

Surface State and Composition of a Disperse Pd Catalyst after Its Exposure to Ethylene

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Pd black was exposed to ethylene alone or in its mixture with hydrogen at 300 and 573 K. The samples were investigated by X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS). Room temperature introduction of C₂H₄ (also in the presence of H₂) induced a binding-energy (BE) shift in the Pd 3d doublet and changed its full width at half-maximum (fwhm). The UPS features indicate shifting of electrons from the Pd d-band to Pd–H, Pd–C, and even Pd–OH species. Vinylidene (BE ~ 284.1 eV) may be the most abundant *individual* surface species on disperse Pd black, along with carbon in various stages of polymerization: “disordered C” (BE ~ 284 eV), graphite (~284.6 eV), and ethylene polymer (~286 eV), and also some “atomic” C (BE ~ 283.5 eV). Introduction of H₂ followed by ethylene brought about stronger changes in the state of Pd than exposure in the reverse sequence. This may indicate that the presence of some surface C may hinder the decomposition of bulk PdH. Formation of Pd hydride was blocked when ethylene was introduced prior to H₂. The C 1s intensity increased, the low-binding-energy C components disappeared, and graphitic carbon (BE ~ 284.6 eV) prevailed after ethylene treatment at 573 K. The loss of the Pd surface state and “PdH” signal were observed in the corresponding valence band and UPS spectra. Hydrogen treatment at 540 K was not able to decrease the concentration of surface carbon and re-establish the near-surface H-rich state. UPS showed overlayer-type C in these samples. The interaction of Pd with components from the feed gas modified its electronic structure that is consistent with lattice strain induced by dissolution of carbon and hydrogen into Pd, as indicated by the d-band shift and the dilution of the electron density at E_F.

Introduction

Palladium is a widely used catalyst for the hydrogenation of double bonds.¹ Of various Pd catalysts, Pd black still has a practical importance in partial selective hydrogenation of hydrocarbons² as well as in fine organic chemistry.³ It proved to be superior to supported Pd catalysts in utilizing modifiers for enantioselective hydrogenations.^{4,5} The surface chemical study of the interaction of C=C structures and Pd black may contribute to the fundamental understanding of the surface species present during the hydrogenation reaction. To this end, ethylene, a reactant of rather simple structure was selected. Ethylene π -bonded to the Pd surface was regarded as the intermediate of hydrogenation.^{6–8} Di- σ -bonded entities and ethylidyne were also present,⁹ possibly as “spectator species”. The chemical state of carbonaceous species accompanying ethylene chemisorption (studied mainly on Pd single crystals) was often a matter of debate. Ethylidyne,^{10–12} vinylidene,^{13,14} vinyl-like C₂H₃,¹⁵ and C₁ fragments¹⁴ were suggested. Their behavior and possible coexistence were summarized in a recent review.¹⁶

The aim of the present work was to study the variation of surface state and the possible surface components (carbonaceous residues and hydrogen) after exposing a disperse Pd black to ethylene and H₂. The application of this more complex system extends the knowledge into polycrystalline materials and macroscopic pressures, which may enable us to study even such

effects as carbon or hydrogen incorporation in the bulk phase. The presence of subsurface hydrogen and its interaction with gas phase ethylene has been proved by tritium tracer experiments on Pt black.¹⁷ Recent results¹⁸ pointed to the role of subsurface hydrogen entities¹⁹ also in ethylene hydrogenation over Pd. Their formation may involve structural rearrangement during catalysis and is in agreement with the “flexible surface” model.²⁰ X-ray photoelectron spectroscopy (XPS) showed an increase of the surface concentration of sodium carbonate impurity on a Pd black sample during ethylene hydrogenation and was regarded as an “indicator” of this rearrangement.²¹ Ceyer summarized the role of subsurface H in catalytic hydrogenation (using mainly Ni) and regarded it as a “reactant with a chemistry of its own”.²² Sárkány,²³ in turn, observed the incorporation of C atoms into the metal bulk during hydrogenation reactions. This was preceded by the formation of CH_x fragments on the surface. They were accumulated on low-Miller-index facets, while hydrogen contributed to keep kinks, edges, and other low-coordination sites clean and free for hydrogenation processes.

