

***In Situ* X-Ray Photoelectron Spectroscopy Studies of Gas/Solid Interfaces at Near-Ambient Conditions**

Hendrik Bluhm, Michael Hävecker, Axel-Knop-Gericke, Maya Kiskinova, Robert Schlögl, and Miquel Salmeron

Abstract

X-ray photoelectron spectroscopy (XPS) is a quantitative, chemically specific technique with a probing depth of a few angstroms to a few nanometers. It is therefore ideally suited to investigate the chemical nature of the surfaces of catalysts. Because of the scattering of electrons by gas molecules, XPS is generally performed under vacuum conditions. However, for thermodynamic and/or kinetic reasons, the catalyst's chemical state observed under vacuum reaction conditions is not necessarily the same as that of a catalyst under realistic operating pressures. Therefore, investigations of catalysts should ideally be performed under reaction conditions, i.e., in the presence of a gas or gas mixtures. Using differentially pumped chambers separated by small apertures, XPS can operate at pressures of up to 1 Torr, and with a recently developed differentially pumped lens system, the pressure limit has been raised to about 10 Torr. Here, we describe the technical aspects of high-pressure XPS and discuss recent applications of this technique to oxidation and heterogeneous catalytic reactions on metal surfaces.

Introduction

One of the main goals in catalysis research is to find a direct correlation between the structure and chemical composition of a catalyst and its catalytic activity and selectivity. This requires the investigation of catalysts under realistic operating pressures, where the chemical composition and structure of the catalyst are monitored simultaneously with its catalytic activity. A number of spectroscopies have been combined with methods that monitor catalytic performance (for recent surveys, see References 1 and 2). Among the techniques

that have been adapted in this way are infrared spectroscopy,³ UV Raman spectroscopy,⁴ sum-frequency generation,⁵ x-ray absorption near-edge structure,⁶ extended x-ray absorption fine structure in the hard-x-ray regime,⁷ electron paramagnetic resonance,⁸ UV-vis spectroscopy,⁹ nuclear magnetic resonance spectroscopy,^{Error! Bookmark not defined.} and Mössbauer spectroscopy.¹⁰ Most of the aforementioned techniques are bulk sensitive (where surface sensitivity can be achieved in some cases if the species at the surface are different from those in the bulk) and thus provide little information about the structure of the surface and near-surface area of the catalyst where heterogeneous catalytic reactions take place.

X-ray photoelectron spectroscopy (XPS) is one of the best analytical techniques for probing the composition and electronic structure at surfaces, and it has been widely used for the characterization of catalyst surfaces. In XPS, the sample is irradiated with monochromatic x-rays. The emitted photoelectrons from atomic core and valence orbitals are collected and analyzed using an electron spectrometer. The binding energy (BE) of the emitted electrons can be calculated from the known energy of the incident x-rays ($h\nu$) and the measured kinetic energy (KE) of the electrons via $BE = h\nu - KE - \Phi$, where Φ is the work function of the electron analyzer. XPS makes possible the quantitative analysis of the surface composition and provides information about the chemical state of elements via the detection of “chemical shifts” in the BEs of the photoelectrons. The probing depth in XPS depends on the kinetic energy of the emitted electrons, with a minimum of a few angstroms at kinetic energies around 100 eV.¹¹ Because the *incident* photon energy ($h\nu$) is <1500 eV in most cases, the kinetic energies of the *detected* electrons are smaller than 1500 eV after interacting with the surface material. The short mean free path of electrons with such kinetic energies in a solid makes XPS a surface-sensitive method. However, electrons in this kinetic energy range are also strongly scattered by gas molecules, and XPS is therefore conventionally performed under high-vacuum conditions. Because the mass density of a gas at 1 Torr is about 10^{-6} times that of the condensed material and because the mean free path of electrons with typical kinetic energies of a few

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hundred electronvolts in a solid is on the order of 1 nm, the mean free path in a gas at 1 Torr is about 1 mm. This is much shorter than, e.g., typical working distances between the sample and the entrance to the electrostatic lens system of an electron analyzer (which is a few centimeters). In addition to the fundamental obstacle of electron scattering by gas molecules, an additional complication for high-pressure (HP)-XPS is the need to operate the electron detector under high vacuum conditions, i.e., to separate it from the high-pressure environment at the sample. For those reasons, most studies of catalysts using XPS have been performed in vacuum systems ($p < 10^{-6}$ Torr) where the chemical potential of reactants in the gas phase is unrealistically low. Another method is the comparison of the surface of the catalyst before and after its participation in a catalytic reaction. The state of a surface measured in such a “postmortem” investigation is not necessarily representative of the surface of the active catalyst, as the presence of, e.g., reaction intermediates at the catalyst surface depends on the partial pressure of the reactants and products in the gas phase.

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In order to perform XPS experiments at elevated pressures ($>10^{-5}$ Torr), the attenuation of the electrons due to scattering by gas molecules has to be kept to a minimum. The attenuation of the photoelectron signal in a gas environment is proportional to $\exp(-z\sigma p/kT)$, where σ is the electron scattering cross section, z is the distance that the electrons travel at pressure p , k is Boltzmann’s constant, and T is the temperature. The electron attenuation can thus be reduced by placing the sample surface close to a differentially pumped aperture, behind which the pressure drops by several orders of magnitude. This basic concept has been used in a number of HP-XPS instruments that were developed over the past 30 years and that operate at pressures of up to 1 Torr.^{12–19} Several of these HP-XPS instruments have been used to study reactions on model catalyst surfaces, such as the interaction of oxygen with silver surfaces,^{20,21} methanol oxidation on Cu,²² CO adsorption on Pd(111),²³ reaction of copper and copper oxide with SO₂,²⁴ the reduction of nickel oxide in H₂,²⁵ and the adsorption of CO on Pd(111).^{Error!}

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Herein, we briefly describe the technical concept of a new type of HP-XPS spectrometer for investigations at pressures higher than 5 torr.^{26–28} Such pressures are of particular importance for environmental science because the vapor pressure of water at the triple point is 4.6 torr. Numerous catalysis-related studies have already been performed with the new-generation HP-XPS instruments. The potential of these investigations is illustrated here using representative examples for reactions on Ru and Pd catalysts.

