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Vacuum 71 (2003) 83–87

VACUUM
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Extending UHV studies to the mbar range: vibrational SFG spectroscopy of high-pressure CO adsorption on Pt(1 1 1) and Pd(1 1 1)

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Received 16 June 2002; received in revised form 21 August 2002; accepted 24 September 2002

Abstract

Vibrational sum frequency generation spectroscopy was employed to study CO adsorption on Pt(1 1 1) and Pd(1 1 1) from ultrahigh vacuum (UHV) to atmospheric pressure. Even by increasing the CO pressure by 10 orders of magnitude the UHV saturation coverages could not be exceeded with the high-pressure CO structures being identical to the corresponding high coverage structures under UHV. No indications of CO-induced surface roughening were found. When CO was exposed at low temperature (100 K) kinetically hindered "non-equilibrium" structures were observed on Pd(1 1 1) and identified as superposition of two ordered structures. Possible reasons for discrepancies between UHV and high-pressure studies are discussed.

Keywords: Sum frequency generation; Catalysis; Vibrations of adsorbed molecules; Palladium; Carbon monoxide; Low index single-crystal surfaces

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1. Introduction

The understanding of heterogeneous catalysis has considerably benefited from the utilization of well-defined single crystals as model catalysts and from surface-sensitive techniques that permit atomic scale characterization [1,2]. However, it was soon realized that discrepancies existed between surface science and heterogeneous catalysis. The so-called "pressure gap" originates from the need of most surface sensitive techniques of ultrahigh vacuum (UHV), in contrast to catalyzed reactions that are carried out at $\geqslant 1$ bar. It has been speculated that at high-pressure UHV saturation coverages may be exceeded and new adsorbate geometries may occur. Even if this is not the case, one has to keep in mind that adsorption studies under UHV are typically carried out at low temperature ($\leqslant 100$ K) in order to obtain high coverages. However, under these conditions the limited mobility of the adsorbed molecules may produce kinetically "trapped" adsorbate species that may not be relevant for catalysis. It has also

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0042-207X/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
doi:10.1016/S0042-207X(02)00718-2

been reported that at elevated pressure/temperature catalysts may restructure (step formation, surface roughening) [3,4] or even alter their composition [5,6] which has a strong impact on the adsorption sites and thus on the adsorbate structure.

A few high-pressure surface-sensitive techniques capable of answering the above-mentioned questions are currently available, among them sum frequency generation (SFG) spectroscopy [1–3]. Because SFG provides vibrational spectra of adsorbed molecules from submonolayer coverages up to ~1 bar, it allows direct comparison of adsorbate structures under UHV and elevated pressure. In this paper we focus on two adsorption systems, CO on Pt(1 1 1) and Pd(1 1 1), where changes in surface morphology and composition are absent. In that way we want to address the inherent effect of the gas pressure on the adsorbed species, without interference from surface structural/compositional changes. Part of the results were published in previous papers [7,8], here we compare both adsorption systems and discuss general trends.

2. Experimental

Experiments were performed in a UHV surface analysis system combined with an SFG-compatible UHV-high pressure cell [3,8]. Pt(1 1 1) and Pd(1 1 1) were prepared by standard procedures, described in [7,8] and characterized by low-energy electron diffraction (LEED), Auger electron spectroscopy (AES) and temperature programmed desorption (TPD). For details about SFG spectroscopy we refer to the literature ([1,3,8–10 and references therein]).

3. Results and discussion

3.1. CO adsorption on Pt(111)

CO on Pt(1 1 1) is one of the "drosophila" systems of surface science and an extensive database was acquired under UHV ([7 and references therein]). The interest to extend these studies to higher pressures is apparent. Due to its high dynamic dipole CO is a perfect probe molecule for vibrational spectroscopy providing information about the surface site distribution (terminal-, bridging-, hollow-sites). Fig. 1 displays SFG spectra of CO on Pt(1 1 1) at 300 K from 10^{-7} to 500 mbar. At 10^{-7} mbar, a single resonance at 2090 cm^{-1} was observed characteristic of the C–O stretching vibration of terminally bonded (on-top) CO. Corresponding LEED/TPD data [7] indicated a coverage of ~0.5 ML where an equal number of CO molecules occupy on-top and bridge sites, as recently confirmed by comparing experimental and simulated scanning tunnelling microscopy (STM) images [11]. The absence of bridge-bonded CO (expected around 1850 cm^{-1}) in the SFG spectra is probably due to a low Raman polarizability [1,9] and/or an inherently broad line width of bridged CO at 300 K [10]. Increasing the pressure up to 200 mbar increased the dipole coupling shifting the frequency to 2097 cm^{-1} (Fig. 1). However, the spectra were still very similar to those under UHV