The present paper reports results obtained on a chemically reduced clean Pd black sample. Since Pd single crystals (even after roughening) were less active in double-bond hydrogenation than small particles,²⁴ the extension of surface chemical studies of this, practically important hydrogenation catalyst seems to be reasonable. Photoelectron spectra were measured after contacting the Pd sample with hydrogen/ethylene mixtures of various concentrations. Although mere evacuation could change the chemical state of chemisorbed carbon inducing the loss of hydrogen,^{6,25} such experiments may supply useful information on the possible amount and state of residual carbon on a disperse sample closer to real-world catalysts.

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Experimental Section

Catalyst and Treatments. Pd black has been reduced from K_2PdCl_4 with aqueous hydrazine²⁶ (sample 5 from that reference). It has been characterized by temperature programmed oxidation.²⁷ Its Brunauer–Emmett–Teller (BET) surface (N_2 adsorption at 77 K) was $7\text{ m}^2\text{ g}^{-1}$ and the particle size 70–100 nm.²⁶ Scanning electron microscopy of various Pt blacks showed aggregation of those elementary particles to give larger, spongelike grains.

Two series of exposure to ethylene have been carried out in the preparation chamber of the electron spectrometer. In series 1, a dry powder sample was placed on a stainless steel sample holder and measured in the “as received” state (0). Next, it was contacted in the preparation chamber of the electron spectrometer consecutively with H_2 at 270 mbar and at 300 K (sample I), with equal mixtures of hydrogen and ethylene (53:53 mbar), II and III. Hydrogen was introduced first, followed by ethylene in sample II, and the reverse order of exposure (ethylene first) was denoted as sample III. The next treatment applied pure ethylene at 53 mbar (IV). Thereafter, an ethylene treatment at 573 K was carried out (V) and finally the sample was heated in H_2 at 540 K (VI). Series 2 applied exposures analogous to III and IV with hydrogen-treated (purified) Pd black (treatment I), denoted as III/2 and IV/2. These treatments, that is, $I \rightarrow III$ or $I \rightarrow IV$, permitted one to distinguish the possible accumulated effect of consecutive exposures. No gas phase analysis could be carried out; the conversions of ethylene could, however, be judged from the pressure drop during exposures. Similar conversions (II, 83%; III, 82%) were found with H_2 /ethylene mixtures, while no pressure drop was observed in the absence of H_2 .

Electron Spectroscopy. Details of electron spectroscopy have been reported earlier.^{21,28} A Leybold LHS 12 MCD instrument was used, XPS used an Al $K\alpha$ anode, and the measurements took place in the pass energy (PE) mode (PE = 48 eV). The binding energy (BE) was calibrated to the Au 4f 7/2 line (BE = 84.0 eV). He I ultraviolet photoelectron spectroscopy (UPS) measurements (excitation energy, 21.2 eV) used a PE of 12 eV. To decompose the C 1s spectra, a mixture of Gaussian–Lorentzian curves (G/L: 0.3 ± 0.05) with a full width at half-maximum (fwhm) of 1.6 were applied. Atomic composition was calculated using homogeneous distribution of the various elements in the information depth.

Results

XPS. The atomic composition of the samples in various states is shown in Table 1. Sample 0 contained some oxygen, as evidenced by a difference spectrum “0–I” (not shown) where the O 1s component (BE \approx 530 eV) appeared as a peak separated from Pd 3p 3/2 (BE \approx 532 eV). The O content of Pd after contacting it with H_2 was negligible, with some O being present as oxidized carbon, as seen in the C 1s region. Hydrogen treatment at 300 K (I) produced a rather clean Pd, with the BE maximum of the Pd 3d peak being at \sim 335.2 eV.^{29,30} Treatments II–IV gave rather similar surface compositions (around 10% carbon), as opposed to the much higher C accumulation in other cases (Table 1). The trace amounts of K (max 0.3% in the untreated sample and below 0.2% after treatments) reported previously³¹ were neglected here. The “as is” sample contained a small Cl impurity (Table 1), in fair agreement with the earlier report for the same catalyst.²⁶ Hydrogen treatment even at 300 K reduced $PdCl_2$ completely; thus, no Cl was detected during subsequent manipulation.

