Oxidation of palladium on Au(111) and ZnO(0001) supports

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Abstract:

The oxidation of supported Pd-deposits on Au(111) and ZnO(0001) single crystals has been studied by x-ray photoemission spectroscopy (XPS). Oxidation has been carried out *ex-situ* in a high-pressure cell with subsequent vacuum-transfer and characterization by XPS in ultrahigh vacuum (UHV), as well as using *in-situ* characterization by synchrotron based near-ambient pressure XPS. On Au(111) alloying of Pd with the substrate competes with oxidation and only sufficiently thick Pd films have been found to oxidize. For Pd on ZnO the oxidation conditions depend on the amount of deposited Pd. Thicker Pd deposits behave similar to bulk Pd, while thinner films oxidize already at lower temperatures. Interestingly, for very small amounts of Pd, *in-situ* XPS shows full oxidation at room temperature and at less than 0.6 mbar O₂ pressure. This indicates a lowering of the kinetic barriers for oxidation of very small supported Pd-clusters. The formed oxide is, however, not stable in UHV and a slow reduction is observed. The instability of this oxide indicates that the Pd-oxide formed at the interface to ZnO may have different chemical properties compared to bulk PdO or surface oxides on Pd.

Introduction:

Supported palladium catalysts are used in a wide array of industrial applications. Such catalysts are involved with methane combustion¹, CO oxidation^{2,3}, methanol reformation^{4,5}, and fuel cells⁶, to name just a few applications. The active phase of Pd depends on the reaction to be catalyzed. For oxidation reactions it may be a (sub) oxide of palladium that is active⁷ and therefore a large number of recent studies were devoted to the characterization of Pd surface and bulk oxide phases. Most of these studies were performed on metal single crystal surfaces⁸⁻¹⁴ and this gave detailed insight in the structure of adsorbed oxygen, surface oxide layers, and bulk oxides. Structural studies were mostly performed in ultrahigh vacuum (UHV) using more reactive oxygen sources than O₂, i.e. ozone, NO₂, or atomic and other activated oxygen species, to form the oxide¹⁵⁻¹⁷. This is necessary because under extremely low pressure conditions, as those accessible in a UHV chamber, the oxidation potential of O₂ is not sufficient to form an oxide on Pd. Alternatively, oxidation of Pd crystals can also be achieved by high pressure (mbar-range) exposure to O₂ at elevated temperatures. This has been exploited in both *ex-situ* studies by oxidizing crystals in a high-pressure cell and subsequent characterization under UHV conditions^{18,19}, as well as in *in-situ* studies by using surface x-ray diffraction under high-pressure conditions²⁰ or high pressure STM². Also, the development of near-ambient pressure XPS has allowed the characterization of the palladium charge state *in-situ* at elevated pressure^{8,21-23}.

On single crystals the oxidation of (111), (110), and (100) faces has been studied. On the (111) and (100) surfaces the formation of a two-dimensional surface palladium oxide (Pd₅O₄) has been observed that precedes the formation of the bulk PdO. On

Pd(110) no such surface oxide has been reported so far ^{24,25}. In addition to forming palladium oxide phases, oxygen can also diffuse into the bulk. Previous ambient pressure XPS studies on Pd(111) have, for example, shown that at 0.4 mbar O₂ pressure the surface palladium oxide phase forms at ~655 K (382°C). The bulk PdO phase forms at 720 K (447°C) and is stable to 815 K (542°C), when the oxygen starts to dissolve into the Pd bulk. The oxidation of Pd(110) was found to proceed at ~100 K lower temperature than on the Pd(111) surface, i.e., at ~347°C ²³. On Pd(100) crystals studies at 0.5 mbar O₂ pressure showed surface oxide formation already at 110 -150°C and bulk PdO formation started at 200°C ²¹. It should be mentioned that the experiments for the (100) surface was done by another group than for the (111) and (110) surface and the reported lower oxidation temperature for the (100) surface is surprising since computational studies predict that the (110) surface should oxidize most readily, i.e. at the lowest oxygen chemical potential ²⁶. Nevertheless the studies on single crystal surfaces show that PdO-formation is dependent on the surface orientation with the more open metal surfaces oxidizing at lower oxygen chemical potential than the densely packed (111) surface. It is also important to note that the formation of bulk PdO in single crystal studies appears to be strongly kinetically hindered²⁰. In oxidation studies of Pd crystals at oxygen chemical potentials at which the oxide is thermodynamically stable, often only adsorbed oxygen adlayers or surface oxides are observed experimentally rather than the thermodynamically expected bulk oxide. Consequently, kinetic considerations are critical for understanding the Pd-oxide formation and kinetics may also influence the different oxidation behaviors of various crystallographic orientations.

