IDENTIFICATION OF THE STATE OF PALLADIUM IN VARIOUS HYDROGENATION CATALYSTS BY XPS

Klaus NOACK and Heinz ZBINDEN

Central Research Units, F. Hoffmann-La Roche & Co.A.G. CH-4002 Basel, Switzerland

and

Robert SCHLÖGL

Fritz-Haber-Institut, Faradayweg 4 D-1000 Berlin 33

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Various commercial supported palladium hydrogenation catalysts were studied by XPS and treated at ambient pressure with hydrogen and air. Unused catalysts exhibit a significant fraction of divalent Pd (oxide) which is reduced by hydrogen treatment at room temperature. Exposure to air in systems with carbonate, alumina, silica or active carbon as support causes the formation of a solid solution of oxygen in Pd characterized by a Pd 3d chemical shift of ca. +0.4 eV. The absolute binding energy of Pd depends strongly on the matrix, indicating a significant contribution of extra-atomic screening, which prevents a direct comparison of reference samples and supported catalysts. Using the oxidation of CO to CO_2 at 300 K as in situ chemical probe it was confirmed that Pd supported on carbonate, silica and alumina exists in the same metallic state which could be activated for the test reaction irrespective of the variation in XPS binding energies.

1. Introduction

Palladium on various supports is widely used as a heterogeneous hydrogenation catalyst. Photoelectron spectroscopy can be applied to determine the chemical nature of the active species and in particular to elucidate any differences in the electronic structures of these materials which may determine their vastly different catalytic activities and selectivities.

The so-called Lindlar catalyst consists of Pd on calcium carbonate, modified with lead. This system has recently been studied in detail [1,2], revealing the complex nature of the active phase. High resolution electron microscopy revealed the existence of aggregates of Pd particles in the less selective catalysts and the

predominant presence of thin platelets of Pd exposing preferentially the (111) orientation in the high performance catalysts. Both morphologies seem to co-exist on various catalysts [1,8].

The determination of the chemical state of Pd from core level shifts proved difficult because of experimental problems with surface differential charging and for more fundamental reasons arising from considerable variations in absolute binding energy data for various forms of palladium in the literature. Thus several catalyst systems were compared to bulk Pd powder samples as reference materials. The binding energy of Pd $3d_{5/2}$ with 335.3 + / − 0.1 eV (Au 4f = 84.0 eV) [3] of bulk polycrystalline metal will be used as reference. Divalent palladium in PdO as a thin layer on a single crystal [4] or on a foil [5] exhibits a shift of +1.6 to +2.0 eV.

2. Experimental

XPS and UPS spectra were measured on a Leybold UHV-LHS11 surface analysis system, equipped with a high pressure cell which permitted treatment of the samples with different gases up to a pressure of 10 bar and transfer directly into the measuring position. The samples could be heated in situ up to 900 K. The base pressure of the system was $1*10^{-9}$ mbar. spectrometric measurements of the CO_2 resulting from the oxidation of CO by the oxygen incorporated in the catalysts were made with a Leybold Quadruvac PGA100 quadrupole mass spectrometer attached to the above UHV-LHS11 surface analysis system. The treatment of the catalysts prior to this measurement was as follows:

The sample was reduced with $1*10^{5}$ Langmuir H_2 (20 min. $1*10^{-4}$ mbar H_2) in the measuring position. N_2 and O_2 exposure took place in the attached preparation chamber for 10 min. at 1 bar. For the air treatment, the sample was positioned outside the instrument for 10 min.

The reaction of CO with the surface or subsurface oxygen was followed by monitoring the 44 dalton mass signal (CO_2) in the following fashion (see also fig. 6):

1) Mass 44 background with the sample in the measuring position under UHV
2) Mass 44 during exposure of the sample to $5.2*10^{-7}$ mbar CO
3) Mass 44 background at $5.2*10^{-7}$ mbar CO with sample removed from the measuring chamber.
4) Mass 44 background (UHV, without sample).

The difference (2-1) minus (3-4) is an indication of the reaction $CO + O = CO_2$ on the catalyst. This procedure is required to discriminate between CO_2 resulting from the catalytic oxidation and desorption from the support materials.