Figure 1a shows the Pd 3d 5/2 peaks after subsequent

TABLE 1: Composition of Pd Black Subjected to Various Treatments

sample	composition, atom %			
	series 1		series 2	
	Pd 3d	C 1s	Pd 3d	C 1s
as is	68	6.5 ^a	70	7.5 ^b
I	96	4	95 \pm 0.3	5 \pm 0.3 ^c
II	89.5	10.5		
III	91.5	8.5	90	10
IV	88.5	11.5	86.3	13.7
			85	15 ^d
V	71.5	28.5		
VI	71.5	28.5		

^a Plus 25.5% O. Cl was not monitored. ^b Plus \sim 20% O and \sim 2.5% Cl. ^c Average of three measurements. ^d An exposure preceded by treating the Pd black by 80 mbar H_2 plus 13 mbar C_2H_4 (cf. sample 2, in ref 21). The sample contained 6.8% C after this previous treatment.

treatments. Normalization and subtraction of the spectra from the cleanest sample (I) was used to indicate changes in spectral shape. The BE(max) value was shifted by \sim 0.1 eV toward higher values after treatment II with the peak becoming slightly more symmetric. Such a change was found to occur when Pd hydride was formed.^{32,33} Surface Pd atoms interacting with adsorbed species (e.g., carbon) have also been found to give a signal at \sim 335.6 eV.³⁴ The BE(max) shift after treatments V and VI can be attributed to these latter species. The fwhm values of the Pd 3d peaks exhibit a peculiar behavior, as fwhm increased upon treatments II–IV (especially II) but was lower at V and VI. The Pd 3d difference spectra (state I subtracted from all other curves, Figure 1b) confirm that a more pronounced BE shift appeared after treatments II, V, and VI. The shape of the difference spectra indicates a BE(max) shift relative to the maximum position of I in all cases. This agrees well with high-resolution XPS data,³⁴ indicating a component at a higher BE after contacting Pd(111) with C_2H_4 .

The difference spectra show a pronounced change in the satellite intensity at \sim 347 eV upon various treatments. Figure 1c attempts to quantify these changes, depicting the satellites with their area calculated after Bezier-background subtraction.²¹ The changes are in good agreement with those shown in Figure 1a and b. The chemical interaction of hydrogen/ethylene mixtures with palladium was more marked when hydrogen was added first (case II); that is, ethylene came into contact with a Pd surface saturated with hydrogen. Much less difference was seen after treatment III, that is, when ethylene was dosed first. Larger differences appeared after treatment IV and especially after V and VI.

The overall maximum BE of the C 1s peak after I was around 284.5 eV. This value was \sim 284.3 eV in cases II–IV (Figure 2a). Approximately 3 times more carbon accumulated upon treatments V and VI (Table 1). The C 1s region was fitted with six lines, but the procedure revealed only four components in samples I, V, and VI. Two different patterns appeared (Figure 2a and b): the main component in samples II–IV had a BE of \sim 284 \pm 0.1 eV. This BE value is close to that attributed to loose hydrocarbon chains attached to deactivated Pt catalyst likely by several bonds to the metal.^{21,35} This peak could also represent ethylidyne or vinylidene.⁹ The component at BE \sim 284.6 eV representing graphite-like entities^{21,28} dominated the C 1s region in I, V, and VI. The component at \sim 286 eV was always present (mainly in II and IV), but its intensity was lower than those of the previous components. This peak corresponds to an aliphatic hydrocarbon polymer, such as ethylene oligomer