In heterogeneous catalysis Pd-clusters supported on metal oxides are used and therefore it is interesting to compare the oxidation behavior of single crystals with that of supported Pd-clusters. Previous studies mainly reported work on larger Pd-clusters with sizes exceeding 10 nm. For 15 and 35 nm Pd-particles it was found that these particles are also forming a surface oxide layer first, similar to the Pd(111) and (100) single crystal surfaces. Furthermore, it is reported that the bulk PdO formation may occur at ~40 K lower temperature than on the (100) surface and the particles are completely oxidized within the probing depth of the XPS measurements at 0.5 mbar O₂ and 210-230°C ²¹. Surface x-ray diffraction studies of Pd-clusters on MgO(100) indicate that at 0.3 mbar O₂ and 300°C bulk PdO was formed but the center of the particles was still metallic Pd ²⁷. Only at 56 mbar and 300°C 5 nm-diameter clusters were completely oxidized. Computational reaction force field (reaxFF) studies predict that 3 nm clusters behave similar to the most-easily oxidized surface orientation, which, according to these simulations, is the (110) orientation ²⁶. DOES THIS HAVE TO DO WITH THE FACETS TERMINATING THE PARTICLES? COMMENT!

In addition to size-effects and exposure of more under-coordinated sites on metal clusters the support/palladium interface may also affect the oxidation of the palladium. In the above mentioned Pd/MgO system, PdO forms an epitaxial relationship with the MgO(100) substrate and this may facilitate the growth of PdO clusters by migration of Pd on the surface, in addition to oxidizing the clusters directly. In molecular beam studies of Pd-clusters supported on a Fe₃O₄ film grown on Pt(111) it was found that PdO preferentially forms at the interface to the oxide support ²⁸⁻³⁰. Thus one may anticipate an oxidation behavior of palladium clusters that is different from single crystals due to

support interactions. In particular the kinetic barriers due to surface oxide species that play such an important role for the oxidation of bulk samples should be modified on supported clusters. Therefore for very small clusters or clusters that interact strongly with a metal oxide support, variations of the oxidation behavior is anticipated compared to single crystal studies.

Here we investigate thin Pd-films on Au(111) and Pd-deposited on ZnO single crystals. We find that alloying between Pd and Au prevents Pd oxidation for thin Pd-films while thicker films behave similar to Pd(111) single crystals, i.e. similar surface oxides are formed that present similar kinetic barriers for bulk oxidation as Pd single crystals. On ZnO, thicker Pd-deposits are behaving similar to the oxidation of larger Pd-clusters reported previously for other metal oxide supports. For small Pd-deposits, which likely results in the formation of sub-nanometer clusters, ambient pressure XPS indicates oxidation in 0.6 mbar O₂ at room temperature. The resulting small Pd-oxide clusters are, however, unstable in UHV, and slowly reduce if left in UHV for a long time period. This study indicates that for very small clusters the oxidation of Pd cannot be extrapolated from the behavior of single crystal surfaces. Our studies suggest that small supported clusters oxidize much more readily than predicted from single crystal studies, possibly due to a lowering of kinetic barriers for oxidation.