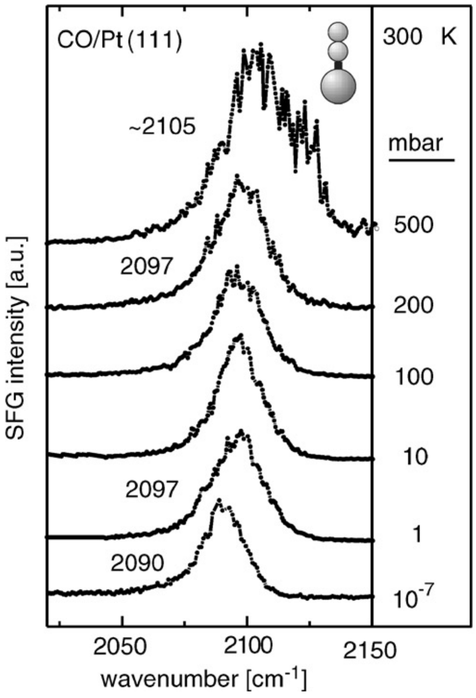

Fig. 1. SFG spectra of CO adsorption on Pt(1 1 1) at 300 K, measured from 10^{-7} to 500 mbar.

with on-top CO being the only species detected by SFG. If the maximum value of the SFG signal is simply taken as a measure of the on-top CO concentration (using 0.5 ML at 10^{-7} mbar as reference), a CO coverage of about 0.7 is calculated for high pressures. This value and the presence of on-top CO is in excellent agreement with a recent high-pressure STM study of CO/Pt(1 1 1) by Vestergaard et al. [12]. SFG spectra at 500 mbar CO showed peak frequencies around 2105 cm^{-1} but with a broader line width due to the smaller signal-to-noise ratio under these conditions (for details see [7]). The SFG spectra were reversible with pressure suggesting the absence of strong surface restructuring.

3.2. CO adsorption on Pd(111)

The adsorption of CO on Pd(1 1 1) is strongly coverage-dependent [8,13] with concomitant rearrangements in the CO layer. SFG spectra of CO/Pd(1 1 1) from 10^{-8}–1000 mbar and 100–500 K can be found in [8,14]. A variety of well-ordered structures was observed, here we focus on high coverages, i.e. the $(4\sqrt{3} \times 8)$rect (0.63 ML) and the (2×2)-3CO (0.75 ML) structures (coverages were determined by TPD, see [8 and references therein]).

Fig. 2a shows a spectrum of 0.63 ML CO (10^{-6} mbar at 190 K), revealing bridge-bonded CO (1954 cm^{-1}) and on-top CO (2086 cm^{-1}). If the coverage was increased, the bridge site intensity decreased, the on-top signal increased and a rearrangement from a bridge/on-top structure to a hollow/on-top structure occurred [15]. Fig. 2c shows a spectrum at saturation coverage (0.75 ML; 10^{-6} mbar at 90 K), where bands at 1894 cm^{-1} (fcc- and hcp-hollow-bonded CO) and 2106 cm^{-1} (on-top CO) were observed. Parallel LEED studies [8] corroborated the presence of ordered 0.63 and 0.75 ML structures (for schematic representations cf. Fig. 2d and f).

However, these well-ordered phases were only obtained upon cooling Pd(1 1 1) from ~300 to 190/90 K in $>10^{-6}$ mbar CO ([8,14–16]). When cooled at lower pressures (10^{-8}–10^{-7} mbar) or when CO was dosed at 90 K, a "less-ordered" saturation structure was observed, exhibiting hollow (1880–90 cm^{-1}), bridge (1958 cm^{-1}) and two on-top CO peaks (2086 and 2100 cm^{-1}) (Fig. 2b). Such phases, sometimes termed "non-equilibrium" structures, may occur in low-temperature UHV surface reaction studies and it seems worthwhile to identify their origin.