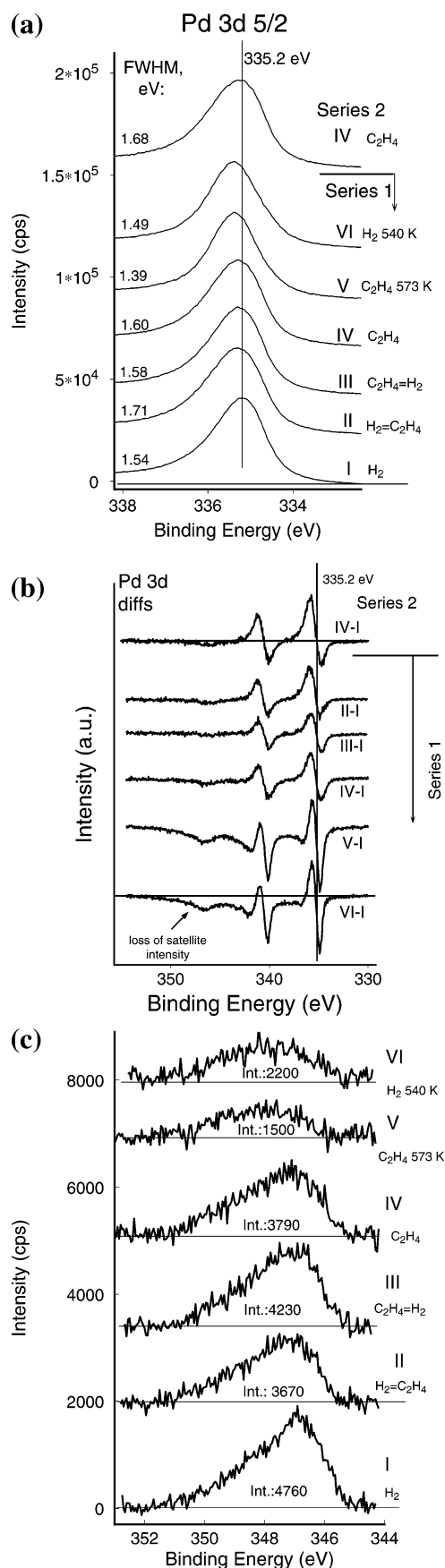


Figure 1. (a) Normalized Pd 3d 5/2 curves and their fwhm values. (b) Difference Pd 3d spectra: spectrum I was subtracted from all other spectra. (c) The Pd 3d shake-up satellites after treatments I–VI after Bezier-background subtraction. The calculated areas are shown on each spectrum.

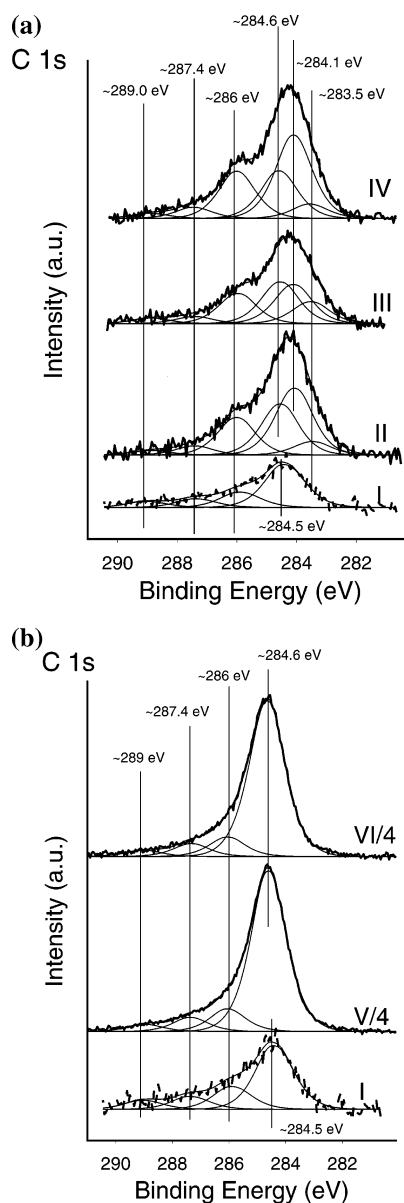


Figure 2. (a) C 1s spectra of samples I–IV and their line fitting. (b) C 1s spectra of samples I, V, and VI and their line fitting (spectra V and VI were divided by 4).

