



High-pressure X-ray photoelectron spectroscopy on palladium model hydrogenation catalysts

Part2: Hydrogenation of trans-2-pentene on palladium

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Abstract

We have performed the first “high-pressure” XPS study on the palladium, hydrogen and olefin (trans-2-pentene) system in order to gain a better insight into the hydrogenation reaction. We report here data collected using a Pd(111) single crystal and a polycrystalline foil. Hydrogenation was observed on polycrystalline foil (RT and 373 K), but not on Pd(111) single crystal, revealed by on-line mass-spectrometry. We observed the reaction in the presence of huge amount of carbon (up to 73 %) in the information depth of XPS. On Pd(111) mainly graphite was present while other components C–H and C–Pd were also formed on the foil in much higher extent. C–Pd characterizes a carbon species in the interaction with palladium whereas C–H represents hydrogenated carbon including chemisorbed species. The d-band of the foil showed a remarkable up-shift towards E_{FERMI} as compared to Pd(111). We concluded that both differences found in the valence and in C 1s region are indicators for different electronic structures that contribute to the variation in activity. The palladium foil lost its activity at elevated temperature (523 K), most probably due to desorption of hydrogen. Using additional UPS measurements we concluded that trans-2-pentene is hydrogenated in σ -bonded chemisorption modus, at least in UHV conditions.

Keywords: high-pressure XPS, palladium, hydrogenation, carbonaceous deposits, d-band, UPS

Introduction

Group 8 transition metals play an important role in heterogeneous catalytic processes. Palladium, as one of the Group 8 metals, is widely employed in industrial processes [1-7] but also in basic research [8-23] mainly as a hydrogenation catalyst. Its interaction with various gases has been extensively investigated with regard to its catalytic [8-12,14,15,17] and surface properties [13,16,18-23].

Most of the mechanistic studies on alkene hydrogenation have focused on the reaction of ethylene. There is little information in the literature about the hydrogenation involving higher hydrocarbons. The first hydrogenation model proposed in 1934 involves a stepwise addition of the surface hydrogen to the σ -bonded ethylene [24]. Fifty years later, π -bonded ethylene was postulated to be the intermediate of the hydrogenation on Pt surfaces [25]. Recent re-

sults from in-situ spectroscopic methods, namely Sum Frequency Generation, gave support for this model [26]. In the last years the involvement of surface hydrogen in the hydrogenation was often questioned and the role of subsurface hydrogen was pointed out by several authors [21,27,28].

Of great interest is also the effect of carbonaceous species that are present on the catalyst surface during the catalytic reaction. First, carbon was considered just to block surface sites, thus leading to deactivation. Later, however, investigations on “coke selectivity” of different hydrocarbon reactions attributed the enhanced selectivity of non-degradative transformations to the formation of carbonaceous adsorbates that prevent the excessive dehydrogenation of the surface intermediates [29-35]. Various carbon species have been observed on the surface of catalysts, ranging from carbides to hydrogen rich aliphatic polymers.

The chemical state of accumulated carbonaceous species on model palladium surfaces was often a matter of debate [36-40]. The majority of these studies were performed ex-situ or in UHV conditions, far away from the real catalytic conditions (pressure gap).

To arrive at a comprehensive understanding of surface catalytic reaction mechanisms and to identify the factors that govern the activity and selectivity of catalysts, the investigation of structural and surface properties of catalysts should be done under real, working conditions. Additionally, the spectroscopic and structural characterization should be combined with on-line catalytic reaction analysis.

X-ray photoelectron spectroscopy (XPS) is one of the most commonly used surface science techniques; it is very powerful owing to its surface sensitivity. In the first part of our paper we demonstrated the importance of gathering spectroscopic informations under relevant (if possible non-UHV) conditions. In the present part, we report on the first "high-pressure" XPS study of hydrogenation reaction on palladium (foil and single crystal), namely the hydrogenation of trans-2-pentene (t-2-p). The *in-situ* measurements will help us to gain a better insight into the hydrogenation reaction.