Technical Aspects

Figure 1a shows the principal approach that is common to all HP-XPS instruments. The sample is placed in a high-pressure cell. X-rays are admitted to the cell through an x-ray-transparent window, usually a silicon nitrate, aluminum, or polymer membrane with a thickness of a few tens to a few hundreds of nanometers and an active window area in the square millimeter range. The x-ray window is necessary to keep the x-ray source (conventional cathode or synchrotron beamline) under vacuum. The sample is placed close to a differentially pumped aperture through which the electrons and also gas molecules escape. The pressure differential across this aperture depends on the size of the aperture, the type of gas, the gas temperature, and the pumping efficiency and is typically on the order of 10^2 – 10^4 .

The ultimate pressure limit in HP-XPS experiments is determined not only by the attenuation of the signal due to electron scattering by gas molecules, but also by the base pressure in the electron detector, which needs to be kept under vacuum. If the sample is to be investigated under pressures of one to several Torr, several differential pumping stages are therefore necessary. This is illustrated in Figure 1b, which shows the principal setup of most high-pressure XPS instruments. From Figure 1b, it is clear that there is a trade-off between the pumping efficiency and the transmission of electrons through the differential pumping stages. Small apertures spaced at large distances improve differential pumping but decrease the effective solid angle of the transmitted electrons. The pressure limit in this type of HP-XPS systems is about 1 Torr.

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The recent development of a new type of HP-XPS design has increased the pressure limit to about 10 Torr, with possible extensions to higher pressures in the future. In this design, electrostatic lenses focus the electrons onto the apertures, thereby increasing the transmission of electrons through the differential pumping system (see Figure 1c). A prototype instrument based on this concept was developed at the Advanced Light Source (ALS) in Berkeley, CA, in 1999.²⁹ A second-generation design was developed soon thereafter, with two instruments now operating at BESSY (Berliner Elektronenspeicherring - Gesellschaft für Synchrotronstrahlung m.b.H., the Berlin 3rd generation synchrotron light source) in Berlin and at the ALS (see Figure 1d). Those instruments use aperture sizes of 2 mm between the differential pumping stages and front apertures of 0.3 mm (ALS) and 1 mm (BESSY), which allow pressures of 100 Torr or higher in the sample cell without compromising the vacuum in the electron analyzer. However, because of the scattering of electrons by gas molecules, the effective pressure limit is about 10 Torr, depending on the gas-phase composition and incident photon flux.

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The key to increasing the pressure limit in HP-XPS is to decrease the effective path length of the electrons through the high-pressure region. This can be achieved by moving the sample closer to the aperture. However, because the pressure drops by several orders of magnitude across the aperture, there is a minimum distance at which the sample should be kept from the aperture to ensure homogeneous pressure conditions across the sample surface. This is illustrated in Figure 2, which shows a closeup of the sample-first aperture region. Below the schematic drawing, the pressure (calculated for molecular flow through the aperture) along the optical axis of the lens system as a function of distance z from the aperture plane in units of background pressure p_0 is shown. At a sample-aperture distance of d (where d is the aperture diameter), the pressure at the sample surface reached $0.95p_0$, and at $2d$, it reached $0.98p_0$. We found in our experiments that the sample-aperture distance needs to be $2d$ ($z=2d$) to ensure homogeneous pressure conditions at the sample surface.

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The effective path length of the electrons through the high-pressure region can be reduced if the aperture diameter is decreased. At Beamline 11.0.2 of the ALS, the x-ray spot has a minimum size of $10\ \mu\text{m} \times 7\ \mu\text{m}$, i.e., the entrance aperture diameter of the differentially pumped lens system could be reduced by 10–30 μm , in turn reducing the minimum working distance between sample and aperture by a factor of 10, which would raise the pressure limit to about 100 Torr. It is possible, however, that the increased photon flux density due to the tight focusing of the x-ray beam could cause beam damage of the sample surface. Therefore, the effective pressure limit in HP-XPS experiments also depends on the susceptibility of the investigated material to radiation damage.

In order to correlate the chemical nature of the surface of the catalyst with its catalytic activity, simultaneous measurements of the gas-phase composition need to be performed. This can be done by using, e.g., online mass spectrometry. Another possibility in some cases is the direct determination of the gas-phase composition from the XPS spectra. Because the incident photon beam irradiates not only the sample surface but also part of the gas phase in front of the sample, gas-phase XPS peaks are observed alongside surface peaks if the partial pressures of the gas-phase species are above ~ 0.05 Torr. The BE shift between gas-phase and surface species is usually large enough to separate these contributions in the spectra.

In the following section, we discuss applications of the synchrotron-based HP-XPS instruments at BESSY and the ALS to oxidation reactions on Ru and Pd catalysts.