(mostly saturated one). A recent simplified classification^{33,36} distinguished just “C–Pd” at ~284.1 eV, “C–C” at ~284.6 eV, and “C–H” at ~285.2 eV, apart from oxidized carbon at higher BE values. Two small peaks of the latter species appeared: at ~287.4 eV (single C–O bonds²⁸) and at ~289 eV (C=O double bonds). They survived all treatments and can be regarded as impurities.

The effect of different carbon types accumulating during subsequent treatments is shown in Figure 3, comparing the C 1s peak after treatment IV, in series 1 and 2. The difference spectra clearly showed the presence of species at BE ≈ 283.5 and 286.0 eV after treatment IV in series 1, where this followed three previous treatments. The lack of the 283.5 eV species in both treatments of series 2 (as shown in the difference spectra a–b and a–c) indicates that this small component in series 1/IV must have remained on the surface from previous contacts with C₂H₄ + H₂.

The valence band XP spectra of samples I and VI and all difference spectra of series 1 relative to I are shown in Figure

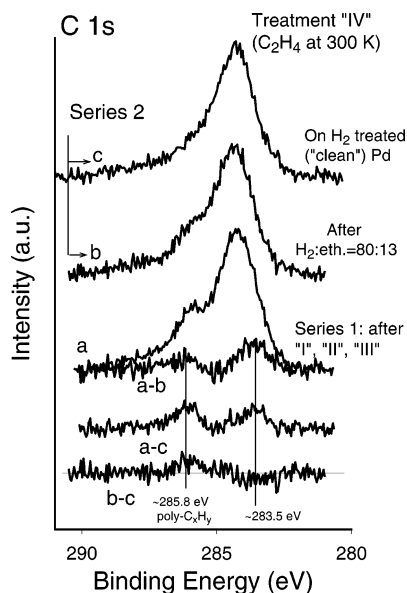


Figure 3. C 1s spectra of IV and IV/2 (treatment IV on H₂-treated Pd black) and that after ethylene treatment with an excess of hydrogen (80 mbar H₂ + 13 mbar C₂H₄) and their differences.

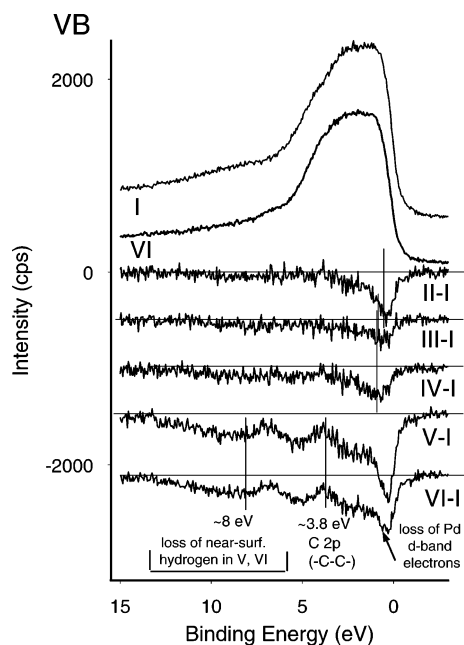


Figure 4. Valence band spectra of two samples and the difference spectra of all samples minus sample I (after intensity normalization at 14 eV).

4. All difference spectra show a minimum just below the Fermi edge, indicating a loss of the d-electron band intensity of Pd after each treatment. Samples III and IV represent the smallest depletion in the Pd 4d density of states. More marked features are visible in the difference spectra V-I and VI-I. The positive feature at ~ 3.8 eV can be attributed to C 2p in $-C-C-$ structures (cf. Figure 2b). The valley between ~ 6 and ~ 12 eV indicates a considerable loss of subsurface hydrogen⁹ in samples V and VI. This feature is almost negligible in the other difference spectra. The small changes in the valence band upon ethylene treatment in III and IV are in accordance with the lowest perturbation of the corresponding Pd 3d peaks (Figure 1b).