Experimental

For experimental details see [Part I]. Briefly, C 1s, Pd 3d and valence band spectra were recorded at normal electron emission. Photon energies of $h\nu = 380, 660$ and 720 eV were chosen for the excitation of the valence band, the C1s and Pd3d core levels, respectively. This insured that the transmission function of the electrostatic lens system had not to be considered since electrons with the same kinetic energies were analyzed and that similar information depth was probed for Pd3d, C1s and VB spectra (inelastic mean free path $\sim 9\text{-}13$ Å). However, higher photon energies were also applied for depth profiling (1160 eV for C1s; inelastic mean free path ~ 24 Å), thus obtaining information on the different surface species along the surface normal. The binding energies were calibrated against the Fermi level of the samples. A Pd(111) single crystal and polycrystalline palladium foil (Goodfellow, purity 99.99 %) were investigated in this study. (Measurements were also carried out on 1% Pd/Al₂O₃ catalysts, but the highly insulating support caused differential charging in such an extent that we were not able to analyze the data.) The hydrogen and trans-2-pentene (t-2-p) gas flow into the reaction cell was controlled using calibrated mass flow controllers. A mixture of 0.6 mbar H₂ and 0.2 mbar t-2-p was introduced, while the temperature was varied in the range from RT to 523 K. Trans-2-pentene was supplied by Sigma-Aldrich (purity 99%), and was purified by several freeze-pump-thaw cycles before the measurements. Gas phase analysis was carried out using a quadrupole mass spectrometer, which was mounted in the second differential pumping stage of the electrostatic lens system, where the pressure is $\sim 10^{-6}$ of the pressure in the experimental cell.

He I UPS (excitation energy 21.2 eV) measurements were carried out in a conventional UHV surface-science chamber. Trans-2-pentene was adsorbed on Pd(111) at 100 K. Multilayer adsorption was achieved by introducing 50 Langmuir of t-2-P (ionization gauge sensitivity corrected). Spectra were measured at different temperatures, from 100 K increased stepwise till RT.

HRTEM investigations were performed in a Philips CM200 FEG electron microscope operated at 200 keV. The microscope was equipped with a Gatan imaging filter (GIF 100) and a Gatan Slow-Scan-Camera in order to enhance the contrast in the images. Cross-section specimen was prepared from a piece of Pd foil that was previously used in the in-situ XPS cell in the hydrogenation of *l-pentyne*.

Results

As already discussed in *Part I*, the palladium samples get quickly contaminated by carbonaceous deposits right after some cleaning treatments because of the high base pressure (10^{-7} mbar) in our experimental cell and also partly because of a beam enhanced carbon accumulation. Nevertheless, under real-life conditions in catalytic reactors the surface of the catalyst will be most likely never ideally clean as in UHV surface science studies. Moreover, the surface quickly adapts to the reaction conditions and the carbonaceous species undergo a massive transformation as pentene is introduced to the gas-phase (see later).

Since the incident X-ray beam does not only irradiate the sample surface but also the gas phase molecules in front of the sample, the *in-situ* XP spectra show gas phase peaks alongside the surface peaks. The binding energy (BE) scale in our Figures is referenced to the Fermi level of the Pd samples, and therefore the apparent BEs of the gas phase peaks are shifted by the amount of the work function of the sample (~ 4.4 eV) relative to literature values, which are conventionally referenced to the vacuum level. Since the vacuum level of the gas phase depends on the vacuum level of the surrounding surfaces (especially that of the sample, since the sample surface is the closest to the detected gas phase volume), changes of the sample work function have an influence on the gas phase peak positions [41]. Small shifts in the gas phase BE position throughout our spectra are therefore a reflection of changes of the work function of the sample surface [42]. *Fig. 1* shows the C 1s spectrum of gas phase trans-2-pentene. The sample was now retracted so that only the gas phase was measured. The spectrum shows a clear shoulder at the low binding energy side and is asymmetrically broadened at the high-BE side. The first rough least-square-fit revealed that at least four peaks are needed to adequately match the measured curve. The first two, main peaks would correspond to the adiabatic ionization of the two different C 1s carbon type, in sp³ and sp² hybridization state. The other two peaks would be due to vibrational excitations [43]. According to the energy separation and the intensity ratios they could be related to the C-H stretching modes of the sp³ carbon atoms with vibra-

tional quantum numbers 1 and 2. However, considering that C(sp²)-H stretching is also present and assuming statistical C(sp³)-H : C(sp²)-H stretching intensity ratios, the fitting analysis provides the picture shown in Fig. 1. The sp³/sp² intensity ratio calculated from the peak fitting is 57 % vs. 43%, which is in good agreement with the expected 3:2 ratio.