Examples

Catalytically Active States of Ru during CO and Methanol Oxidation

Reactions

The oxidation of CO over a Ru catalyst, used in exhaust gas converters, is a textbook example of a reaction that exhibits a so-called “pressure-gap” behavior, where results obtained under ultra-high vacuum in classical surface science experiments differ from those obtained under realistic, atmospheric pressure conditions. The difference between ultra-high vacuum studies and

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studies under realistic conditions is attributed to kinetic limitations at low oxygen potentials ($P_{\text{O}_2} < 10^{-4}$ mbar) to form the catalytically active $\text{RuO}_2(110)$ phase with active lattice oxygen and coordinatively unsaturated Ru atoms at the surface.³⁰ RuO_2 is also considered as the active state catalyzing such reactions as oxygen reduction in fuel cells and the partial oxidation of alcohols.^{31,32} In reality, the catalytically active state under operating conditions is largely determined by dynamic processes and can deviate from the well-defined equilibrium metal oxide phases used in modeling the mechanisms of oxidation reactions.³³ It has been suggested that the catalytically active transient states can also be formed under operating conditions by incorporation of critical amounts of oxygen within the top few layers of metal catalysts or by partial reduction of the stoichiometric metal oxide phase.³⁴⁻³⁹ These transient oxidation states RuO_x ($1 < x < 2$) with variable amounts of incorporated subsurface oxygen not only can catalyze CO oxidation⁴⁰ but might be the catalytically active state for partial oxidation of methanol to formaldehyde.^{41,42}

The RuO_x ($1 < x < 2$) transient states precede the nucleation and growth of the stoichiometric RuO_2 phase or mediate the reduction of RuO_2 to metallic Ru. They can coexist with the RuO_2 phase in a wide range of temperatures for $P_{\text{O}_2} > 10^{-4}$ mbar and can also form at temperatures < 500 K where the growth of stoichiometric RuO_2 is kinetically hindered.⁴³ Under reaction conditions, the RuO_x states can be stabilized by “reducing” reactants (e.g., CO, H_2 , CH_3OH , etc.) that drive the oxidation state away from the equilibrium achieved in a pure O_2 environment.⁴⁴ Fortunately, the RuO_x transient has characteristic Ru 3d core-level features, different from those of the RuO_2 phase and metallic Ru. Thus, the Ru oxidation states and their catalytic performance, evolving under variable millibar operating conditions, can be identified by HP-XPS combined with online mass spectrometry, which monitors the gas-phase products.^{Error! Bookmark not defined.} The experiments described in this section were performed using the HP-XPS instrument located at BESSY.

The Ru $3d_{5/2}$ core-level spectra in Figure 3, measured during CO oxidation reactions, illustrate the transformation of a metallic Ru(0001) precatalyst into a RuO_x transient in the 420–500 K range and the following growth of the RuO_2 phase above 500 K. The plot of the CO_2 yield in Figure 3 shows a sharp onset far below the RuO_2 formation temperature, which practically coincides with the temperature (420 K) at which the development of RuO_x is apparent in the Ru $3d_{5/2}$ spectra. The growth of RuO_2 does not affect the monotonic increase of the CO_2 yield with temperature, indicating comparable catalytic activities of the RuO_x and RuO_2 states.^{Error! Bookmark not defined.} The catalytic activity of the transient RuO_x can be tentatively attributed to several possible factors, such as the modification of the catalyst surface due to lattice stress induced by incorporation of O or the presence of undercoordinated atoms or other structural irregularities.⁴⁵

The nonequilibrium RuO_x states play a decisive role in tuning the catalyst selectivity, an issue addressed by studies of CH_3OH oxidation, the simplest system representing the important class of alcohol oxidation catalytic reactions. The CH_3OH oxidation reaction has several possible pathways, which can be summarized as (1) partial oxidation with dominant products CO, H_2 , and H_2O ; (2) partial oxidation with dominant products $H_2CO + H_2O$; and (3) full oxidation to $CO_2 + H_2O$, with pathway 2 being the desired one. Monitoring the dynamic response of a RuO_2 or Ru precatalyst simultaneously with the yield under different operating conditions has revealed the dynamic coupling of the possible pathways and corresponding catalytically active states to the chemical potentials of reactants and temperature.^{Error! Bookmark not defined.,Error! Bookmark not defined.}

The results of these experiments have shown that the desired partial oxidation pathway to formaldehyde is catalyzed only when the reduction–oxidation equilibrium maintained by the reactant chemical potentials stabilizes a specific RuO_x state that evolves independently of the initial Ru precatalyst state (RuO_2 or Ru).^{Error! Bookmark not defined.} The summary of some representative results in Figure 4 illustrates the dynamics of the catalyst oxidation state and the dramatic changes in the catalyst selectivity with small variations in the stoichiometry of the

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RuO_x transient. The Ru 3d_{5/2} spectra of the catalyst in steady state at 600 K (see Figure 4) demonstrate that both partial oxidation to CH₂O and full oxidation to CO₂ are catalyzed by RuO_x transient states. However, these states contain different amounts of oxygen, apparent in the relative weight of the RuO_x component in the corresponding Ru 3d_{5/2} spectrum. This observation implies that there is a critical amount of incorporated and surface oxygen that selectively activates the catalyst surface to provide the most favorable energetics of interlinked processes of adsorption, desorption, surface diffusion, and surface reactions for the desired reaction channel. The CH₂O pathway also exhibits pressure-gap behavior: it is activated in the 10⁻¹ mbar range, although the specific catalytically active RuO_x state can be formed in the 10⁻⁴ mbar pressure range.^{Error!}

Bookmark not defined. The observed pressure gap in the RuO_x activity to CH₂O formation can be ascribed to kinetic limitations at low reactant potentials to obtaining the optimal coverage of reacting species with specific adsorption configurations, favoring the immediate desorption of CH₂O to prevent further oxidation.

In conclusion, the example of the dynamics of the Ru oxidation state and its catalytic performance up to Torr pressures demonstrates the compositional complexity of the catalytically active states under operating conditions that are often found at phase boundaries. These results underscore the need for measurements under technically relevant ambient pressures.

In Situ Study of Palladium Oxidation

Despite their general importance, the atomic-scale processes leading to the oxidation of metals are not understood. Here, we discuss an example where HP-XPS has been used to experimentally follow the oxidation of Pd.

A recent *in situ* surface x-ray diffraction (SXRD) study identified different crystalline phases of oxidized Pd(100) over an extended pressure and temperature range.⁴⁶ For that reason, new photoemission measurements were carried out on Pd(111) by Ketteler et al. using the ALS HP-XPS instrument at beamline 11.0.2 under oxygen pressures of up to 1 Torr.⁴⁷ This spectroscopic study revealed for the first time the various steps leading to the complete oxidation of the Pd surface.

