

## C–O bond scission on “defect-rich and perfect” Pd(1 1 1)?

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### Abstract

To investigate the influence of surface defects on CO adsorption and dissociation, well-annealed and “defect-rich” Pd(1 1 1) were examined by sum frequency generation (SFG) and X-ray photoelectron spectroscopy (XPS) within the pressure range  $10^{-6}$ –1 mbar. Ar<sup>+</sup> ion sputtering was employed to produce surface defects which exhibited vibrational and photoemission characteristics different from the regular adsorption sites on Pd(1 1 1). Even under high-pressure, SFG and XPS indicated that no CO dissociation occurred on both surfaces at 300–400 K. By contrast, C–O bond scission was observed during methanol decomposition producing carbonaceous deposits beside CO and H<sub>2</sub>. A possible relationship between the adsorption geometry and C–O bond scission is discussed.

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### 1. Introduction

The interaction of CO with palladium has been studied extensively in the past, due to its relevance in automobile emission control and due to the high sensitivity of CO vibrational and photoemission characteristics towards binding sites and adsorbate structure ([1] and references therein). In preceding studies monitoring CO structures on Pd(1 1 1) from ultrahigh vacuum (UHV) up to 1 bar we have shown that the high-pressure CO structures

were comparable to high-coverage structures under UHV, and that surface rearrangements and CO dissociation were absent even at mbar pressures [2,3]. By contrast, in a number of studies on mica, alumina or MgO supported palladium catalysts carbon deposits were observed, resulting from CO dissociation or disproportionation via the Boudouard reaction [4–6]. It was reported that the dissociation activity increased with decreasing particle size and that carbon preferentially blocked strongly bonding adsorption sites [4]. The rate of formation was accelerated by high pressure (coverage) and high temperature (maximum at ~400 K) [5]. This process is important for technical catalysis since carbon deposition is a major reason for catalyst deactivation. However, there are also conflicting reports on supported Pd, where CO dissociation was not observed [6–9].

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To explain the disagreement between different studies on Pd nanoparticles, Henry et al. [7] suggested that CO dissociation proceeds on a special type of defect site, which is present only on “ill-shaped” (rough) clusters and not on well-faceted nanoparticles. This was supported by an XPS study where partial CO dissociation occurred on sputtered Pd foil, but was absent on a well-annealed foil [10]. Another reason, which may contribute to the observed disagreement, may be metal–support interactions as described by Matolín et al. [6]. Furthermore, CO was reported to dissociate on Pt(1 1 1) [11] and Rh(1 1 1) [12,13] at mbar pressures (most likely due to surface roughening), while CO dissociation was absent under UHV. Apparently, the exact origin of CO dissociation is still under debate.

These considerations led us to revisit the CO/Pd system, in order to study CO adsorption on Pd surfaces with different defect concentration, using physical methods which are sensitive both to the nature of adsorbed CO and to carbonaceous residues. As a first step, we have recently examined CO adsorption on well-annealed Pd(1 1 1) up to 1 mbar using sum frequency generation (SFG) and X-ray photoelectron spectroscopy (XPS) [3]. Here, we report the next step, i.e. high-pressure CO adsorption on defect-rich (strongly sputtered) Pd(1 1 1). For comparison, we also present results from methanol decomposition illustrating the different nature of the C–O bond within carbon monoxide and methanol.

## 2. Experimental

The experiments were carried out in two UHV chambers, both equipped with high-pressure reaction cells for in situ studies (SFG: [14]; VG ESCALAB “high-pressure” electron spectrometer) [3,15]. Pd(1 1 1) was cleaned as described in [2] until no contaminants were registered by XPS or Auger electron spectroscopy (AES) and the surface exhibited a sharp (1 × 1) low-energy electron diffraction (LEED) pattern. “Defect-rich” Pd(1 1 1), i.e. slightly misoriented Pd(1 1 1) or strongly sputtered surfaces (20  $\mu$ A, 2–3 keV at  $2 \times 10^{-5}$  mbar Ar at 100–300 K, 60 min, no sub-

sequent annealing) were also utilized. According to previous studies, the defect-rich surface is stable at 300–400 K and annealing to  $\sim$ 600 K is necessary to completely remove the defects [1]. AES and XPS indicated that the sputtered surface was clean, but LEED showed a (1 × 1) pattern with rather broad spots. CO (purity  $\geq$  99.997%) was cleaned using a liquid nitrogen cold trap and a carbonyl absorber cartridge, while methanol (p.a.) was purified by freeze-thaw cycles. No Ni or Fe impurities were registered in survey XPS spectra even after high-pressure CO treatments of several hours.