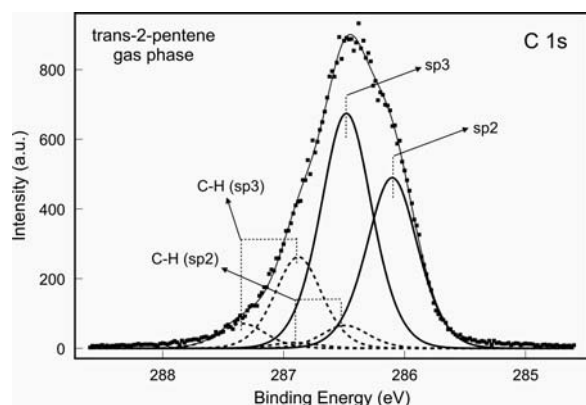


Figure 1: C 1s spectrum of gas-phase trans-2-pentene, $h\nu = 660$ eV. Dots: measured data, full line: adiabatic ionisation and dashed line: C-H stretching modes

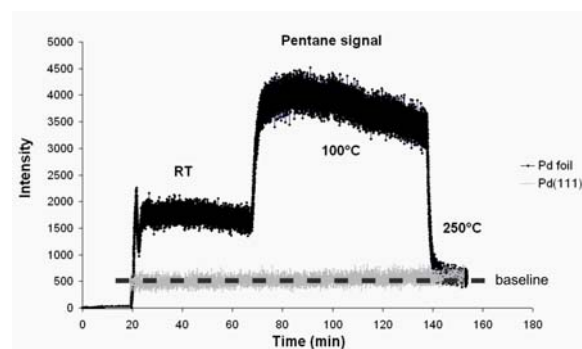


Figure 2: Pentane signal (MS data) in the hydrogenation of trans-2-pentene on Pd foil and on Pd(111). H₂ (0.6 mbar) was introduced first followed by t-2-p (0.2 mbar) at min. 20 (RT). Temperature was increased to 373 K at min. 70 and increased further to 523 K at min. 140.

The hydrogenation of t-2-p over the two palladium samples was measured in our high-pressure XPS set-up. The pentane MS response is plotted in Fig. 2 as a function of reaction time at three reaction temperatures. For both samples hydrogen (0.6 mbar) was introduced first. After 20 min 0.2 mbar t-2-p was introduced. The sample temperature was increased to 373 K after 70 min and to 523 K after 140 min. We observed catalytic activity for the Pd foil sample already at room temperature. The foil reached its maximum activity at ~ 373 K. At 523 K the foil was not active anymore as can be seen from the comparison with the amu “62” baseline. The pentene response (not shown) reveals also no additional pathway at 523 K. Contrary to the Pd foil, the Pd(111) single crystal showed no measurable activity at all temperatures, although the apparent surface area of the foil and the single crystal were comparable.

The inactivity of the single crystal is in line with the TDS results of Doyle et al. [44] measured in UHV conditions.

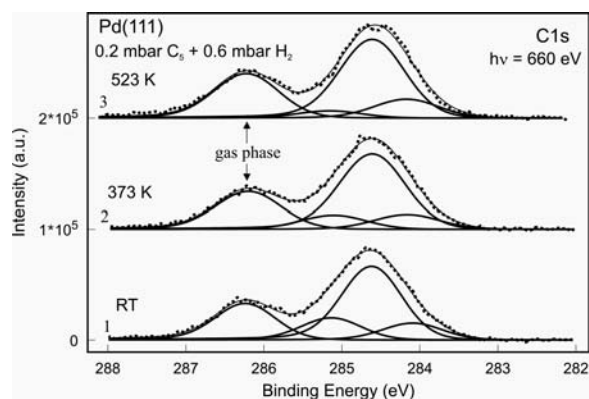


Figure 3: C 1s region of Pd(111) single crystal in the reaction mixture of 0.6 mbar H₂ + 0.2 mbar t-2-p at 3 temperatures (RT, 373 K and 523 K). Incident photon energy, $h\nu = 660$ eV. Dashed line: measured data, full line: fits. The reason for the different height of the gas phase peak is described in [45].