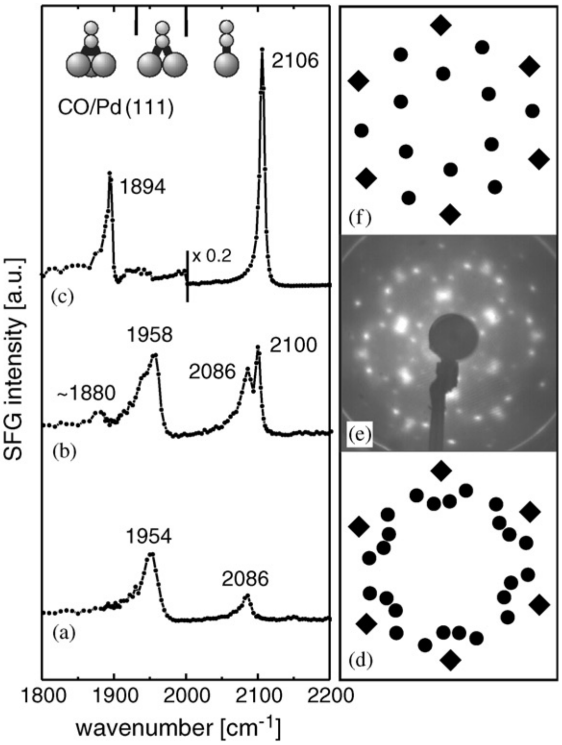

Fig. 2. SFG spectra of various CO structures on Pd(1 1 1): (a) 0.63 ML, $(4\sqrt{3} \times 8)$rect, (b) a "non-equilibrium" phase, and (c) 0.75 ML, (2×2). Approximate frequency ranges of hollow, bridge, and on-top CO are also shown. The LEED image of a "non-equilibrium" structure in (e) is a superposition of 0.63 and 0.75 ML domains schematically shown in (d) and (f), respectively (circles: CO reflections; squares: Pd reflections).

The spectrum in Fig. 2b clearly represents a superposition of the spectra at 0.63 ML (Fig. 2a) and at 0.75 ML (Fig. 2c), particularly evident from the double on-top peak (small variations in frequency are due to different dipole coupling). The LEED image of the non-equilibrium phase (Fig. 2e), indicative of a superposition of a $(4\sqrt{3} \times 8)$rect (0.63 ML; Fig. 2d) and a (2×2) (0.75 ML; Fig. 2f) structure, further corroborates this picture. In fact, when the non-equilibrium layer in Fig. 2b was heated in 10^{-6} mbar CO to ~250 K and cooled back to 90 K, a typical (2×2)

spectrum was obtained (such as the one in Fig. 2c). These data (together with previous cooling experiments [8]) indicate that the formation of a well-ordered (2×2) saturation structure requires a sufficiently high CO mobility (temperatures of ~150 K to overcome the CO diffusion barrier) and a sufficient CO flux (e.g. $\sim 10^{-6}$ mbar at 150 K) to avoid "quenching" of domains with lower coverages.

It is now interesting to examine which structures occur under catalytic reaction conditions. Fig. 3 shows SFG spectra between 10^{-6} and 1000 mbar CO on Pd(1 1 1) at 300 K. At 10^{-6} mbar, the 1937 cm^{-1} peak indicated a coverage of about 0.5 ML [8]. The coverage increased with pressure and reached about 0.6 ML at 100 mbar (1951 cm^{-1}—bridge and 2083 cm^{-1}—on-top CO). Upon further increasing the pressure, the bridge peak decreased and the on-top peak increased. Between 400 and 1000 mbar CO "non-equilibrium" structures with hollow, bridge and on-top peaks were observed. This suggests that at certain temperature/pressure combinations (falling into the transition range between 0.63 and 0.75 ML) such structures may be even present during catalytic reactions. A perfect hollow/on-top (0.75 ML) structure could not be obtained at 300 K and would presumably require pressures > 1 bar.