All materials and catalysts were of commercial origin. The characterization of the Lindlar catalysts (5% Pd + 5% Pb on $CaCO_3$) is given in ref. [1]. The following were from Degussa: 5% Pd/Al_2O_3, Type E207 N/D, BET surface area

400 m^2/g (all BET informations from supplier). 5% $Pd/CaCO_3$, Type E 406 R/D, BET surface 10 m^2/g. 5% Pd/SiO_2 (Aerosil), Type E 31 B/D, BET surface 200 m^2/g. From Heraeus: 5% Pd + 5% $BaCO_3$ (no information on BET surface). From Fluka: PdO (sample A), ca. 78% Pd and from Degussa: PdO (sample B) 86.86% Pd.

3. Results

REFERENCE MATERIALS

Pd-black. Figure 1 shows the Pd $3d_{5/2}$ spectrum of a Pd-black sample "as delivered" (a) and after heating to 775 K (b), a procedure which is intended to decompose any oxide precursors present. It is clearly seen that the original Pd-black has two Pd $3d_{5/2}$ maxima, at 336.8 (oxide) and 335.3 eV (zerovalent palladium). The peak at 336.8 eV disappears after heating. The line at 335.3 eV is insensitive to hydrogenation of the palladium at 300 K and 2 bar for 30 min. This is in line with other observations [1,6] which find no or very small chemical shift for hydrogenated palladium. In a reference experiment palladium foil hydrogenated under the same conditions did not show any core level shift and a subsequent study by X-ray diffraction revealed the formation of beta Pd hydride as the dominant crystallographic phase.

The treatment of Pd-black was also studied with HeI-UPS as shown in fig. 2. In the "as delivered" state the Pd-black exhibits a small fraction of metallic

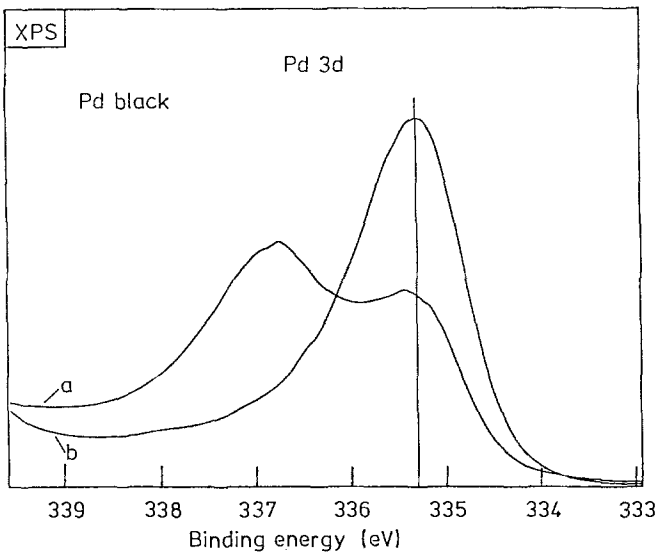

Fig. 1. Pd black, XP-spectra. (a) Pd $3d_{5/2}$ at 300 K, (b) after heating to 775 K.