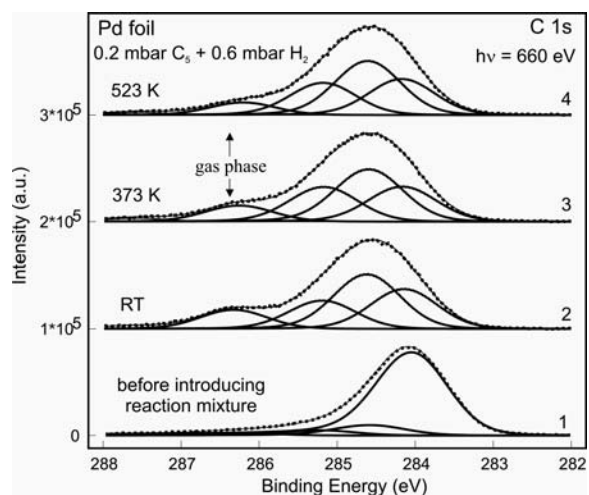


Figure 4: C 1s region of Pd foil in the reaction mixture of 0.6 mbar H₂ + 0.2 mbar t-2-p at 3 temperatures (RT, 373 K and 523 K). The spectrum before introducing the reaction mixture is also included. Incident photon energy, $h\nu = 660$ eV. Dashed line: measured data, full line: fits. The reason for the different height of the gas phase peak is described in [45].

Simultaneous to the mass spectrometric analysis, the surface of the samples was measured by XPS. Fig. 3 and 4 display the corresponding C 1s spectra. With pentene in the gas mixture we see a new peak compared to the spectra presented in Part 1. This peak at ~ 286.2 eV corresponds to the gas phase spectra as in Fig. 1. For the sake of simplicity, the gas phase was fitted here just by one peak (not as in Fig. 1). Concerning the different height of the gas-phase peak, please, read paragraph [45] in References. For the least square analysis the same surface components were used as discussed in Part 1, with the three types of carbon: carbon connected to palladium (C-Pd; 284.1 eV), carbon connected to carbon (C-C; 284.55 eV) and carbon con-

nected to hydrogen (*C-H*, 285.2 eV). Similar to the observation described in *Part 1* for the measurements in H_2 and high vacuum, in the reaction mixture much less carbon was found on the single crystal, and the dominant part of the carbon was also graphitic (*C-C*). When the temperature was increased the *C-H* component on the single crystal decreased (*Fig. 3* curves 2 and 3) until almost vanished at 523 K. An opposite tendency was found for *C-Pd*. Its abundance was the highest at 523 K, while the total amount of surface carbon at 523 K was at its lowest. These tendencies are quite similar to the hydrogen and temperature effects presented in *Part 1*, consequently the single crystal recognizes the presence of pentene rather weakly. Contrary to this, on the foil (*Fig. 4*) the absolute amount of *C-Pd* and *C-H* are much higher at all temperatures. Additionally, the spectrum before introducing the reaction mixture (1) clearly indicates the thorough transformation of the carbonaceous deposits. From RT to 373 K (when the activity increases), *C-H* gets slightly higher and *C-Pd* slightly lower. Interestingly, the C 1s region (at 660 eV excitation energy) reveals no changes coming from 373 K to 523 K, although the catalytic activity disappears. No additional carbonization occurs that might give rise to activity loss. The comparison of the foil with the single crystal however, shows that the foil in the reaction mixture does not follow the tendencies observed in hydrogen. No disappearance of *C-H* and no increase of *C-Pd* were obtained. Please, note as well, that the total carbon content of the foil was rather high (~70%). A very rough calculation of one monolayer of carbon on palladium would give about 45% carbon content using the applied excitation energy and assuming an exponential decay of information with depth. Therefore, as a first approximation, we can consider a full surface coverage, however the situation is far more complex, since the relative position of carbonaceous species (3D islands, on/in/sub-surface) and their abundance would drastically effect and complicate the calculation.

The corresponding Pd 3d spectra in the reaction mixture (not shown) reveal very similar pattern as was already discussed in *Part 1*. (The fitting analysis supplied no clean surface palladium and the spectra were thus fitted by two components, i.e. by bulk palladium and by adsorbate-induced surface Pd.) The tendencies here are similar to those found for the experiment in pure hydrogen, where the surface related component decreased with increasing temperature. This effect was more dominant on the Pd(111) single crystal than on the foil.

