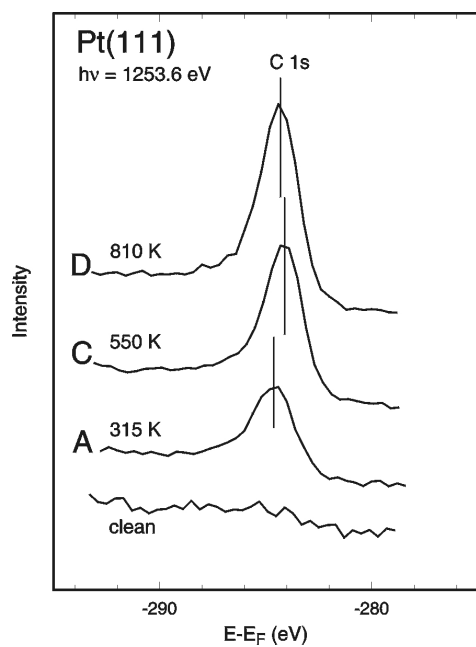


Fig. 9:

C 1s XP spectra of chemisorbed g-styrene (A), of g-styrene annealed under „Sty-on“ conditions to 550 K (C) and 810 K (D), corresponding to the positions marked A, C and D in fig. 6.