Methods

Substrates used in this study were Au(111) and Ga-doped ZnO samples. Generally, high-resolution photoemission studies on oxide supports are often limited by the poor conductivity of many interesting oxide materials including ZnO. Here we use

Ga-doped ZnO crystals to avoid charging effects. Ga-doping is known to make ZnO a good conductor and thus no charging during XPS studies was observed. We used both polar surface orientations of ZnO, i.e. ZnO(0001)-Zn and ZnO(000-1)-O, where this nomenclature indicates that one surface is Zn- and the other O-terminated. Sample surfaces were prepared using repeated cycles of 1 keV Ar⁺ sputtering and annealing. ZnO surfaces were annealed to 600°C, and Au surfaces were annealed to 400°C.

The *ex-situ* experiments were done at the University of South Florida (USF), with a dual anode x-ray source and a hemispherical electron energy analyzer. Samples were mounted on a four-axes translation stage. Samples were transferred directly between the UHV chamber and a high-pressure cell with no exposure to atmosphere. The high-pressure cell contained a sample holder fitted with a ceramic button heater allowing for sample temperatures above 600°C in reactive gas environments. Static volumes of O₂ were introduced to the high-pressure cell, and the pressure monitored with an Inficon capacitance gauge. The cell was evacuated with a turbomolecular pump. For the experiments reported here, the samples were held at room temperature when first exposed to O₂ pressure, ramped to the target temperature, and then allowed to cool to below 50°C. The O₂ was then evacuated and the samples returned to the UHV system.

Palladium was deposited by e-beam heating of a solid Pd rod, while the ion flux was monitored. Approximate thickness of Pd films grown on Au(111) was calculated from the Au 4d to Pd 3d core level intensity ratio as a function of emission angle. This analysis assumed uniform Pd-layers on top of the bulk Au crystal³¹. For ZnO substrates, effective Pd coverage was calibrated using the method described by Bera et al³².

Near-ambient pressure XPS (AP-XPS) allows collection of XPS spectra with high background pressure (< 1 mbar). Such *in-situ* experiments were carried out at Brookhaven National Laboratory, using an AP-XPS endstation the National Synchrotron Light Source (NSLS) beamline X1A1 operated by the Center for Functional Nanomaterials. The system contains sputtering and annealing capabilities, as well as a Pd evaporation source similar to that used for the experiments at USF. For the in-situ experiments, ZnO surfaces were cleaned under UHV conditions and then Pd films were grown. Films grown at NSLS were also transferred to the USF ex-situ apparatus for rough comparison of the relative amount of Pd deposited in the two setups. In-situ XPS experiments at the synchrotron were conducted by backfilling the chamber to the required O_2 pressure. The sample temperature could be increased in the O_2 environment as well. The incident photon energy used was 610 eV, and the photoelectrons were collected in a differentially pumped SPECS Phoibos 150 NAP hemispherical analyzer. The angle between x-ray beam and analyzer was 70° and the photoelectrons were collected 20° off the surface normal.

Results

XPS spectra for palladium deposited on Au(111) are shown in Figure 1. Figure 1(a) is from a Pd film thickness estimated to be 2 nm, while Figure 1(b) shows a film estimated to be 6 nm in thickness. Three XPS features are visible in these spectra: Pd $3d_{3/2}$ and overlapping Pd $3d_{5/2}$ and Au $4d_{5/2}$. For both figures, black lines represent as-deposited films, while blue lines denote spectra taken after exposure to oxidation conditions. Both films were heated to 350°C in O_2 . The 2 nm Pd film in Fig. 1(a) was

exposed to 8 mbar O₂ while the 6 nm Pd film in Figure 1(b) was exposed to 6 mbar O₂. The 2 nm Pd film in Figure 1(a), shows a significant contribution from the Au 4d_{5/2} feature. The XPS spectrum is unchanged after exposure to oxidizing conditions. The 6 nm Pd film in Figure 1(b) shows significant differences after exposure to oxygen at elevated temperature. New features, attributed to oxidized Pd, are observed near the Pd 3d_{3/2} and 3d_{5/2} peaks, approximately 1.6 eV higher in binding energy.