One of the essential advantages of using synchrotron as X-ray source is the opportunity to vary the incident photon energy and hence the KE of the photoelectrons. This allows to perform depth-profiling experiments. *Fig. 5* gives a comparison of the C 1s spectrum excited with 660 eV photons (= KE ~ 370 eV) with measurements obtained using higher photon energy (1160 eV). The inelastic mean free path for 370 eV KE electrons in C is ~ 13 Å, and for 870 eV electrons (hv = 1160 eV) is about 24 Å [46]. The comparison of the 373 K spectra shows that the *C-Pd* component is higher and the *C-H* component is lower at higher

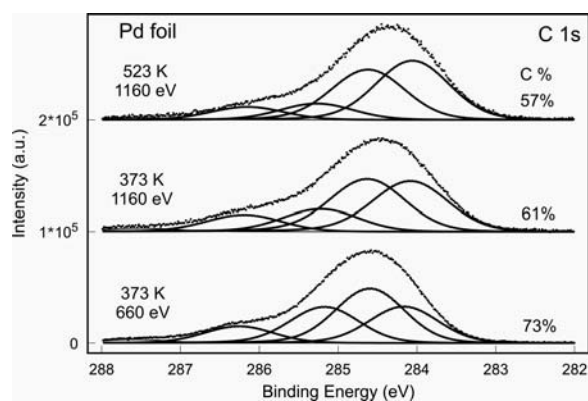


Figure 5: C 1s region of Pd foil at higher incident photon energy (1160 eV) in the reaction mixture at 373 K and at 523 K, compared to the 373 K spectrum taken at 660 eV. Dashed line: measured data, full line: fits.

incident photon energy, meaning that the *C-H* component is situated above the *C-Pd* component, with the *C-C* component in the middle. This indicates that *C-Pd* is located partly *in* the palladium surface and also in the subsurface region, in good agreement with the suggestions in *Part 1*. The distribution of the C 1s species supports our C 1s peak assignment, as well. At higher photon energy the surface sensitivity decreases i.e. the total carbon to palladium ratio is reduced (C%: 73% vs. 61%). Comparing the two upper spectra in *Fig. 5* (hv 1160 eV at 373 and 523 K), we do see some minor differences between the active (373 K) and inactive state (523 K) of the sample. (There was not any difference using 660 eV excitation; see *Fig. 4*) At 523 K the *C-Pd* component is more pronounced, which indicates that the interaction of palladium and carbon is stronger.

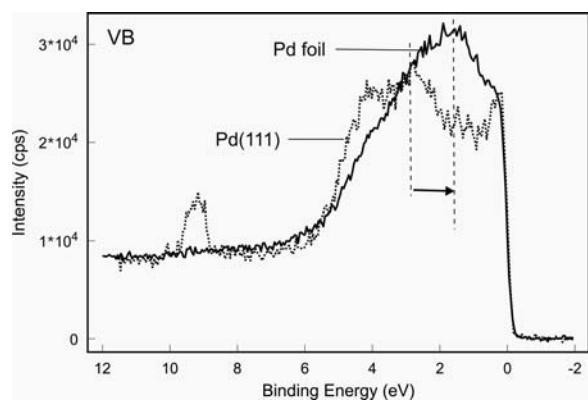


Figure 6: Valence band spectra of Pd(111) (dashed line) and Pd foil (full line) in the reaction mixture (0.6 mbar H_2 + 0.2 mbar t-2-p) at 373 K.

Fig. 6 depicts the valence band of the Pd foil and the single crystal at 373 K, in the reaction mixture, i.e. at the condition when the foil had its highest activity and the single crystal was inactive. The d-band of the foil is distinctly narrower and its center is shifted towards the Fermi-edge when compared to the single crystal. This change of the electron density in the valence region might contribute to the presence or lack of catalytic activity of palladium.