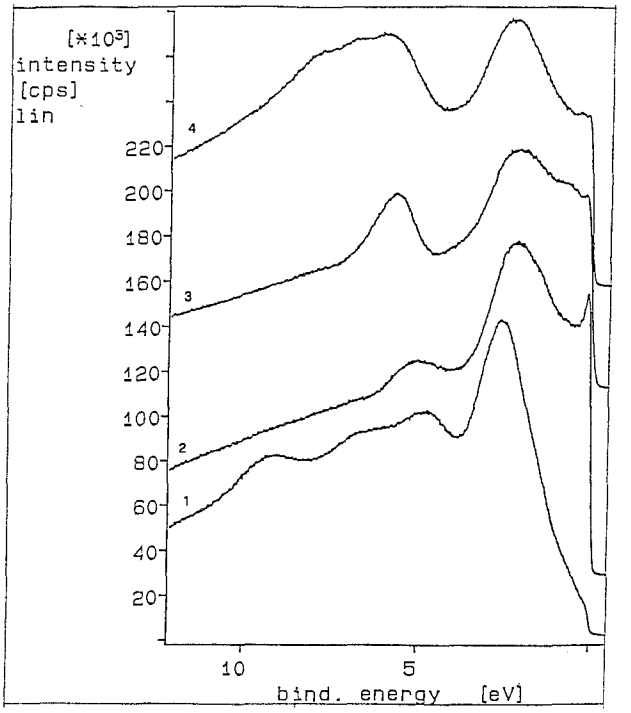

Fig. 2. UP He I spectra of Pd black. 1. as delivered, 2. after 3 hrs at 775 K, 3. after 36000 Langmuir H_2 at 300 K, 4. after 20 min. 2 bar H_2.

surface (step at the Fermi energy, E_F) and a dominant narrow Pd 4d band which is characteristic of a chemical compound (spectrum 1 in fig. 2). The features between 5 and 10 eV are attributed to oxygen 2p states of atomic (5.5 eV) and molecular species like water and OH (6.5 eV, 9.5 eV) [7]. Thermal decomposition at 775 K for 3 hrs in situ leads to entirely metallic palladium characterized by the broad d-band containing the Fermi edge with a small surface state superimposed (spectrum 2 in fig. 2). The peak at 5.5 eV indicates the presence of atomic oxygen. We ascribe this species to subsurface oxygen since an attempt to hydrogenate it at 300 K and 36000 Langmuir H_2 exposure caused the oxidic species only to increase in concentration (see spectrum 3 in fig. 2). The shift of the oxygen peak to 5.8 eV after the hydrogen treatment is due to segregated surface oxygen (cf. quenched surface state at E_F) and not to palladium hydride as it was shown in [6]. An increase of the hydrogen pressure to 2 bar with 30 min. exposure caused the formation of hydroxyl groups as result of the hydrogenation of subsurface oxygen (spectrum 4 in fig. 2). In reference experiments with clean Pd foil it was demonstrated that gas phase impurities or transfer artifacts could not have caused the structures in the top spectrum of fig. 2. These changes in the chemical state of the surface are not detected by XPS, only a damping of the 3d–4d shake-up transition after high pressure hydrogenation was observed. XPS of powdered Pd

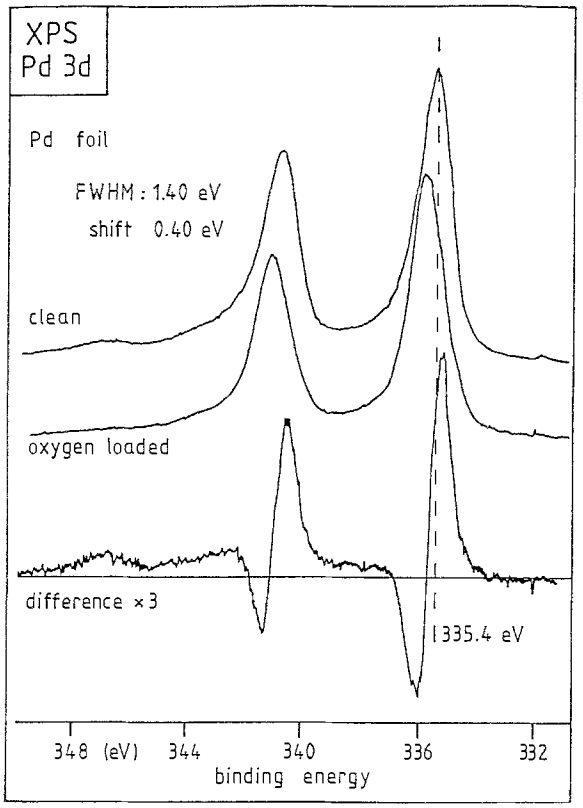

Fig. 3. XPS of clean and oxygen loaded Pd foil.

metal is thus insensitive to the presence of hydrogen or small amounts of dissolved oxygen.