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Following standard surface-science preparation and characterization methods in the preparation chamber, which are described in detail in the original work,^{Error! Bookmark not defined.} the clean Pd(111) sample was introduced into the high-pressure chamber and exposed to O₂ at various pressures and temperatures. In addition to the (2 × 2) chemisorbed phase, various other phases of the O–Pd system could be identified. They were characterized by well-defined XPS peaks in the O 1s and Pd 3d and Pd 3p regions, as shown in Figure 5. After the chemisorbed phase has formed, the topmost surface layer oxidizes, forming a two-dimensional one-layer-thick surface oxide, as found previously with a characteristic LEED pattern corresponding to a $\sqrt{6} \times \sqrt{6}$ superstructure for $p \geq 10^{-6}$ Torr and for $T < 750\text{--}900$ K.⁴⁸ This phase is characterized by Pd 3d_{5/2} peaks at 334.9 eV (I), 335.5 eV (II), and 336.3 eV (III) that have been attributed to Pd atoms with two (II) and four (III) O neighbors^{Error! Bookmark not defined.} and bulk Pd (I) (see Fig. 5a).⁴⁹ The O 1s region shows two peaks at 529.0 and 529.7 eV with an intensity ratio of ~1 that have been assigned to two different oxygen species (3-fold- and 4-fold-coordinated O atoms). The stoichiometry of this surface oxide phase can be written as PdO_{0.3}. For $10^{-4} < p < 0.3$ Torr and $450 \text{ K} < T < 800 \text{ K}$, respectively, the surface oxide transforms into a new phase with XPS peaks at binding energy positions identical to those of the surface oxide, but with a Pd 3p/O 1s peak ratio corresponding to the stoichiometry PdO_{0.6±0.1} over the probed sample thickness (see Fig. 5b and 6a). The ratio between the Pd 3d_{5/2} peak areas at 336.3 and 335.5 eV has increased from 1:4 in the surface oxide to values between 1:2 and 1:1. Following the same assignment of coordination numbers as before, the fraction of highly coordinated Pd atoms (four O neighbors) has increased. Peak positions are also unchanged in the O 1s region, although the O intensity has increased. These observations indicate that the chemical states of the Pd and O atoms are similar to those of the surface oxide phase. Therefore this new phase was assigned to a thicker oxide, probably two layers. This new phase is referred to as “subsurface oxide.” Interestingly, the subsurface oxide is formed always upon cooling in O₂ only. During heating to reduce the oxide, the PdO phase transforms directly into the surface oxide phase, indicating that the subsurface oxide is a metastable phase.

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When the oxygen pressure was increased into the Torr range PdO formed (see Fig. 5c). The Pd $3d_{5/2}$ region shows one single peak that is shifted by ~ 1.6 eV compared to bulk metallic Pd (peak I in Figs. 5a and b). The experimental observations at many pressures and temperatures were used to construct the phase diagram in Figure 6a. Each point in the diagram represents an independent experiment in which no change was observed in the spectra over several minutes. Four different regions can be observed in the diagram. The top left pink region corresponds to the vacuum, high temperature chemisorbed (2×2) phase. Below this, the green area represents p, T conditions where the one-layer-thick surface oxide phase is stable. The p, T region where the new subsurface oxide is observed is marked blue, and the dark region corresponds to the PdO bulk oxide when the pressure is reduced from 1 Torr at fixed temperature. The solid line indicates the phase boundary between Pd and PdO as calculated by tabulated values of the enthalpies and heat capacities.⁵⁰ As can be seen, the boundary agrees well with that observed between PdO and the surface oxide at the higher temperature. However, the surface oxide phases are not predicted by classical standard thermodynamics. The surface phase diagram calculated by atomistic thermodynamics⁵¹ is shown in the bottom phase diagram (see Figure 6b). It is clear that kinetic limitations are present that prevent thermodynamic equilibrium from being reached at the lower temperatures. Perhaps the most interesting result of the HP-XPS observations is the existence of the metastable subsurface oxide, which is stabilized by a large activation energy separating the clean metal and surface oxide from bulk PdO. The origin of this activation energy is likely in the large crystallographic restructuring that occurs when going from the metal to the bulk oxide. As a result, the surface oxide structure, which is in epitaxial relationship with the (111) metal substrate, can grow into a two- (and perhaps more) layer-thick film before finally transforming into PdO.

Methane Combustion over Pd(111)

Following the example of Pd oxidation, we now discuss the role of Pd in a heterogeneous catalytic reaction. Palladium is well-known for its catalytic activity in the combustion of methane in gas-powered turbines. Compared to other metals,

it shows the highest rate per unit metal surface for methane oxidation.^{52,53} PdO is the thermodynamically stable phase at low temperatures, whereas Pd metal is stable at high temperatures. There is controversy about the activity of PdO and Pd metal in methane combustion.⁵⁴⁻⁶⁰

Methane combustion over Pd(111) was investigated by HP-XPS at 0.33 mbar in a mixture with $\text{CH}_4/\text{O}_2 = 1:5$. The heating ramp was programmed to 6.6 K min^{-1} . The HP-XPS spectra and the mass spectrometry data were continuously recorded.⁶¹ Figure 7 shows mass spectroscopic data of the formation rates of CO_2 (Fig 7a) and water (Fig 7b) during a heating/cooling cycle as a function of the sample temperature. In analogy to previous observations, a kinetic hysteresis, which was assigned to spectroscopically observed differences in the surface oxidation state, was found.^{62,63} During the heating cycle, the conversion starts above 500 K and reaches a maximum at 650 K. Between 650 and 700 K, the activity decreases again, and it finally increases exponentially above 700 K. During cooling, the reaction rate does not abandon its exponential decrease, and consequently, the low-temperature maximum at 650 K is missing.