Discussion

The hydrogenation of trans-2-pentene was investigated using high-pressure XPS. In the previous section we have shown that while the single crystal was inactive at all the temperatures applied, the polycrystalline foil was active already at room temperature with a maximum activity at 373 K and a loss of activity at 523 K. In the C1s region we found different types of carbonaceous deposits, as was discussed in *Part I*, and in addition the t-2-p gas-phase peak was also observed. Photon-dependent depth profiling supported the assignment of the C1s peaks to different carbon species. Rather remarkably, the total carbon content of the active sample was 70-80%, but only half of that was observed on the inactive single crystal. The amount of graphitic deposit was just slightly (x 1.1-1.6) higher on Pd foil compared to single crystal. On the other hand, C-Pd and C-H was much more abundant (x 4-10) on the foil. The hydrogen coverage and the amount of solved hydrogen should be on the same order of magnitude for both samples. According to the palladium/hydrogen phase-diagram [47,48] the samples at room temperature should be in the α hydride phase. At 523 K, however, the hydrogen concentration on the surface and in the bulk (subsurface) should dramatically decrease.

In the following part we attempt to answer three questions. 1, what causes the different activities of foil and single crystal? 2, what contributes to the observed activity difference at different temperatures on the Pd foil? 3, How chemisorbs t-2-p on palladium?

Doyle et al. [44] investigated the t-2-p hydrogenation under UHV conditions by TDS on thin film deposited Pd nanoparticles and on Pd(111). The authors found *pentane* desorption only on the nanoparticles and not on Pd(111). It was concluded that the accessibility of subsurface hydrogen should be the key parameter governing the hydrogenation. Hydrogen/deuterium TDS measurements [20,35,49-51] on different palladium surfaces reveal a rather general pattern for hydrogen species, with differences on the order of a factor of 2-10 in the ad(ab)sorption capacity. The presence or absence of different hydrogen species was mainly governed by the amount and temperature of hydrogen exposure and the prehistory of the samples. Introduction of a macroscopic amount (mbar) of hydrogen, contrary to the exposure to just some Langmuir of H₂, populates the available surface and subsurface sites in such an extent that the inactivity of the single crystal *under mbar condition* cannot be caused by the lack of a particular hydrogen type. (Both of our samples were exposed to hydrogen already prior to the introduction of t-2-p.) Since we performed the same measurements with the same hydrogen pressure and temperature on both samples, we believe that it is not the hydrogen availability, which causes the difference in the catalytic activity of our samples. Additionally, the higher carbon content on the Pd foil might represent a higher energetic barrier for hydrogen entering the foil compared to the Pd(111). A major difference is found in the valence band spectra of the samples, where the active Pd foil shows an

up-shift of its d-band – relative to the d-band center of Pd(111) – towards E_F. The reasons for the d-band shift could be variations in the electron density caused by morphological changes (reduced Pd coordination) and the interaction of palladium with non-stoichiometric species e.g. carbon [22,52,53]. As was shown before [54-56] the position of the d-band center can be correlated with chemisorption strength of an adsorbate, and therefore with the reactivity of the system. Other differences between the foil and the single crystal sample are their ability to interact with carbon, to hydrogenate surface carbon and to maintain the hydrogen rich (chemisorbed) state. This can be concluded from the higher absolute amount of C-Pd and C-H components on Pd foil in gaseous atmosphere as compared to the single crystal. As the C-Pd component was assigned to in/subsurface carbon, the much higher C-Pd component on the foil would indicate a much stronger distortion of the palladium lattice (see next paragraph). Interaction of the palladium with carbonaceous entities that are not directly involved in the main reaction can perturb the initial (inactive) state and change the dehydrogenation strength of Pd and thus promote a modified chemisorption strength of t-2-p. We think that the d-band position and the different ability to interact with carbon are interconnected and therefore both are indicators for the activity.