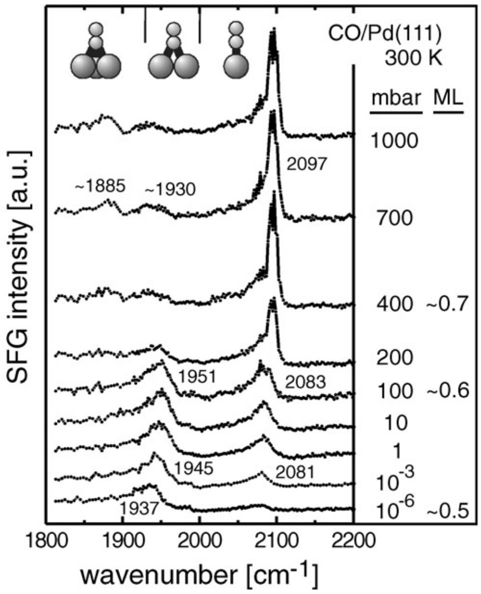

Fig. 3. SFG spectra of CO adsorption on Pd(1 1 1) at 300 K, measured from 10^{-6} to 1000 mbar. Approximate CO coverages are also indicated.

At 190 K, the 0.63 ML structure was observed at 10^{-6} mbar, while the 0.75 ML saturation structure was obtained at 1 mbar (identical to Fig. 2a and c) [8]. At 10^{-4} and 10^{-3} mbar, non-equilibrium structures again occurred. Increasing the pressure from 1 to 1000 mbar did not induce changes in the SFG spectrum, i.e. the CO saturation structures on Pd(1 1 1) under UHV and high pressure were identical. The reversibility of the spectra at 300 and 190 K indicated the absence of irreversible CO-induced restructuring.

4. Conclusions

SFG spectra of CO on Pt(1 1 1) and Pd(1 1 1) have shown that the high-pressure structures (up to 1000 mbar) were identical to the corresponding high coverage structures under UHV, with "regular" CO adsorption sites (on-top, bridge, and hollow bonded) [3,7,8]. Even by increasing the CO pressure by 10 orders of magnitude, the UHV saturation coverage could not be exceeded. For Pd(1 1 1), "non-equilibrium" structures were identified as superposition of two ordered structures occurring when CO was exposed at low temperature (100 K) and/or when the CO flux was insufficient.

Excluding "new" high-pressure adsorbate structures and CO-induced surface structural and compositional changes, based on our data several scenarios for the "pressure gap" can still be suggested. When elevated temperatures are required to stimulate reactions between molecules, typical UHV pressures (10^{-9}–10^{-6} mbar) may lead to rather low coverages. For instance, at 300 K UHV exposures of CO on Pd(1 1 1) would produce coverages $\leqslant 0.5$ ML, while above 100 mbar 0.6–0.7 ML are obtained. Even more important than the simple coverage difference are differences in the site occupation. At 300 K, CO is bound to hollow sites under UHV, while being mainly bridge and linearly bonded at 100 mbar. Therefore, UHV studies may not be characteristic for a specific reaction, e.g. when the active species is weakly bound on-top CO which only appears at high coverage after the stronger adsorbing sites (hollow, bridge) are occupied. Of course, applying low temperatures in UHV (~100 K) can produce high CO coverages but would simultaneously prompt another problem. At low temperature the reduced mobility of adsorbed CO molecules may produce different (kinetically hindered) adsorbate structures and the catalytic reaction may proceed in a different way.

Consequently, to connect surface science and catalysis one has to make sure that both types of studies are carried out under comparable conditions, i.e. with identical surface coverages *and* identical adsorbate structures (site occupation). Finally, it should also be noted that single crystals cannot fully represent the complex structure of a supported catalyst. We have recently shown that the specific morphology of supported Pd nanoparticles exhibiting (nanosize) smooth facets and, even more important, steps and other low-coordination sites has a strong influence on the UHV and high-pressure CO adsorption behavior [3,8,17].

Acknowledgements

Work supported by the German Science Foundation (DFG) through priority program SPP1091.

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