Palladium 3d_{5/2} spectra from approximately 1 ML-equivalent Pd deposited on ZnO(0001) are shown in Figure 2. Spectrum (i) represents the as deposited film, while spectrum (ii) represents the film after exposure to 6 mbar O₂ at 200°C. Also shown are peak shape fits for each spectrum. The spectrum of the as-deposited film can be constructed with a single component, represented as black squares. After exposure to oxidizing conditions, the film is best fit with two components. One metallic-component with the same shape and position as the spectrum for the as-deposited Pd-film, represented with black dots, and a second component with the same shape parameters but 1.6 eV higher in binding energy, shown as blue triangles. The area of this second component varies as a function of oxidation conditions, as described below. While not shown here, annealing in vacuum above 150°C removes the higher binding energy component, leaving only the metallic Pd peak. This temperature is close to the expected PdO phase stability temperature in UHV of around 200 °C^{12,26} and may fall within the uncertainty of our temperature measurement. The observed XPS Pd/Zn ratios after vacuum reduction at ~150°C are similar to those of the original as grown Pd film.

A summary of the *ex-situ* oxidation experiments is shown in Figure 3. The relative area of the oxide 3d_{5/2} component (with respect to the total 3d_{5/2} peak area) is

plotted as a function of oxidation temperature. All oxidation experiments were done with an O₂ pressure of ~6 mbar. Peak areas are determined using the peak fitting described in Figure 2. In addition a Pd(111) single crystal was also exposed to 6 mbar O₂ as a reference, and the onset temperature of bulk PdO formation was observed to be ~400°C. This result is in good agreement with reported *in-situ* experiments using ~0.4 mbar O₂ report initial PdO formation on Pd(111) between ~440°C⁸ and ~380°C²³, with the amount of PdO being exposure time dependent.

For ~ 6nm thick Pd films grown on Au(111), shown as square symbols in Fig. 3, the relative oxide area remains low for temperatures below ~300°C and only increases at 350°C. The small amount of oxide detected at low temperatures may be related to a surface oxide and the increase in the oxide component at 350 °C is assigned to bulk PdO formation. Thus the bulk oxide formation temperature is ~ 50 K lower for the Pd-film on Au compared to that on Pd(111). This lowering in the oxidation temperature may be a consequence of polycrystallinity of the film and exposures of e.g. (110) faces. In addition the much more rapid saturation of the thin Pd-film with dissolved oxygen compared to bulk Pd single crystals may also facilitate oxidation of the film at a lower temperature compared to bulk single crystals.

The ratio of the oxide component to the total Pd-3d peak are shown as circles for Pd deposits of ~4 ML-equivalent on ZnO substrates. Oxide formation again remains low below 300°C and the oxide component only increases at 350°C. Thus the oxidation behavior is similar to that of the Pd-films on Au(111). Also for the temperature range studied here we always observe a metallic component, i.e. the clusters do not completely

oxidize. This is consistent with previous studies of large supported Pd clusters that indicate the formation of an oxide shell and the presence of a metallic core^{18,28}.

The oxidation behavior of thinner Pd-films (~1 ML equivalent) grown at room temperature in UHV on ZnO is indicated as triangles in Figure 3. Significant oxidation is already observed at temperatures as low as 200°C. However, again the Pd does not completely oxidize and metallic Pd is always observed in the XPS spectra. This lowered oxidation temperature is similar to that previously reported of 15-35 nm Pd-particles²¹. Interestingly, if the ~1ML Pd film is oxidized and then reduced by vacuum annealing at 150°C the resulting Pd-deposit is not as easily oxidized the second time. The measurements of oxidation experiments of such vacuum-reduced samples is shown by the diamond symbols in Fig. 3. In contrast to the as-grown films, the same sample after vacuum reduction shows significant PdO formation only above 300°C. This means that after a cycle of oxidation and reduction the Pd deposit behaves similar to the thicker Pd-deposits. This suggests that the oxidation and reduction treatment results in sintering of the Pd-clusters and the larger clusters then exhibit a higher oxidation threshold compared to the smaller clusters. This history effect is only observed for thinner (~1 ML) Pd films grown on ZnO substrates.