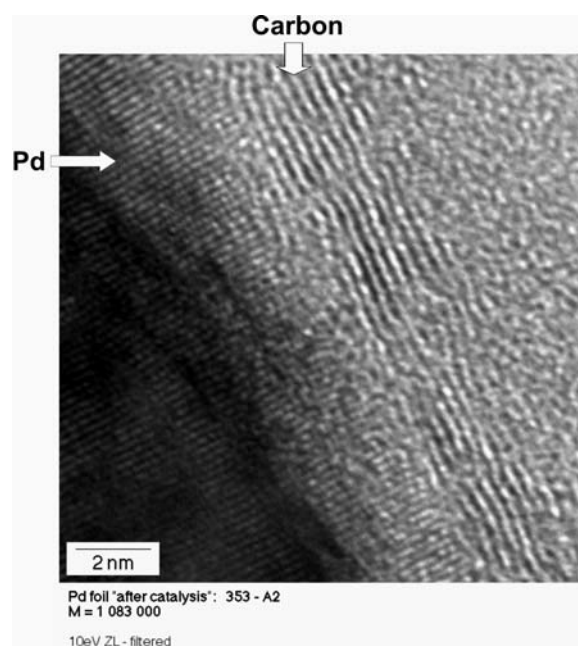


Figure 7: High resolution TEM image of a Pd foil taken out of our in-situ XPS set-up. The sample was used prior the microscopic investigation in the hydrogenation of *1-pentene*.

To understand more complex (selective) hydrogenation, our intention was to increase chemical complexity step by step, starting from a single hydrogenation (t-2-p) and then moving toward systems with multiple functionalities. As a second step, 1-pentyne was used with the possibility to partial and total hydrogenation. In a forthcoming paper [57] we will give a detailed report on that study with

a focus on the morphological changes observed with the palladium foil that was taken out from the experimental cell after reaction. In that system, we observed by XPS also very high carbon content, which apparently did not cause any activity decrease. A representative HRTEM image is shown in *Figure 7*. The high resolution imaging of the “post-reaction” Pd surface revealed in numerous places graphitic structures of up to 10 or 12 graphene layers directly on the Pd surface. The graphitic nature is confirmed by the (002) lattice fringes of the graphene layers with spacing of 0.335-0.355 nm. In a very few cases weaker (100) and (102) graphite lattice fringes were also detected, indicating a higher degree of graphitic order in small regions. On the left side (111) lattice fringes of the Pd surface are clearly visible. (Note that the sample was the same type of palladium foil as was used in the trans-2-pentene study.) Pd (111) lattice fringes near the surface seem to be expanded by a few % in comparison to Pd bulk values. This expansion can be explained by carbon incorporation to the palladium lattice. This incorporated, subsurface type of carbon would fit very well the C-Pd XPS feature and would indicate that a certain degree of lattice distortion is needed to create active centers for hydrogenation reactions.

We will now discuss the effect of temperature on the catalytic activity of the Pd foil. (*Fig. 2*) The Pd foil was active at RT; its activity increased at 373 K and vanished at 523 K. Since we observed no additional reaction path at 523 K and no further carbonization, the blocking of active centers by carbonaceous species can be ruled out as a possible explanation for the deactivation at 523 K. Palladium was most likely in α phase at RT [47,48], and as the temperature increased the reaction rate increased (Arrhenius term) as long as hydrogen was available. TDS measurements on different palladium surfaces [20,35,49-51] show hydrogen desorption mainly in the temperature range of 150-400 K, depending on the initial exposure temperature. The hydrogen partial pressure in our experiment (0.6 mbar in the presence of 0.2 mbar pentene) might not be high enough to populate at elevated temperature the available ad(ab)sorption sites, and therefore the Pd/C/H equilibrium shifts towards the energetically more favorable carbon-palladium interaction. This can be deduced from the slightly higher C-Pd component at 523 K (as compared to 373 K) in the depth profiling experiment (*Fig. 5*). The C-H component at 523 K was still observed indicating no strong dehydrogenation of the chemisorbed overlayer (no loss of hydrogen from carbon). We conclude that under this condition chemisorbed t-2-p is still present on the surface, and therefore at higher temperature the availability of active hydrogen is rate limiting.

Regarding our third question about the chemisorption geometry of trans-2-pentene on palladium, we performed UPS measurements of adsorbed t-2-p on Pd(111). Trans-2-pentene was adsorbed on Pd(111) at 100 K. Multilayer adsorption was achieved by dosing 50 Langmuir of t-2-P (*Fig. 8* upper curve). The UPS spectrum of the multilayer is similar to the gas phase spectrum of t-2-butene [58], showing π and σ contributions, (no gas phase UPS of t-2-p is