UPS. The He I spectrum of the hydrogen-treated Pd (I) corresponded to a clean Pd state, with pronounced Fermi-edge

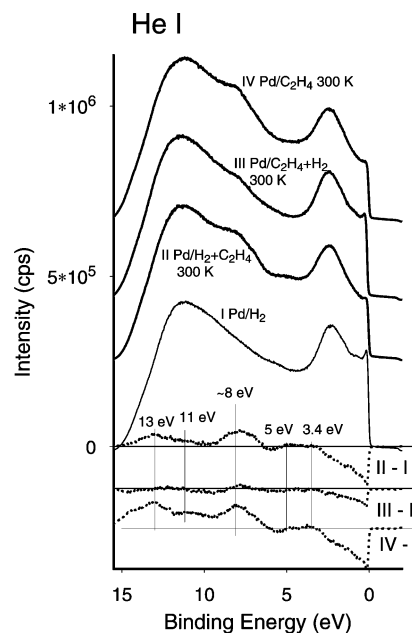


Figure 5. He I spectra of Pd treated at 300 K and the difference spectra with clean Pd (I).

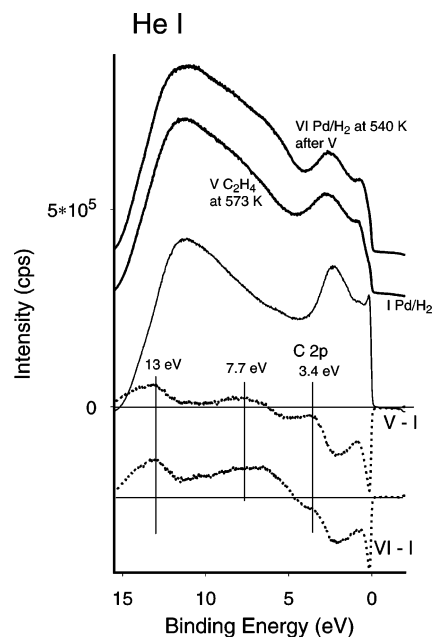


Figure 6. He I spectra of Pd treated at elevated temperatures and their differences with clean Pd (I).

intensity (Figure 5). The difference spectra II-I, III-I, and IV-I show depletion of the Pd d-band electron density. Pd-C (~ 3.4 and ~ 5 eV), Pd-H (~ 8 eV), and Pd-OH (~ 11 and ~ 13 eV) can be suggested on the spectrum II-I, and also on IV-I,^{9,18,32,36,37} together with individual hydrocarbonaceous adsorbates (see below). Features found in III and IV are analogous to those in II. The least pronounced peaks appeared on the difference spectrum III-I.

Difference spectra after high-temperature treatments are shown in Figure 6. Here, the electron density depletion at the Fermi edge as well as at ~ 2 eV is rather large. Three energy regions containing positive peaks are worth mentioning: 3–5 eV, 6–9 eV, and around 12–13 eV. The C 2p intensity growth at ~ 3.4 eV appeared here, too, although it did not reach the zero level of the difference spectrum. The peak at ~ 7.7 eV was broad and resembled the carbon overlayer structure described

on Pt black,^{35,38} rather than a PdH feature.^{39,40} Analogous values (BE \sim 3.6, 7.2 eV) were reported after annealing acetylene precovered Pd(111) up to 470 K and were assigned to C and CH derivatives, respectively.¹⁴ The formation of CH fragments from C₂H₂ and C₂H₄ at 400–500 K was also confirmed by high-resolution electron energy loss spectroscopy (HREELS).¹¹ Similar peak positions (4.9, 7.4, 8.7, and 11.8 eV) and intensity ratios were found upon acetylene chemisorption on hydrogen precovered Pd(111) at room temperature.¹³ Those peaks were assigned as σ -CH₂*, σ -C–C, σ -CH₂, and σ _S*, respectively. The authors strongly argued in favor of them being associated with vinylidene. Lloyd and Netzer¹⁰ observed a pattern with peaks at 4.8, 7.0, and 8.3 eV after ethylene exposure over Pd(111) and interpreted the spectra as originating from ethylidyne. Graphite support for metal clusters gave also a broad peak at about 8 eV.⁴¹ Thus, not only CH fragments but also graphite-like entities as a result of gradual polymerization contribute to the broad feature around 7–8 eV, in good agreement with the main component in the C 1s line (Figure 2b). The quantitative disagreement between the XP and He I spectra of V can be due to the different surface sensitivities of the two methods, with XPS underestimating the topmost surface layer and being more sensitive to detecting the 3D graphitic phase. High-temperature H₂ treatment decreased the peak intensity at 3.6 eV and increased that around 8 eV, with the latter appearing as a broad featureless peak. The changes can be best described as hydrogenating the “disperse” part of the carbonaceous overlayer, converting the C species (3.6 eV) to CH species around 7 eV. No Pd–OH is likely here.