Figure 8a and b shows the corresponding HP-XPS O 1s/Pd 3p_{3/2} spectra recorded *in situ* during heating and cooling, respectively, together with the deconvolution into their peak components. During the heating ramp, an increased intensity of the O(I) and O(II) peaks was detected between 530 and 650 K compared to temperatures below 500 K and above 700 K. The limited time resolution did not allow to detect an XP spectrum at exactly 650 K. In the temperature range between 530 and 650 K the catalyst exhibits a steep rate increase toward the 650 K activity maximum. At temperatures below 500 K the reaction rate is low. At higher temperatures oxygen is removed from the surface and the reaction takes place at the metal surface (see Figure 7). Below 500 K, the O(III) component is dominant in the O 1s spectra. This component was assigned to a compressed O_{ads} layer formed by adsorption of clean oxygen at temperatures low enough to avoid surface oxide formation.^{64,65} A contribution of carbon/oxygen species (such as CO) to the O(III) peak can be ruled out, given that the intensity of the C 1s peak was negligible above 420 K. The O(III) peak

decreases with increasing temperature from 420 to 530 K, whereas the O(I) and O(II) peaks grow, reaching a coverage of approximately 0.3 ML at 530 K, reflecting the conversion of the compressed O_{ads} layer to the Pd_5O_4 surface oxide below 530 K. At 530 K, the total coverage of oxygen species characterized by only O(I) and O(II) peaks reaches 0.6 ML, which is very close to stoichiometric Pd_5O_4 . As mentioned in the previous section, the O(I) and O(II) peaks at 528.9 and 529.5 eV were assigned to 3-fold- and 4-fold-coordinated O atoms within the Pd_5O_4 surface oxide structure, respectively. **Error! Bookmark not defined.** **Error! Bookmark not defined.**⁻⁶⁶ In addition to the O(I) and O(II) component, the Pd_5O_4 surface oxide is characterized by the Pd_{ox1} and Pd_{ox2} peaks at 335.5 and 336.3 eV, which were attributed to Pd atoms neighboring two (Pd_{ox1}) and four (Pd_{ox2}) O atoms. For pure Pd_5O_4 , the expected ratio between the Pd_{ox1} and Pd_{ox2} components is 4:1. This value was not obtained in the temperature region up to 700 K. The Pd_{ox1}/Pd_{ox2} ratio remains approximately at 2.4, i.e., the relative contribution of the Pd_{ox2} peak is larger than expected for Pd_5O_4 . The ratio of 2.4 is rather typical for the metastable state of the surface characterized as PdO seeds growing within the largely Pd_5O_4 covered surface. **Error! Bookmark not defined.** The presence of PdO seeds coincides with the pronounced catalytic activity increase between 500 and 650 K (see Figure 7). It is therefore proposed that the PdO seeds in Pd_5O_4 represent a particularly active phase for methane oxidation. The Pd_{ox2} component showed a steady increase and reached a maximum at 550 K, before gradually decreasing. The Pd_{ox1} component remained approximately constant up to 650 K and then started to decrease, indicating the beginning decomposition of the Pd_5O_4 surface oxide above 650 K. **Error! Bookmark not defined.**

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In summary, the surface oxidation state of Pd correlates with the reaction rate. The catalytic activity exhibits a strong increase between 530 and 650 K, which is the stability region of PdO seeds within the Pd_5O_4 surface oxide. Above 650 K, this most active "PdO seeds + Pd_5O_4 " surface state decomposes, and the activity decreases. The further increase in the reaction rate observed above 700 K is exponential with temperature, and it is associated with the activated reaction on the metallic catalyst. During cooling, a surface oxide phase that is more reduced

than Pd₅O₄ formed, and no evidence of PdO seed growth within this phase was found.

Conclusions

The results presented above demonstrate that HP-XPS is able monitor the active state of a catalyst and its performance at Torr pressures, thus significantly narrowing the pressure gap between classical surface-science studies and industrial conditions. The examples of metals as oxidation catalysts highlight the necessity to perform *in situ* high-pressure surface analysis. In all examples, atomic oxygen species are formed when the bare metal is in contact with oxygen gas. For the understanding of the selectivity of these metal catalysts, it is not sufficient to consider only atomic oxygen as an adsorbed species with varying coverages on the metal surface. Instead, the pressures present in these experiments approach chemical potentials of real catalytic processes where the oxygen chemical potential can lead to the formation of subsurface compounds. These subsurface species cannot be observed under vacuum conditions because they either are not formed in vacuum because of the lack of oxygen chemical potential, or they decompose into surface oxides and bare metal when the sample is transferred from high pressure back into vacuum.

Subsurface compounds are electronically distinctly different from oxides in that they have a metallic surface termination. These metal sites are deprived of electron density, and therefore, their chemisorptive interaction with surface atomic oxygen will be different from metal sites in the absence of subsurface compounds. As a result of these differences, atomic oxygen can be bound to a metal atom either as electrophilic (oxidizing) or nucleophilic (C–H activating) oxygen. With respect to reacting molecules, the subsurface oxygen compounds support the adsorption of nonactivated reactants.

In the cases of CO and methanol oxidation, the roles of the activated oxygen species differ from each other: Whereas CO can only react with electrophilic oxygen, methanol either will be transformed to formaldehyde by nucleophilic oxygen or will be deeply oxidized to CO₂ by the combined action of nucleophilic and electrophilic oxygen. Exactly this combined action is desired in

methane combustion, where a strongly oxygen-modified metal surface is also required to bind the nonactivated substrate.