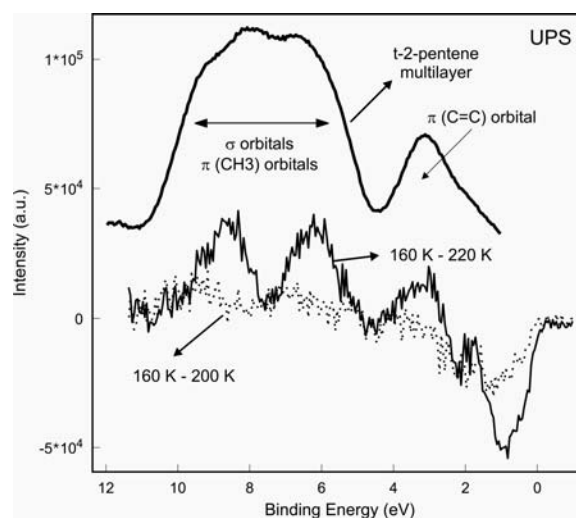


Figure 8: He I UPS spectra (after background subtraction) of multilayer of t-2-p on Pd(111). Difference spectra (160 K – 200 K and 160 K – 220 K) of the chemisorbed layer on Pd(111).

available in the literature). Due to strong desorption in the temperature range of 100-160 K only a chemisorbed monolayer was present at $T > 160$ K. A TDS measurement by Doyle et al. [44] reveals molecular desorption from weakly bound multilayer at ~ 130 K, desorption from π -bonded species at ~ 170 K. In addition a third peak (~ 270 K) was also present, corresponding to σ -bonded pentene molecules. In our experiment we observed no changes in the UPS spectra up to 220 K, thus we believe that the species corresponding to the second TDS peak in Ref. [44] (assigned to π -bonded t-2-p) is also desorbed. However the spectra of the chemisorbed species were rather comparable to the physisorbed t-2-p, indicating no dramatic alteration of the molecule during chemisorption. As the multilayer desorbs the palladium d-band evolves and overlaps strongly with the π orbital of t-2-p. This overlap makes it difficult to unambiguously identify the presence of the π orbital in the original spectra. However, the use of difference spectra can clear this question. At 220 K the UPS spectrum changes dramatically as the π orbital and some contribution from the $\sigma/\pi(\text{CH}_3)$ region were removed (160 K – 220 K curve). Furthermore, the difference spectrum (160 K – 200 K) clearly indicates that the π orbital is present up to 200 K. From this we conclude that t-2-p changes its chemisorption modus at ~ 210 -220 K. The combination of UPS and TDS [44] reveals that, as the π -bonded molecules desorb, there is still σ -bonded t-2-p on the surface. The π bond is intact; therefore the chemisorption occurs via losing hydrogen (probably in position 2 or 3). At ~ 220 K the molecule loses the double bond, and consequently the bonding to the surface changes as well. However the molecule still can desorb as t-2-p (the third TDS peak at ~ 270 K), therefore the changes should not be irreversible. The same adsorption behaviour (TDS) was found on Pd(111) single crystal and on supported Pd clusters. The latter were active in the hydrogenation of t-2-p (pentane desorption). The result of our UPS experiments is, that t-2-p reacts with hydrogen in σ -

bonded chemisorption modus, at least in UHV conditions. Whether this chemisorption modus is transferable to realistic pressures needs further investigations.

Conclusion

The hydrogenation of trans-2-pentene was investigated on palladium foil and Pd(111) single crystal using combined high-pressure XPS and MS analysis. We found activity on the polycrystalline foil sample (RT, 373 K) in the presence of huge amount (up to 70%) of carbon in the information depth of about 1 nm. Pd(111) was inactive, its carbon content was about 40%. The different activity of the two samples was related to their d-band position in the valence band and the widely different distribution of carbonaceous species. The importance of lattice expansion by carbon incorporation was addressed. The foil sample lost

its activity at 523 K, most likely due to hydrogen desorption. Separate UPS measurements revealed that adsorbed t-2-p loses its double bond at about 210 K, and therefore it is the σ -bonded chemisorbed species, which is the intermediate of this hydrogenation, at least at UHV conditions.

Acknowledgements

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the intensity of the gas phase signal depends also on the width of the gas phase irradiated by the X-ray between the sample and the first aperture. Consequently, on the distance of the sample from the aperture. This distance might be not exactly the same for the two samples, contributing to the differences in the relative intensity of the gas phase signal seen in Fig. 3 and Fig. 4. Note that mechanical stress in the heating stage moves also the sample (and its surface) relative to the first aperture; therefore the height of the gas phase peak might not be constant at different temperatures.

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