In order to investigate where the oxide and metal Pd components are located within the Pd-films we conducted XPS measurements as a function of emission angle. Spectra of partially oxidized Pd films on Au and ZnO (6nm and 4 ML-equivalent respectively) substrates were taken. Emission angles were varied from 0° (normal to the surface) to 60°. The ratio of PdO 3d_{5/2} area to the total Pd 3d_{5/2} area as a function of emission angle θ for both films are shown in Figure 4. On the Au substrate the relative

intensity of the oxide signal increases with increasing emission angle, indicating that the oxide is located at the surface. For the Pd-deposit on the ZnO substrate the opposite behavior is observed, i.e. the oxide signal decreases with increasing emission angle, suggesting that the Pd-oxide is located at the interface to the ZnO-substrate. This behavior is similar to that reported for Pd on iron-oxide/Pt(111)³³ as well as for oxidation of copper supported on ZnO³⁴.

In-situ oxidation experiments were performed by synchrotron AP-XPS. For all *in-situ* experiments, Pd was first deposited on ZnO in UHV. Both Zn- and O- terminated polar surfaces of the ZnO crystal were examined, but the results were nearly identical and thus we are not distinguishing between these samples in the following. Since the above-described *ex-situ* experiments suggested that only for thin Pd films on ZnO a variation of the oxidation behavior of Pd is observed compared to single crystals, the synchrotron studies were performed on very thin Pd-films with less than 1 ML-equivalent. These studies with small amounts of Pd were also aided by the higher surface sensitivity at the synchrotron due to the accessibility of lower photoelectron kinetic energies.

In-situ near ambient-pressure XPS results are shown in Figure 5. Pd 3d_{5/2} XPS spectra of <1 ML Pd films at constant O₂ pressure (~0.1 mbar) are shown in Figure 5(a). Spectrum (i) shows the sample at 30°C before introduction of O₂. The Pd 3d_{5/2} peak position is measured to be ~336.1 eV. Although a small shift of the binding energy of Pd on ZnO compared to bulk Pd has been previously reported³², our peak position is about 0.7 eV higher than the expected binding energy. This difference is likely due to uncertainties in the calibration of the spectrometer and the true binding energy should be around 335.4 eV. After O₂ exposure at room temperature a small amount of oxide is

observed, as shown in spectrum (ii) of Fig. 5(a). After increase of the sample temperature to 120°C in the oxygen atmosphere the oxide component has increased significantly in spectrum (iii). At 300°C sample temperature, (iv), the Pd is nearly completely oxidized. Upon cooling to 50°C in O₂ and returning to UHV conditions, the oxide remains stable for at least several hours.

Figure 5(b) shows 3d_{5/2} XPS spectra of <1 ML Pd films on ZnO acquired at a constant temperature of 30°C. Spectrum (i) shows the as grown film, and spectrum (ii) is acquired during 0.6 mbar O₂ exposure. At this pressure near total oxidation was observed even at 30 °C. Immediately after removal of the O₂ (iii) the film remains oxidized. Leaving the film under UHV conditions, remaining at 30°C, partial reduction to metallic Pd is observed after 120 minutes (iv). The conversion back to metallic Pd continues over time, as seen after ~300 minutes in UHV (v). Such a reduction of the oxidized Pd-film is only observed after oxidation of very thin deposited Pd-films. The oxide formed by after annealing and oxidation at elevated temperatures is stable at room temperature in UHV, suggesting that the instability of the room temperature as-deposited Pd film is related to the morphology and/or size of the clusters.

Discussion

Thicker Pd films (6nm) on Au(111) show similar oxidation parameters as single crystal Pd(111). Significant PdO formation is observed above 300°C at 6 mbar O₂ pressure. Thinner Pd films (~2 nm), however, do not form PdO, even at temperatures above 400°C at 8 mbar O₂ pressure. Increasing the substrate temperature leads to loss of Pd, through diffusion into the Au bulk. Consequently, we propose that the inhibition of PdO formation for thin Pd-films is a consequence of Pd-Au alloy formation³⁵. For thicker

films alloying competes with oxidation of the Pd-film and it may be the slow kinetics of the interdiffusion process of Pd and Au at the oxidation threshold temperature around 400°C that enables oxidation of the Pd-surface before it can alloy with the Au-substrate. The observation that the Pd cannot be completely oxidized and the metallic Pd-component is located at the interface to the Au substrate may also be a consequence of an interface Pd-Au alloy.