## 3. Results and discussion

Fig. 1 shows SFG and XPS spectra of CO adsorbed on perfect “p” and defect-rich “d” Pd(1 1 1) at 300 K. Comparison of “p” and “d” SFG spectra at  $10^{-6}$  mbar CO (Fig. 1a) evidences that ion sputtering gave rise to an additional feature at  $1980 \text{ cm}^{-1}$  which is attributed to CO bridge bonded to defects (see [1] for details). The two common features at 1935 and  $\sim$ 2075  $\text{cm}^{-1}$  originate from CO on bridge (and hollow) and on-top sites on (1 1 1) terraces, respectively.

XPS C1s core-level spectra at  $10^{-6}$  mbar CO are very similar for “p” and “d” surfaces exhibiting a single peak at 285.6 eV with slight asymmetric shape (Fig. 1b, traces 2,3). According to our previous SFG/XPS study [3], the C1s peak corresponds to bridge and/or three-fold hollow CO at a coverage of  $\sim$ 0.5 ML (using the 0.63 ML CO structure at  $10^{-6}$  mbar/200 K as reference for quantitative analysis). However, there are two differences between “p” and “d” surfaces: First, the C1s intensity is  $\sim$ 20% higher on the sputtered surface which reflects an increased palladium surface area after ion sputtering. Second, the C1s binding energy is slightly higher (285.8 eV) than on perfect Pd(1 1 1), as illustrated by the difference spectrum in Fig. 1c (trace 3–2). Despite the small value of this shift ( $\sim$ 0.2 eV), the corresponding SFG data (Fig. 1a) suggest an additional CO state. Accordingly, the C1s binding energy of 285.8 eV is tentatively ascribed to CO bridge-bonded to sputtering-induced defects such as steps, kinks or

vacancies. Of course, high-resolution XPS [16,17] using synchrotron radiation would be required for confirmation.

Raising the CO pressure to 1 mbar on the “d” surface shifted the frequency of all CO species (dipole-coupling) and increased their intensity, especially for on-top CO (Fig. 1a). In agreement with SFG, the C1s intensity increased (Fig. 1b, trace 4) due to a growing feature at  $\sim 286.2$  eV (Fig. 1c, difference spectrum 4–3). As shown earlier [3,16] this feature arises from on-top CO. Spectra of 0.1 mbar CO on “p” Pd(111) (presented in [3]) indicated the same changes (the C1s intensity was again  $\sim 20\%$  higher on the sputtered surface).

Core-level C1s spectra of 0.1 mbar CO on “p” and “d” surfaces at 400 K are compared in Fig. 2a. Again, a  $\sim 20\%$  increase in CO coverage was observed due to the formation of and adsorption on defect sites. The influence of the defect sites can be rationalized by calculating the difference C1s spectrum which shows an obvious shift when compared to the  $10^{-6}$  mbar CO spectrum from “p” Pd(111) (adsorption on hollow sites only) (Fig. 2b). Consequently, we again assign the C1s feature at 285.8 eV to CO bridge-bonded to sputtering-induced surface defects.

With respect to CO dissociation, carbon deposits (amorphous, graphitic, etc.), which typi-

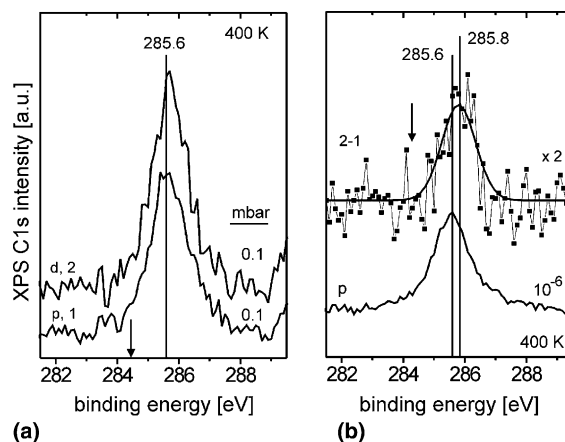


Fig. 2. (a) C1s core-level spectra measured during CO adsorption at 400 K. “p” and “d” refer to a well-annealed (perfect) and defect-rich (ion-bombarded) Pd(111) surface. (b) To illustrate the contribution of CO adsorption on defect sites, the difference spectrum (2–1) is compared with the C1s spectrum of  $10^{-6}$  mbar CO on “p” Pd(111).

cally appear at  $\sim 284.5$  eV (marked by arrows in Figs. 1 and 2), were not detected on both surfaces. In the following, we discuss possible mechanisms of CO dissociation on transition metals and briefly recall the nature of CO bonding. According to the frequently used Blyholder model, the CO–metal bond results from a charge transfer from the  $5\sigma$