Discussion

XPS and UPS indicate that the surface of a polycrystalline Pd sample was rather pure after a hydrogen treatment at room temperature (sample I). This treatment assumedly created a hydride phase,^{1,29} which, however, must have decomposed during subsequent evacuation. Thus, sample I can be regarded as the cleanest of all Pd samples, and was used as a standard for comparison of treated Pd samples.

The Pd 3d peak (Figure 1), the valence band, and He I UPS all indicated that when hydrogen exposure was followed by introduction of ethylene rather than evacuation (sample II), a surface state rather different from clean palladium (I) arose. The features mentioned, namely, Pd 3d BE shift, smaller shake-up satellite, additional UPS intensity at \sim 8 eV, point to the presence of some Pd hydride in state II which was rather active in ethylene hydrogenation (conversion $>$ 80%). The formation of subsurface hydrogen was not hindered on carbon-covered Pt.⁹ Our present results indicate that carbon-containing surface species formed *after* hydrogen saturation may hamper the decomposition of bulk PdH and desorption of subsurface hydrogen. Of course, the H concentration is much lower here than that reported for a “saturated” hydride⁴⁰ (PdH_x with $x \approx$ 0.65). At the same time, some peaks appearing in the difference spectrum II–I can also arise from vinylidyne or other C and CH species.¹⁴ If hydrogen was introduced after ethylene (III), most of the π -chemisorbed ethylene would be hydrogenated (the conversion was the same as in case II). The residual ethylene was not sufficient to give intense peaks of chemisorbed C_xH_y entities (spectrum III–I). The difference UP spectra after treatment IV were similar to II–I, with the larger and narrower peak at \sim 8 eV indicating, likely, C₂H_x species^{10,13} rather than PdH. The deep negative peak at \sim 2 eV below the Fermi edge after V and VI points to a pronounced transfer of the Pd d-band to binding states of various surface entities (appearing in Figures

5 and 6 as various positive peaks). These were harmful for double-bond hydrogenating activity.

High-resolution XPS was able to differentiate between bulk and surface Pd 3d components^{34,42} situated at 334.95 and 334.67 eV in clean Pd(111), respectively. After dosing five monolayers (ML) of H₂, the Pd 3d peak broadened toward higher BE, indicating a shift of the surface component due to interaction with hydrogen. Introducing 120 ML of C₂H₂ shifted the surface component further (335.51 eV), now clearly distinguishable from the bulk peak. Bearing this information in mind, the observations in Figure 1 are easy to understand. After room temperature ethylene treatments (II–IV), ethylene interacted with the surface component to different extents (as discussed above), shifting the 3d overall maximum and increasing the fwhm. High-temperature treatments (V and VI) decreased the Pd intensity (high carbon content, Table 1) with the highest disturbance of the 3d doublet. The marked loss of the Fermi-edge intensity (see also Figures 4–6) was concomitant with the peaks being more symmetrical and decreasing the fwhm again, even below the original value. The symmetry changes may be connected to the incorporation of other elements: hydride formation³³ and/or incorporation of interstitial carbon in the Pd lattice during treatments V and VI.^{23,43}