For both *ex-situ* and *in-situ* experiments, Zn- and O- terminated polar ZnO substrates were studied. No systematic differences were observed and thus we conclude that the surface termination of the oxide support does not critically affect the oxidation behavior of the supported metal deposits. In experiments, all thicknesses of Pd films on ZnO were found to form PdO given sufficient oxidation conditions. Thicker Pd films on ZnO exhibited similar oxidation behavior as reported previously for Pd clusters larger than 10 nm, i.e. requiring temperatures above 300°C at 6 mbar to show significant oxidation. Thinner Pd films required lower temperature, ~200°C to exhibit oxidation, as seen in Figure 3. This reduced oxidation temperature may be a consequence of the formation of separate PdO clusters by oxidation of Pd-atoms released from the Pd-clusters, similar to what has been reported for the Pd/MgO(001) system²⁷ or due to the exposure of more reactive facets on the Pd-clusters that have shown a significant lowering of the oxidation temperatures compared to the (111) face. After vacuum reduction the Pd-deposit likely sinter into larger clusters³² and in a second oxidation the film behaves similar to the thicker Pd-deposits.

XPS as a function of photoelectron emission angle was used to examine the location of the oxide within the partially oxidized Pd-films. For films grown on Au, the

ratio of PdO to Pd XPS signal increased with increasing emission angle. This indicates that the surface region of the film contains a higher proportion of PdO, suggesting the oxide formation begins at the film surface, with alloys of Pd and Au at the interface. In contrast, films grown on ZnO show a decreasing amount of PdO as the emission angle is increased. This suggests PdO formation begins at the film/substrate interface. A similar oxidation behavior of metals on ZnO was reported previously for Cu on ZnO system³⁴. This difference in the oxidation may be a consequence of the oxidation kinetics. On bulk samples the surface is the only interface from which oxidation can proceed and thus the formation of a surface oxide may contribute to the kinetic hindrance of bulk oxidation. Our measurements do not exclude the formation of a passivating monolayer surface oxide layer but suggest that the kinetic barrier for oxidation is lowered at the interface to the oxide support.

The *in-situ* experiments for thinner Pd-films shown in Figure 5 give results very similar to the ex-situ results for Pd on ZnO. The oxide forms during the temperature ramp, completely oxidizing below 300°C. No intermediate oxide was observed in these experiments. After cooling in the oxygen environment, the oxide film was stable at room temperature under UHV. When slightly larger O₂ pressures (0.6 mbar instead of 0.1 mbar) were used (Figure 5(b)), the oxide was found to form quickly at room temperature. This oxide formed without sample annealing was unstable, and after some hours began to reduce back to metallic Pd at room temperature in UHV. Complete oxidation of Pd-clusters at room temperature at mbar pressures was not observed previously. Thermodynamically PdO is the stable phase under these conditions (300 K and 0.6 mbar) and thus the formation of PdO is thermodynamically expected, however kinetic barriers

prevented PdO formation on bulk samples or large clusters in the past. Furthermore for sub-monolayer of Pd on ZnO two-dimensional Pd-clusters were previously reported³², i.e. the Pd-clusters may consist of a single monolayer Pd. For such clusters there obviously does not exist any bulk-Pd and the oxidation becomes similar to the formation of a surface oxide on a single crystal that can occur under these thermodynamic conditions. Possibly the clusters remain in close to 2D form after oxidation at room temperature. As the slow decay of this oxide under UHV conditions shows this form of supported PdO is however not thermodynamically stable at 30°C if the oxygen background is removed. This is different to bulk PdO, which remains stable in UHV. The difference in the stability of the oxide for deposits annealed for oxidation (Fig. 5(a)) also suggests a different morphology, i.e. 3D for slightly annealed samples versus 2D for clusters oxidized at RT.