In summary, we have shown that, through the use of HP-XPS, a detailed picture of the selectivity control in oxidation reactions emerges. The examples in this article demonstrate the potential to determine ratios of surface to subsurface species and their influence on the reactivity. This insight into selectivity was hitherto available only through indirect analysis using surface science experiments. Because single-crystal surfaces are not required for the type of HP-XPS experiments that we have presented here, we expect that HP-XPS will also be a valuable tool for the synthesis of nanostructured catalysts and the investigation of their catalytic properties, even for classes of reactions other than oxidations.

Acknowledgments

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References

1. B.M. Weckhuysen, Ed., *In-Situ Spectroscopy of Catalysts* (American Scientific Publishers, 2004).
2. J.W. Niemandsverdriet, *Spectroscopy in Catalysis* (Wiley, Weinheim, Germany, ed. 2, 2000).
3. C. Lamberti, E. Groppo, G. Spoto, S. Bordiga, A. Zecchina, *Adv. Catal.* **51**, 1 (2007).
4. P.C. Stair, *Adv. Catal.* **51**, 75 (2007).
5. G. Rupprechter, *Adv. Catal.* **51**, 133 (2007).

6. A. Knop-Gericke, M. Hävecker, T. Schedel-Niedrig, R. Schlögl, *Top. Catal.* **10**, 187 (2000).
7. A.M.J. van der Eerden, J.A. van Bokhoven, A.D. Smith, D.C. Koningsberger, *Rev. Sci. Instrum.* **71**, 3260 (2000).
8. A. Brückner, *Adv. Catal.* **51**, 265 (2007).
9. M. Hunger, J. Weitkamp, *Ang. Chem. Int. Ed.* **40**, 2954 (2001).
10. J.-M.M. Millet, *Adv. Catal.* **51**, 309 (2007).
11. S. Tanuma, C.J. Powell, D.R. Penn, *Surf. Interface Anal.* **21**, 165 (1994).
12. K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P.F. Heden, K. Hamrin, U. Gelius, T. Bergmark, L.O. Werme, R. Manne, Y. Baer, *ESCA Applied to Free Molecules* (North-Holland Publishing Company, Amsterdam, 1969).
13. H. Siegbahn, K. Siegbann, *J. Electron Spectrosc. Relat. Phenom.* **2**, 319 (1973).
14. H. Fellner-Feldegg, H. Siegbahn, L. Asplund, P. Kelfve, K. Siegbahn, *J. Electron Spectrosc. Relat. Phenom.* **7**, 421 (1975).
15. H. Siegbahn, S. Svensson, M. Lundholm, *J. Electron Spectrosc. Relat. Phenom.* **24**, 295 (1981).
16. R.W. Joyner, M.W. Roberts, K. Yates, *Surf. Sci.* **87**, 501 (1979).
17. H.J Ruppender, M. Grunze, C.W. Kong, M. Wilmers, *Surf. Interface Anal.* **15**, 245 (1990).
18. M.A. Kelly, M.L. Shek, P. Pianetta, T.M. Gür, M.R. Beasley, *J. Vac. Sci. Technol. A* **19**, 2127 (2001).
19. J. Pantförder, S Pöllmann, J.F. Zhu, D Borgmann, R. Denecke, H.-P. Steinrück, *Rev. Sci. Instrum.* **76**, 014102 (2005).
20. R.W. Joyner, M.W. Roberts, *Chem. Phys. Lett.* **60**, 459 (1979).
21. A.I. Boronin, V.I. Bukhtiyarov, A.L. Vishnevskii, G.K. Boreskov, V.I. Savchenko, *Surf. Sci.* **201**, 195 (1988).
22. V.I. Bukhtiyarov, I.P. Prosvirin, E.P. Tikhomirov, V.V. Kaichev, A.M. Sorokin, V.V. Evstigneev, *React. Kinet. Catal. Lett.* **79**, 181 (2003).
23. V.V. Kaichev, I.P., Prosvirin, V.I. Bukhtiyarov, H. Unterhalt, G. Rupprechter, H.-J. Freund, *J. Phys. Chem. B* **107**, 3522 (2003).

24. J.P. Baxter, M. Grunze, C.W. Kong, *J. Vac. Sci. Technol. A* **6**, 1123 (1988).
25. M. Grunze, D.J. Dwyer, M. Nassir, Y. Tsai, *ACS Symp. Ser.* **482**, 169 (1992).
26. D.F. Ogletree, H. Bluhm, G. Lebedev, C.S. Fadley, Z. Hussain, M. Salmeron, *Rev. Sci. Instrum.* **73**, 3872 (2002).
27. H. Bluhm, M. Hävecker, K. Ihmann, E. Kleimenov, D. Teschner, D.F. Ogletree, M. Salmeron, A. Knop-Gericke, R. Schlögl, *to be submitted to Rev. Sci. Instrum.*
28. H. Bluhm, K. Andersson, T. Araki, K. Benzerara, G.E. Brown, J.J. Dynes, S. Ghosal, M.K. Gilles, H.-Ch. Hansen, J.C. Hemminger, A.P. Hitchcock, G. Ketteler, A.L.D. Kilcoyne, E. Kneedler, J.R. Lawrence, G.G. Leppard, J. Majzlam, B.S. Mun, S.C.B. Myneni, A. Nilsson, H. Ogasawara, D.F. Ogletree, K. Pecher, M. Salmeron, D.K. Shuh, B. Tonner, T. Tylliszczak, T. Warwick, T.H. Yoon, *J. Electron Spectrosc. Relat. Phenom.* **150**, 86 (2006).
29. F.G. Requejo, E.L.D. Hebenstreit, D.F. Ogletree, M. Salmeron, *J. Catal.* **226**, 83 (2004).
30. H. Over, Y.D. Kim, A.P. Seitsonen, E. Lundgren, M. Schmid, P. Varga, A. Morgante, G. Ertl, *Science* **287**, 1474 (2000).
31. H. Liu, E. Iglesia, *J. Chem. Phys. B* **109**, 2155 (2005).
32. E.A. Seddon, K.R. Seddon, *The Chemistry of Ruthenium* (Elsevier Science, New York, 1984).
33. P. Mars, D.W. van Krevelen, *Chem. Eng. Sci.* **3**, 41 (1954).
34. C.I. Carlisle, T. Fujimoto, W.S. Sim, D.A. King, *Surf. Sci.* **470**, 15 (2000).
35. J.A. Labinger, K.C. Ott, *Catal. Lett.* **4**, 245 (1990).
36. H. Bluhm, M. Hävecker, A. Knop-Gericke, E. Kleimenov, R. Schlögl, D. Teschner, V.I. Bukhtiyarov, D.F. Ogletree, M. Salmeron, *J. Phys. Chem. B.* **108**, 14340 (2004).
37. L. Zhou, S. Gunther, D. Moszynski, R. Imbihl, *J. Catal.* **235**, 359 (2005).
38. W. Vogel, N. Alonso-Vante, *J. Catal.* **232**, 395 (2005).
39. V. Narkhede, J. Assmann, M. Muhler, *Z. Phys. Chem.* **219**, 979 (2005).
40. R. Blume, M. Hävecker, S. Zafeiratos, D. Teschner, E. Kleimenov, A. Knop-Gericke, R. Schlögl, A. Barinov, P. Dudin, M. Kiskinova, *J. Catal.* **239**, 354 (2006).