The subsurface oxygen can not only be generated by reduction of oxides as in [5] or in the present example but may be introduced in clean palladium by exposure to oxygen at pressures above ca. $1 * 10^{-3}$ mbar at room temperature. In this way a concentrated Pd + O phase has been prepared [3]. In fig. 3 the formation of the Pd + O phase characterised by UPS, ISS and AES and temperature programmed reaction profiles of CO oxidation is demonstrated using high resolution spectra of the Pd core level. A change to a symmetric line shape can be seen resulting in a shift of the peak maximum of +0.4 eV upon incorporation of large amounts of oxygen. A fuller discussion of this effect is presented elsewhere [3]. Any quantification of the amount of oxygen by XPS is difficult since the concentration profile within the depth information is not known.

In summary, these data show that metallic particles of palladium exhibit a b.e. of 355.3 eV irrespective of the presence of hydrogen (hydride) or surface chemisorbed oxygen or water. High concentrations of oxygen below the surface result in a shift or 0.4 eV, whereas oxidation to divalent PdO causes a significantly larger shift of +1.6 to 2.0 eV [4,5].

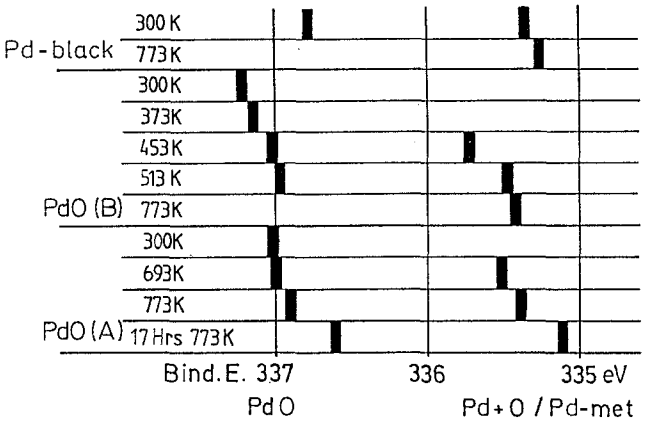

Fig. 4. Schematic positions of Pd $3d_{5/2}$ binding energies of Pd black and PdO on heating.

PdO. Two different samples of PdO powders were heat treated in situ. In the first sample (A) at 300 K there is a sharp O 1s peak at 530.3 + /− 0.05 eV near the Pd $3p_{3/2}$ line which persisted even on heating to 773 K as shoulder on the shifting Pd $3p_{3/2}$ peak.

The effects of treatment at various temperatures on the binding energy of the Pd $3d_{5/2}$ are summarized in fig. 4. For sample A at 300 K only one peak with b.e. 337.0 eV is present. It shifts with heat treatment continuously towards lower b.e. and at 693 K a second peak at a distance of 1.5 eV appears. Both Pd $3d_{5/2}$ peaks shift to lower b.e. on further heating and persist even after 17 hours at 773 K in UHV, whereas the O 1s remains at its initial position.

The second sample (B) behaves somewhat differently upon heating. Its O 1s peak exhibits a b.e. of 530.9 eV at 300 K. The Pd $3d_{5/2}$ peak, corrected for the oxygen b.e. shift of 0.6 eV is situated at 337.2 eV and shifts towards lower b.e. upon heat treatment. At 453 K a second peak appears at a distance of 1.3 eV to lower binding energy. Upon further heating to 773 K both peaks shift and the high b.e. peak disappears.

We state the continuous shift of both Pd peaks for the oxide and the metal in both samples over a range of 0.4 eV. The shift is not due to charging effects since the corresponding UP spectra exhibit electron density at the Fermi edge and show a constant position of the Pd 4d band edge.