C 1s peaks with binding energies between 283.1 and 285.4 eV were reported upon the adsorption of a few langmuirs of ethylene (and acetylene) on Pd surfaces.^{14,44} Exposures at or annealing up to \sim 300 K favored higher binding energies. Two C 1s components at BE values of 283.75 and 284.3 eV were reported after annealing a Pd(111) surface at 300 K which was precovered by hydrogen and exposed to acetylene at 125 K.³⁴ That paper attributed this C 1s doublet to ethylidyne, showing an analogous structure to that obtained on CCH₃/Rh(111).⁴⁵ The decomposition of C 1s in II to IV showed a contribution at \sim 284.1 eV which may indicate analogous surface species. The peak at BE \approx 284.1 eV (Figure 2a) correlates well with the features observed in the He I spectra. They appear only in samples II–IV (Figure 5), where the C 1s contribution at 284.1 eV also appears. Difference C 1s spectra (Figure 3) revealed that a species with a C 1s BE at 283.5 eV was produced in the presence of H₂ (II, III). It might represent C₁ entities, being the precursors of intercalated carbon in the Pd surface.²³ The reality of subsurface carbon was also shown on Pt black where the intensity of the residual C 1s peak increased when an ultrahigh vacuum (UHV)-treated Pt (C \sim 11%) was exposed subsequently to H₂ (C \rightarrow \sim 15%).⁴⁶ This was explained by hydrogen entering in subsurface positions and “pushing” carbon to the surface where it may have partly graphitized.

Various UPS features on single crystals were earlier assigned to individual surface species, such as ethylidyne^{10,12} or vinylidene.^{13,14} The migration of electrons from the Pd d-band to surface species decreased upon introducing ethylene first, followed by hydrogen (III compared to II), indicating the role of H in this phenomenon. All of these are in accordance with the flexible surface concept,²⁰ inasmuch as these H, C, and alkali impurities can affect the reconstruction of the surface.

Olefins adsorb on Pd at low temperature (LT \approx 50–100 K) as π -bonded species, leaving the molecule highly intact.^{14,44,47} Annealing to or direct exposure at room temperature (RT) results in the dehydrogenation of the chemisorbed species and creates new bonds to the surface.⁹ Recent studies show that π -bonded ethylene is the intermediate for hydrogenation as opposed to di- σ -bonded species for pentene.^{24,36,37} Carbonaceous entities that are not directly involved in the reaction can block certain sites or can change the flexibility of the surface.^{20,46} Lattice strain

caused by interstitial carbon atoms can also be the origin of peculiar selectivities. Annealing at higher temperature (V) can decompose RT species, leaving behind C and CH_x and creating a three-dimensional graphitic phase (Figure 2b). High-temperature hydrogen treatment at 540 K (VI) restructured the disperse part of the overlayer but was not able to remove the massive phase (Figure 6). A stable PdC_x phase, containing up to 10 atom % carbon was observed upon ethylene treatment at 473 K.⁴³ Another paper⁴⁸ reported $x \approx 0.06$ at 423 K. The shift of the d-band (as indicated by the minimum at ~ 2.2 eV in Figures 4 and 6) and the loss of electron density at the Fermi edge could be induced by penetration of carbon in the Pd lattice at higher temperature. This effect correlates well with the highest disturbance of Pd 3d. Similar strong attenuation of the Fermi edge was detected after annealing Pt(111) pre-exposed to ethylene or acetylene at temperatures up to 500 K, although the carbonaceous ionization features were more or less removed.^{12,15}

The present studies reveal that the surface spectroscopy of Pd black exposed to macroscopic pressures of ethylene at ~ 300 K exhibited more or less similar features of the surface carbon-containing residues as observed on single crystals with much lower exposures. Thus, the surface science approach with well-defined surfaces and exposures can answer questions coming from the catalytic community. On the other hand, despite a lot of useful information,^{21,49,50} the use of dispersed materials and macroscopic pressures cannot tackle all important problems if used quasi-ex situ. Real in situ techniques, such as a specially built high-pressure XPS,^{33,36} would be more helpful to obtain appropriate answers for catalytic research.

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