For films below 1 ML examined with AP-XPS, the oxide feature was ~1.3 eV higher in binding energy than the metallic feature. While this shift is less than the 1.6 eV shift commonly reported for PdO (and observed in our ex-situ studies for thicker Pd-deposits) it is consistent with the surface component of PdO²¹ which is very similar to the shift reported to the Pd₅O₄ surface oxide phase on Pd(100) and Pd(111). This could further suggest that the oxide we observe is closer to a two-dimensional palladium oxide supported on ZnO than bulk PdO.

Conclusion

The oxidation behavior of Pd is well described by previous single crystal studies for thin Pd films and Pd clusters of sufficient size. For Pd deposited on gold substrates

the competing formation of a Pd-Au alloy may impede oxidation of the palladium. For Pd-clusters supported on ZnO we find that the oxidation temperatures may be reduced for small clusters. This is similar to previous reports for the oxidation of 3 nm Pd clusters and may be a consequence of the exposure of more reactive facets and/or the oxidation of Pd-adatoms released from the Pd-cluster, as has been observed for Pd/MgO system. Interestingly, for very small amounts of Pd deposited on ZnO we find that the Pd may already completely oxidize at RT and sub-mbar O₂ pressure. This could be a consequence of lowering of kinetic barriers for oxidation due to the interface with the oxide support or simply the consequence of the Pd-deposits only being one or a few monolayers thick and thus not exhibiting any bulk-Pd. Interestingly though these very thin Pd-oxides on ZnO substrates are not stable in UHV and slowly (over hours) decompose to the metal. Such different thermodynamic stability compared to bulk PdO also suggests different chemical behaviors for example for oxidation catalysis. Clearly to investigate the size regime at which the Pd is oxidized at room temperature, a combination of the *in-situ* XPS studies with e.g. ambient pressure STM would be desirable. Such instruments are becoming available and thus these studies may be performed in the future. Importantly, our studies show that there exists a size regime for ZnO-supported Pd at which Pd is oxidized already at RT and moderate O₂ pressures. This may yet indicate that oxidation catalysis for supported nanosized Pd-clusters is different to that probed on bulk Pd-surfaces³⁶.

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Figure 1. Pd 3d spectra of 2 nm (a) and 6 nm (b) Pd films on Au(111). Spectra collected before (black lines) and after exposure to oxygen (blue dotted line) at 8 mbar and 6 mbar O₂ at 350°C, respectively.

Figure 2. Pd 3d_{5/2} spectra from 1 ML Pd film grown on ZnO(0001), before (i) and after (ii) exposure to oxidation conditions, 6 mbar O₂ at 200°C. Shown are peak fitting for metallic Pd (black squares) and PdO (blue triangles).

Figure 3. Ratio of PdO 3d_{5/2} area to total Pd 3d_{5/2} area after exposure to 6 mbar O₂ at various substrate temperatures. Results are shown for 6 nm Pd on Au(111)(squares), 4 ML Pd/ZnO(0001) (circles), as grown 1 ML Pd/ZnO(0001) (triangles), and reduced and re-oxidized 1ML Pd/ZnO(0001) (diamonds). PdO formation on Pd(111) was observed at 400°C, dotted line.

Figure 4. Ratio of the Pd 3d_{5/2} oxide-component to the total 3d_{5/2} peak area as a function of emission angle. Pd films grown on Au(111)(squares) exhibit an increase of the oxide component with increasing angle. Pd films grown on ZnO(0001) (circles) exhibit a decrease of the oxide component with increasing angle.

Figure 5. *In-Situ* AP-XPS Pd 3d_{5/2} spectra of <1 ML Pd/ZnO(0001). The background O₂ pressure (0.1 mbar) is introduced and held constant (a), (i) before O₂, then the temperature is raised from 30°C (ii) to 120°C (iii) to 300°C (iv). The spectra a(ii) and a(iii) exhibit a small shift to lower binding energy due to effects of the sample heater. In (b), the sample is held at 30°C at UHV (i), then exposed to 0.6 mbar O₂ (ii). The sample is returned to UHV and measured after 120 minutes (iii) and 600 minutes (iv).