CATALYSTS

a) $Pd/CaCO_3$ catalysts. We report here briefly the main results of in situ treatment of $Pd/CaCO_3$ catalysts with H_2, O_2 or air. Typical spectra of a Lindlar catalyst ($Pd/CaCO_3$, treated with a lead salt) are displayed in fig. 5. Commercial Lindlar catalysts showed a complex Pd 3d spectrum, the features of which could not be correlated with catalytic properties [1]. If those catalysts are treated with 1

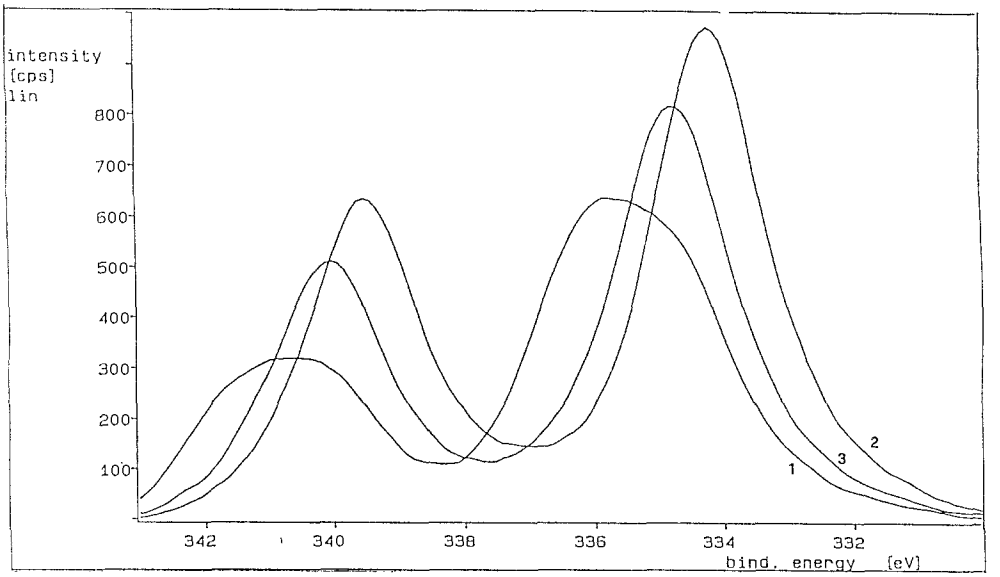

Fig. 5. Lindlar catalyst. XP spectra of the Pd 3d region, 1. as delivered, 2. after 10 min. 2 bar hydrogen, 3. 1 bar ambient air after hydrogen treatment.

bar H_2 for 10 min., the complex features in the Pd 3d spectra disappear and a single sharp Pd $3d_{5/2}$ emission is observed with a b.e. of 334.9 eV, referenced to the Ca $2p_{3/2}$ peak at 347.5 eV. If the sample, after the XPS measurement under UHV conditions, is treated with 1 bar O_2 or ambient air, a new peak at 335.4, shifted by 0.5 eV to higher b.e., is consistently observed (fig. 5). After a new hydrogen treatment, the peak shifts again back to 334.9 eV. If, however, the sample is exposed to air after previous hydrogen treatment and without UHV pumping, the identical b.e. of 334.9 eV as directly after the H_2 treatment is obtained.

$Pd/CaCO_3$ catalysts with and without lead modification do not differ in their behaviour on these treatments.

b) Pd on other supports. Similar experiments (reduction with H_2 and subsequent treatment with O_2) as with $Pd/CaCO_3$ were also performed with Pd on $BaCO_3$, Al_2O_3, SiO_2 and on carbon. Table 1 summarises the results. The Pd $3d_{5/2}$ b.e.'s of the hydrogen treated samples are given first. Their absolute values depend on the chosen reference lines which are indicated in the table. For comparison, a $Pd/CaCO_3$ sample is also included. The shift of the Pd $3d_{5/2}$ due to the oxygen treatment is shown in the second column. Catalysts supported on $BaCO_3$, Al_2O_3 and SiO_2 show a similar shift of some tenths of an eV as $Pd/CaCO_3$. Palladium on active carbon was somewhat different from the other samples. The conductivity of the support was such that no charging correction had to be applied. Furthermore, the conducting sample gave rise to a much narrower line width of

Table 1

Sample	b.e. after H_2 treatment (eV)	b.e. shift after O_2 treatment (eV)
$Pd/CaCO_3$	334.9	+0.5
$Pd/BaCO_3$	334.2	+0.2
Pd/Al_2O_3	335.5	+0.5
Pd/SiO_2	334.7	+0.5
Pd/C	335.5	+0.2
Pd/C (+Pb)	335.5	+0.2