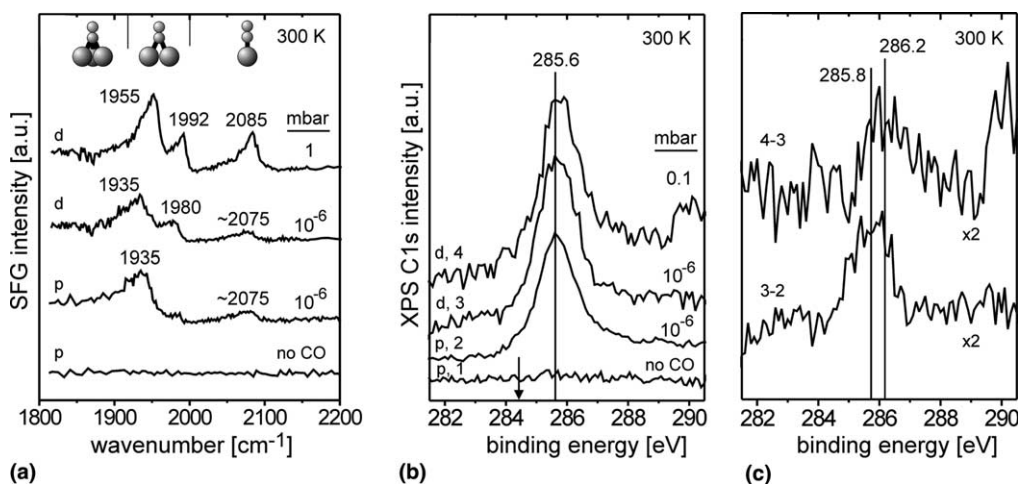


Fig. 1. (a) SFG and (b) XPS C1s core-level spectra measured during CO adsorption at 300 K. “p” and “d” refer to a well-annealed (perfect) and defect-rich (ion-bombarded) Pd(111) surface. In (c) difference spectra are shown revealing adsorption on defect (3–2) and on-top (4–3) sites. XPS spectra were normalized to the Pd3d<sub>5/2</sub> integral intensity at 334.9 eV.

molecular orbital of CO into a free d orbital of the metal and an electron back-donation from an occupied d orbital of the metal into the unoccupied  $2\pi^*$  antibonding orbital of CO. As discussed by Broden et al. [18], the activation energy for dissociation may be related to the degree of population of the  $2\pi^*$  antibonding CO orbital (which weakens the C–O bond). CO dissociation seems to be also facilitated if CO bends towards the surface [19–21]. For CO dissociation on rhodium, deKoster et al. [19] reported a tilting of the C–O bond, with an angle of about  $70^\circ$  between the C–O axis and the surface normal. For Fe(1 0 0), Moon et al. [20] suggested CO molecules tilted  $45^\circ \pm 10^\circ$  with respect to the surface normal as precursor state for CO dissociation. Shinn and Madey [21] proposed a CO dissociation precursor with an axis nearly parallel to the Cr(1 1 0) surface. The tilted CO molecule may allow for a better overlap between the CO  $2\pi^*$  orbitals and the metal valence electron density, thus weakening the CO bond. The influence of surface defects on these low-index surfaces cannot be fully ruled out though. The ability of CO to adopt a tilted geometry on early transition metals has been explained in terms of their ability to accept electrons (due to their d-electron-deficiency) [22]. In contrast to the above-mentioned metals, Pd has a filled d-band ( $4d^{10}$ ) and CO adsorbs perpendicular on Pd(1 1 1) [23,24]. The upright adsorption geometry may be one of the reasons explaining the non-occurrence of CO dissociation.

This model is further supported by results on methanol decomposition on Pd(1 1 1). Methanol decomposition proceeds via O–H bond scission forming  $\text{CH}_3\text{O}$  (methoxy) groups, which are stepwise dehydrogenated via  $\text{CH}_x\text{O}$  to adsorbed CO [25]. A simultaneous formation of  $\text{CH}_3\text{O}$  and  $\text{CH}_3$  species by dehydration of two adsorbed neighboring methanol molecules was also suggested [26,27]. Both cases involve  $\text{CH}_x\text{O}$  or  $\text{CH}_3\text{OH}$  adsorption geometries where the C–O axis deviates from a perpendicular orientation [27,28]. For instance, a  $\text{CH}_3\text{O}$  group bonded to the surface via the oxygen atom has to turn over in order to produce CO bonded via the carbon atom. If the above-mentioned model of C–O bond scission applies we should expect carbon (or carbonaceous

species  $\text{CH}_x$ ) as side products of methanol decomposition on Pd. It can, however, not be ruled out that the additional hydrogen atoms within  $\text{CH}_x\text{O}$  also facilitate C–O bond scission.