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41. R. Blume, M. Hävecker, S. Zafeiratos, D. Teschner, E. Vass, P. Schnörch, A. Knop-Gericke, R. Schlögl, S. Lizzit, P. Dudin, A. Barinov, M. Kiskinova, *Catal. Today* **124**, 71 (2007).
42. R. Blume, M. Hävecker, S. Zafeiratos, D. Teschner, A. Knop-Gericke, R. Schlögl, P. Dudin, A. Barinov, M. Kiskinova, *Phys. Chem. Chem. Phys.* **9**, 3449 (2007).
43. R. Blume, H. Niehus, H. Conrad, A. Böttcher, L. Aballe, L. Gregoratti, A. Barinov, M. Kiskinova, *J. Phys. Chem. B* **109**, 14052 (2005), and references therein.
44. K. Reuter, M. Scheffler, *Phys. Rev. B* **73**, 1 (2006), and references therein.
45. M. Mavrikakis, B. Hammer, J.K. Nørskov, *Phys. Rev. Lett.* **81**, 2819 (1998).
46. E. Lundgren, J. Gustafson, Mikkelsen, J.N. Andersen, A. Stierle, H. Dosch, M. Todorova, J. Rogal, K. Reuter, M. Scheffler, *Phys. Rev. Lett.* **92**, 046101 (2004).
47. G. Ketteler, D.F. Ogletree, H. Bluhm, H. Liu, E.L.D. Hebenstreit, M. Salmeron, *J. Am. Chem. Soc.* **127**, 18269 (2005).
48. E. Lundgren, G. Kresse, C. Klein, M. Borg, J.N. Andersen, M. De Santis, Y. Gauthier, C. Konvicka, M. Schmid, P. Varga, *Phys. Rev. Lett.* **88**, 246103 (2002).
49. M. Todorova, W.X. Li, M.V. Ganduglia-Pirovano, C. Stampfl, K. Reuter, M. Scheffler, *Phys. Rev. Lett.* **89**, 096103 (2002).
50. I. Barin, *Thermochemical Data of Pure Substances* (VCH, Weinheim, Germany, 1992).
51. K. Reuter, M. Scheffler, *Appl. Phys. A* **78**, 793 (2004).
52. R.B. Anderson, K.C. Stein, J.J. Feenan, L.J.E. Hofer, *Ind. Eng. Chem.* **53**, 809 (1961).
53. C.F. Cullis, B.M. Willatt, *J. Catal.* **83**, 267 (1983).
54. R.F. Hicks, M.L. Young, R.G. Lee, H. Qi, *J. Catal.* **122**, 280 (1990).
55. M. Lyubovsky, L. Pfefferle, *Catal. Today* **47**, 29 (1999).
56. R. Burch, F.J. Urbano, P.K. Loader, *Appl. Catal. A* **123**, 173 (1995).
57. J.N. Carstens, S.C. Su, A.T. Bell, *J. Catal.* **176**, 136 (1998).
58. R.S. Monteiro, D. Zemlyanov, J.M. Storey, F.H. Ribeiro, *J. Catal.* **199**, 291 (2001).

59. R.S. Monteiro, D. Zemlyanov, J.M. Storey, F.H. Ribeiro, *J. Catal.* **201**, 37 (2001).
60. G.B. Hoflund, H.A. Hagelin, J.F. Weaver, G.N. Salaita, *Appl. Surf. Sci.* **205**, 102 (2003).
61. H. Gabasch, K. Hayek, B. Klötzer, W. Unterberger, E. Kleimenov, D. Teschner, S. Zafeiratos, M. Hävecker, A. Knop-Gericke, R. Schlögl, B. Aszalos-Kiss, D. Zemlyanov, *J. Phys. Chem C* **111**, 7957 (2007).
62. J.G. McCarty, *Catal. Today* **26**, 283 (1995).
63. P. Salomonsson, S. Johansson, B. Kasemo, *Catal. Lett.* **33**, 1 (1995).
64. D. Zemlyanov, B. Aszalos-Kiss, E. Kleimenov, D. Teschner, S. Zafeiratos, M. Hävecker, A. Knop-Gericke, R. Schlögl, H. Gabasch, W. Unterberger, K. Hayek, B. Klötzer, *Surf. Sci.* **600**, 983 (2006).
65. H. Gabasch, W. Unterberger, K. Hayek, B. Klötzer, E. Kleimenov, D. Teschner, S. Zafeiratos, M. Hävecker, A. Knop-Gericke, R. Schlögl, B. Aszalos-Kiss, D. Zemlyanov, *Surf. Sci.* **600**, 2980 (2006).
66. E. Lundgren, G. Kresse, C. Klein, M. Borg, J.N. Andersen, M. De Santis, Y. Gauthier, C. Konvicka, M. Schmid, P. Varga, *Phys. Rev. Lett.* **88**, 246103 (2002).