[1] referenced for Ca $2p_{3/2}$ = 347.5 eV
Ba $3d_{5/2}$ = 780.2
Al 2p = 74.7
Si 2p = 103.4
Cl s = 284.5.

the Pd $3d_{5/2}$ line (1.26 eV in comparison to 2.6 eV for $Pd/CaCO_3$). The narrow line allows the identification of a small fraction of divalent Pd which resisted hydrogen reduction and increased after oxygen treatment at room temperature. The oxygen treatment also affected the b.e. of the support. Difference spectra of the C 1s line showed that some oxidation of carbon had occurred increasing the C 1s intensity at ca. 286 eV and broadening the O 1s peak. The dispersion of Pd was remarkably high for a carbon support and remained completely unaffected by all chemical treatments.

It was observed that the Pd 3d b.e. of the oxygen-treated Pd/SiO_2 shifts slowly back towards the position prior of the oxygen treatment during the accumulation of the XP spectra. In 60 min. half of the shift is reversed. The value in table 1 was taken after about 5 min. acquisition time. The b.e.'s of the other samples are not shifted after 1 hr of measurement.

A further qualitative observation concerns the apparent dispersion of Pd on the various supports. In those cases where we observe a chemical shift upon treatment with oxygen, the ratio of the Pd 3d intensity to a core level of the support diminished by 5–20%.

c) Reaction of carbon monoxide with oxygen in the catalysts. In order to probe the presence of chemically active oxygen the catalysts were treated with CO in situ and the resulting CO_2 was monitored as described in the experimental part. Figure 6 shows the result of two such experiments with hydrogenated (A) and oxygen treated (B) Lindlar catalysts. It can clearly be seen that only the oxygen treated sample produces catalytically CO_2. XPS spectra of the Lindlar catalysts were taken before and after the reaction with CO. The Pd $3d_{5/2}$ b.e. after the reaction with CO was again the same as before the oxygen treatment of the H_2-reduced sample. This proves the removal of the oxygen by the CO treatment and shows the correlation of the XPS shift with the presence of oxygen in

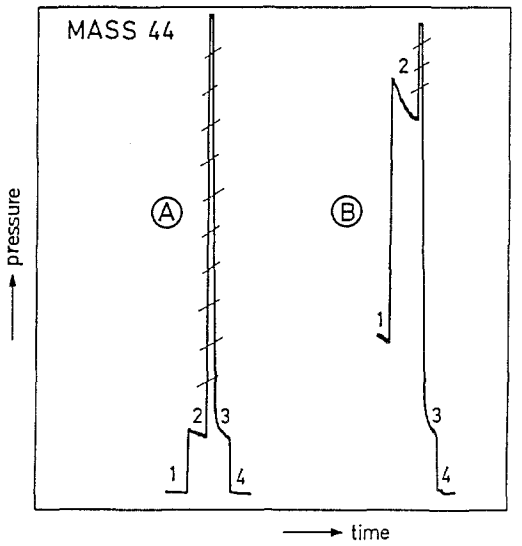

Fig. 6. Reaction profil of CO oxidation, A. hydrogen-reduced Lindlar catalyst, B. Lindlar catalyst air exposed after hydrogen reduction. The reaction rate is proportional to the difference in height of the steps (1-2) and (3-4) (see experimental part). Experiment A shows no catalytic activity for CO oxidation, in experiment B the oxygen on the Pd oxidises CO to CO_2. The high spike between 2 and 3 is an artifact of the sample transfer.

zerovalent palladium. Similar experiments with identical results were also performed on Pd foil loaded with oxygen [3]. Pd/SiO_2, Pd/Al_2O_3 and Pd/C also form CO_2 from CO in their oxygenated state under similar conditions. A qualitative estimate of the intensities of the CO_2 signals referenced to the quantity of sample shows that under identical conditions Pd/SiO_2 and Pd/Al_2O_3 give off only about 1/6 of the amount of CO_2 from $Pd/CaCO_3$ and Pd/C.