Fig. 3 shows SFG and XPS C1s spectra acquired during methanol decomposition on well-annealed (p) Pd(1 1 1). The SFG spectrum ( $10^{-6}$  mbar  $\text{CH}_3\text{OH}/300$  K; Fig. 3a) displays the C–O stretching region revealing a peak at  $1915\text{ cm}^{-1}$  indicating approximately 0.5 ML hollow/bridge bonded CO originating from  $\text{CH}_3\text{OH}$  decomposition. In the corresponding XPS spectrum (Fig. 3b) two peaks can be identified and attributed to adsorbed CO and  $\text{CH}_x\text{O}$  ( $285.6\text{ eV}$ ;  $\sim 0.5$  ML) and to carbon or carbonaceous species ( $\text{CH}_x$ ;  $283.8\text{ eV}$ ). The amount of carbonaceous species is  $\sim 0.15$  ML

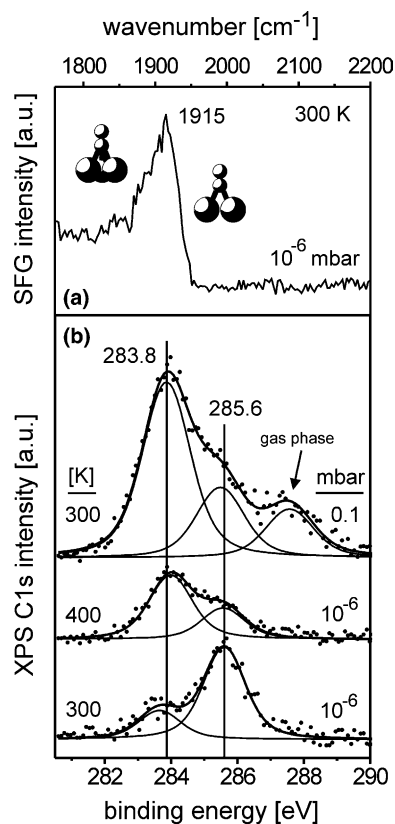


Fig. 3. (a) SFG spectrum of  $10^{-6}$  mbar  $\text{CH}_3\text{OH}$  on “p” Pd(1 1 1) at 300 K (exposure time 90 min). (b) C1s XPS spectra of  $10^{-6}$  mbar  $\text{CH}_3\text{OH}$  at 300 and 400 K, and of 0.1 mbar  $\text{CH}_3\text{OH}$  at 300 K (exposure time 90 min) revealing carbonaceous deposits; see text.

which is apparently too low to induce significant changes in the SFG spectrum, which shows no indications of carbon deposition. Increasing the temperature or CH<sub>3</sub>OH pressure increased the amount of carbon(aceous) deposits, as shown in Fig. 3b (10<sup>-6</sup> mbar/400 K: ≈0.3 ML; 0.1 mbar/300 K: ≈1 ML). Consequently, C–O bond cleavage occurs during methanol decomposition and presumably proceeds via intermediates including a tilted C–O bond.

Based on these results we suggest that CO molecules adsorbed on sputter-induced defects are not enough tilted to provide the geometry required for CO dissociation. With respect to the reported CO dissociation on small Pd particles, we suggest that either the geometric and/or electronic structure of surface sites on nanoparticles are different from sputter-induced defects or that an additional influence comes from the oxide support (interface sites, metal–support interaction, hydroxyl groups etc.). Along these lines, discrepancies between various studies on Pd/Al<sub>2</sub>O<sub>3</sub> were attributed to differences in catalyst preparation/composition, e.g. Matolín et al. [6] reported PdAl alloys produced by partial reduction of the alumina support. In this case carbon and oxygen of the CO molecule may bind to Pd and Al, respectively, and the tilted geometry may lead to CO dissociation. For Pd particles on mica, potassium may promote CO decomposition [4,29].

#### 4. Conclusions

CO adsorption on defect-rich Pd(1 1 1) resulted in an additional peak in both SFG and XPS spectra which was attributed to CO bridge-bonded to defect sites. This assignment is based on the CO frequency of ~1990 cm<sup>-1</sup> and a C1s feature at 285.8 eV that are higher than the corresponding values for bridge bonded CO on (1 1 1) terraces (1955 cm<sup>-1</sup> and 285.6 eV, respectively). Nevertheless, even in the mbar regime both methods did not detect carbon deposits indicating the absence of CO dissociation. Based on the comparison with CO dissociation on other metals and with methanol decomposition, the perpendicular adsorption geometry of CO on Pd(1 1 1), which is also main-

tained at high pressure, is presumably responsible for the non-occurrence of CO dissociation. To further elucidate the mechanism of CO dissociation on Pd catalysts, analogous experiments on oxide supported Pd nanoparticles are planned for the near future.

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