Figure Captions

Figure 1. (a) Principal idea of HP-XPS. The sample is placed in a high-pressure chamber that is separated from the x-ray source by an x-ray-transparent window. Electrons and gas escape through a differentially pumped aperture. (b) Conventional HP-XPS setup. Several differential pumping stages are needed to keep the electron analyzer under vacuum when the pressure in the sample cell is close to 1 Torr or higher. There is a tradeoff between the pumping efficiency, given by aperture sizes and spacings, and the solid angle of transmission of electrons through the differential pumping stages. (c) Principle of HP-XPS using a differentially pumped electrostatic lens system. The electrons are focused onto the apertures using electrostatic lenses in the differential pumping stages, which increases the efficiency of electron collection and allows for a reduction of the size of the apertures for improved differential pumping. (d) Differentially pumped electrostatic lens system and hemispherical analyzer (Phoibos 150, Specs GmbH, Berlin) of the HP-XPS instruments at ALS beamline 11.0.2 and BESSY.

Figure 2. Closeup of the sample–aperture region. The incident x-rays irradiate not only the sample surface but also part of the gas phase in front of it, leading to the appearance of gas-phase peaks in the XPS spectra. The bottom panel shows the pressure along the optical axis as a function of the aperture–sample distance. The

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pressure drops in the plane of the aperture to $0.5p_0$ and is $0.98p_0$ at a distance of two aperture diameters.

Figure 3. (b) Selected Ru $3d_{5/2}$ spectra monitored during CO oxidation reaction by HP-XPS, showing the evolution of the Ru(0001) precatalyst with increasing temperature. The components corresponding to bulk metallic Ru (black), Ru surface with adsorbed O and CO (orange), RuO_x transient (green) and RuO_2 (blue) appear at different binding energies, as indicated by the dashed lines. The decrease of the relative intensity of the bulk Ru component reflects the increasing thickness of the RuO_x transient and RuO_2 phase. (a) CO_2 yield as a function of reaction temperature. The dashed line indicates the onset of the RuO_2 growth. Reaction conditions: $P_{CO} = 0.5 \times 10^{-1}$ mbar, $P_{O_2} = 0.5 \times 10^{-1}$ mbar.

Figure 4. Surface plot with the Ru $3d_{5/2}$ spectra illustrates the partial reduction of a RuO_2 precatalyst to RuO_x transient with increasing reaction temperature at specific CH_3OH and O_2 potentials ($P_{CH_3OH+O_2} = 2.4 \times 10^{-1}$ mbar, $P_{CH_3OH}/P_{O_2} = 1.5$) favoring formaldehyde production. Similar evolution of the Ru $3d_{5/2}$ spectra is observed for reactant potentials ($P_{CH_3OH+O_2} = 2.4 \times 10^{-1}$ mbar, $P_{CH_3OH}/P_{O_2} = 0.75$) favoring full oxidation, but it terminates at the oxygen-richer transient, RuO_{x2} . The difference in the stoichiometry of the two steady catalyst states at 600 K, RuO_{x1} and RuO_{x2} , is reflected by the relative intensity of RuO_x component (green) in the deconvoluted Ru $3d_{5/2}$ spectra, shown in the left and right panels. The panel above each Ru $3d_{5/2}$ spectrum shows the corresponding product yield plotted as a function of temperature. The dashed-line plots in the panel for the CH_2O channel are measured for metallic Ru precatalyst, which apparently evolves to the same catalytically active state above 550 K

Figure 5. Pd $3d_{5/2}$ (left) and O $1s$ /Pd $3p_{3/2}$ (right) XPS spectra during different stages of oxidation of Pd(111): (a) $\sqrt{6} \times \sqrt{6}$ surface oxide, (b) subsurface oxide, and (c) bulk PdO. Peaks are normalized to the total Pd $3d_{5/2}$ and Pd $3p_{3/2}$ areas, respectively.

Figure 6. (a) Phase diagram showing the experimentally observed stability regions of the different palladium oxide structures as a function of pressure and temperature. The points mark the conditions under which XPS spectra were acquired during isotherm measurements (oxidizing conditions). At these points, the spectra were stable over several minutes. The solid line indicates the phase transition of bulk Pd to bulk PdO as calculated from tabulated enthalpy and heat capacity values. The hatched region shows the PdO bulk oxide stability region when the pressure is reduced from 1 Torr at fixed temperatures. (b) Corresponding surface phase diagram, as calculated by transforming results from atomistic thermodynamics into a p, T plot.

Figure 7. Mass spectroscopic data of CO_2 and water formation through the oxidation of methane on Pd(111) as a function of temperature at a heating–

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cooling rate of 6.6 K min^{-1} . The O_2/CH_4 mixture was 1:5 at a total pressure of 0.33 mbar.

Figure 8. HP-XPS spectra corresponding to the mass spectrometry data in Figure 7. (a) O 1s/Pd 3p_{3/2} (left) and Pd 3d_{5/2} (right) core-level spectra recorded during heating in an O_2/CH_4 mixture. The raw data after Shirley background subtraction are indicated by open circles. The intensity was normalized to the Pd 3p_{3/2} (left) and the total Pd 3d_{5/2} (right) areas. (b) O 1s/Pd 3p_{3/2} (left) and Pd 3d_{5/2} (right) core-level spectra recorded during cooling in an O_2/CH_4 mixture. The raw data after Shirley background subtraction are indicated by open circles. The intensity was normalized on the Pd 3p_{3/2} (left) and the total Pd 3d_{5/2} (right) areas.