4. Discussion and conclusions

The *reference experiments* showed for polycrystalline materials at realistic hydrogenation conditions the following chemical effects:

a) There is only metallic Pd present at 1 bar H_2 and 300 K irrespective of any precursor oxide.

b) H_2 and small amounts of O_2 do not affect the b.e. of metallic "clean" Pd. Large amounts of subsurface oxygen lead to a shift of the Pd $3d_{5/2}$ b.e. of $0.4 + / - 0.1$ eV to higher b.e.

c) The reactivity of PdO towards thermal decomposition to Pd was found to be different for different samples. The less stable form leads to spectroscopically pure Pd, the more stable form leads to Pd with significant amounts of oxygen remaining in the sample. The different reactivity may be due to the presence of

structural OH in the less stable sample ($PdO_{1-x}OH_x$) and a different thermal pretreatment during manufacture of the commercial samples.

d) Intermediate stages in the thermal decomposition of PdO comprise mixtures of Pd metal and Pd oxide. The variation in b.e. of the oxide and of the metal is ascribed to extra-atomic screening effects arising from the intimate contact of metal nuclei in the oxide (beginning of the process) and of oxide remaining enclosed in metal particles (end of the process). The screening is particularly large for Pd because of the dramatic difference of the density of states near E_F on transformation of oxide to metal (see height of the Fermi edge feature in fig. 3). A possible cluster effect on the b.e. due to very small particle size is excluded from ex situ XRD measurements showing only varying fractions of crystalline oxide and metal with no pronounced change in line shape during reaction. The N_2 BET surface area measured on sample A as a function of reaction progress increases only slightly from 0.7 to ca. 2 m^2/g for the reduced material which is also consistent with large particles interconverting internally via growth of metal nuclei within the oxide matrix to large metal particles. The increase in surface area is likely to be due to formation of porosity as consequence of oxygen gas evolution.

The *results on the catalyst samples* allow the following *conclusions* to be drawn:

The in situ treatment with 1 bar hydrogen at room temperature removes all surface differential charging, i.e. the charging corrections using support signals as reference lead to the "true" b.e. of Pd. In all examples of table 1 the charging correction was done either with the cation, the contamination carbon or the hydroxylated oxygen from the support as standard and all methods gave, within 0.2 eV, the same results. The "true" b.e.'s of the various samples in table 1 differ far more than the experimental error. The chemical state of the supported Pd in the hydrogen-treated as well as in the subsequently oxygen treated samples is always metallic. This is shown for the oxygen treated samples by the chemical probe of Co-oxidation (only metallic Pd catalyses this reaction). These experiments which in all cases gave CO_2 only after preloading of Pd with oxygen show that the initial state (after hydrogen treatment of the as-received material followed by UHV pumping) is metallic Pd free of oxygen of hydrogen. The in situ gas charging experiments showed that supported Pd particles can occur in this "initial" reactive state (clean). When this material is loaded with hydrogen (removable by UHV pumping) or oxygen (removable by chemical reaction such as CO oxidation) it becomes inert towards oxidation to PdO at 300 K in air. We thus conclude that the b.e. of supported clean Pd particles cannot be compared to bulk metal or between different catalysts. The apparent XPS shifts of table 1 are not chemical shifts but are characteristic of Pd in different support environments, i.e. they are extra-atomic screening shifts. This Madelung shift which is caused by the electrostatic field of the support ions in close contact to Pd or by a large difference in the morphology of the Pd particles (clusters vs. large particles) contains information on the metal-support interaction. An interpretation of the

data in table 1 in these terms requires additional information on dispersion and particle morphology and will not be pursued here. These phenomena also control the activity of the samples in the CO oxidation reaction which is, therefore, not interpreted here in a quantitative way. The extra-atomic screening effect does not prevent spectroscopic discrimination by XPS of the oxygen loaded state from the empty and hydrogen loaded state of Pd. This loading results in a constant relative shift of $0.5 + / - 0.2$ eV which is in agreement with the bulk reference experiment.

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