Bridging the Pressure and Materials Gaps: High Pressure Sum Frequency Generation Study on Supported Pd Nanoparticles

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Infrared-visible sum frequency generation vibrational spectroscopy is applied for the first time to monitor CO stretching vibrations on alumina supported Pd nanoparticles in a pressure range from 10^{-7} to 200 mbar. The adsorption behavior of Pd aggregates with 3 and 6 nm mean size is dominated by surface defects and two different adsorption sites (twofold bridging and on-top) were identified. The CO adsorption site occupancy on Pd nanocrystals is mainly governed by the gas phase pressure while the structure of the particles and their temperature have a smaller influence.

To close the gaps between fundamental research and applied heterogeneous catalysis is one of the major challenges in catalysis science. The "pressure gap" originates from the need of most surface sensitive techniques of a vacuum environment, in contrast to catalyzed reactions that are carried out at atmospheric pressure or higher. The "materials gap" is due to the fact that many fundamental studies use model systems (e.g., single crystals) that cannot represent the complex structure of a supported catalyst. In this Letter we demonstrate that both gaps can be simultaneously bridged by applying optical sum frequency generation (SFG) vibrational spectroscopy on a well-defined model catalyst of Pd nanoparticles grown on an ordered alumina film. As a photon-based inherently surface sensitive technique, infrared-visible sum frequency generation spectroscopy can be used from ultrahigh vacuum (UHV) to ambient conditions. The effectiveness of SFG spectroscopy as an *in situ* diagnostic tool to monitor adsorbates on single crystal metal and oxide surfaces at low and high pressure has been demonstrated in a number of studies [1–4]. SFG has also been carried out on thin oxide films grown on metal single crystals [5] and on polycrystalline metal foil [6], but to our knowledge no SFG spectra of adsorbates on nanometer-sized metal aggregates were published.

The present study shows the ability of SFG spectroscopy to study gas adsorption on supported Pd nanoparticles over a wide pressure (10^{-7} to 200 mbar) and temperature (190–300 K) range. The CO adsorption site occupancy on Pd nanocrystals was found to be substantially different from single crystal surfaces and it is mainly governed by the gas phase pressure while the structure and the temperature of the particles have a smaller influence.

The SFG process has been reviewed in the literature [1–7]. SFG is a second-order nonlinear optical process which involves the mixing of tunable infrared (ω_{IR}) and visible light (ω_{vis}) to produce a sum frequency output ($\omega_{SFG} = \omega_{IR} + \omega_{vis}$) (Fig. 1). The process is allowed only in a medium without inversion symmetry (in the electric dipole approximation), e.g., at surfaces (or interfaces)

where the inversion symmetry is broken. The dominant SFG signal is hence generated by the adsorbate. The applicability of SFG spectroscopy to nanostructured supported catalysts has been questioned for several reasons. Rough surfaces may considerably scatter the laser beams, and the high dispersion and structural heterogeneity of a supported catalyst, possibly leading to disordered adsorbates
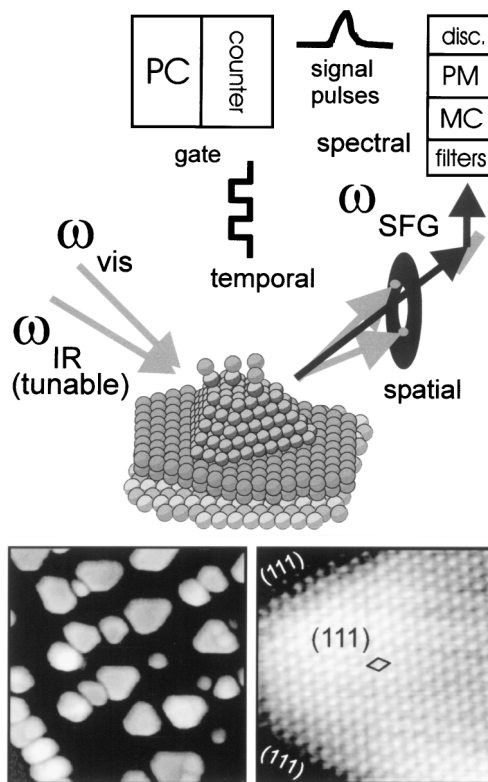

FIG. 1. Schematic representation of the sum frequency generation process and the detection of the SFG signal utilizing spatial, spectral, and temporal filtering (MC: monochromator; PM: photomultiplier; disc.: discriminator). The STM images show an overview of Pd nanoparticles grown on aluminum oxide at 300 K (left: 500×500 Å^2) and atomically resolved facets on a Pd nanocrystal.

and small coverages, could prevent the acquisition of SFG spectra. These limitations were circumvented in the present study by using a well-defined model catalyst, consisting of UHV-grown metal nanoparticles on an ordered thin alumina film [8,9]. Because of the "flatness" and the very small thickness of the alumina film, the high reflectivity of the metal substrate, and the mean size of the Pd particles that is well below the wavelength of the incident light, the reflectivity of our model catalyst is similar to that of a single crystal. Consequently, pronounced light scattering did not occur.

The experiments were carried out in a newly designed two-level apparatus that combines a UHV surface analysis chamber (1×10^{-10} mbar) with an elevated pressure cell that is SFG and UHV compatible. This system allows us to prepare and characterize supported nanoparticles under well-controlled conditions in UHV, to transfer the sample to an SFG-compatible UHV-high pressure cell (equipped with CaF_2 windows), and to monitor adsorbates from submonolayer coverages up to several 100 mbar by SFG spectroscopy. CO is introduced via a manifold after passing a cold trap (to remove carbonyl impurities) and the pressure is measured using an ionization and Baratron gauge. The source of the visible radiation (790 nm, 2 mJ/pulse, 2 ps, 500 Hz) is an amplified titanium sapphire laser, and 90% of the output is used to generate tunable infrared light (3–6 μm, ca. 10 μJ/pulse) with an optical parametric generator/amplifier (OPG/OPA). The two ps-laser pulses are spatially and temporally overlapped on the sample and the SFG output is detected by a photomultiplier (Fig. 1). All experiments were carried out using parallel (p) polarized infrared and visible beams which resulted in a p-polarized SFG output (denoted "p, p, p geometry"; for details, see [4]). The infrared power is nearly constant between 2000 and 3300 cm^{-1} but decreases below 2000 cm^{-1} due to a reduction of the transmission of the AgGaS$_2$ crystal in the OPG/OPA.

Supported Pd nanoparticles were prepared following a procedure that is described in detail in [8,9]. A NiAl(110) single crystal was used as substrate to grow an ordered aluminum oxide film by oxidation in 10^{-5} mbar O$_2$ at 523 K and Pd was subsequently deposited by electron beam evaporation. The cluster size and number density can be adjusted by accurately controlling the substrate temperature and the amount of metal. Two different model catalysts were prepared: Pd particles of 3 nm mean size (or 300 atoms per particle) grown at 90 K by depositing 0.4 nm Pd (particle density 10^{13}/cm^2), and Pd particles with 6 nm mean size (or 3000 atoms per particle) grown by depositing the same Pd amount at 300 K (particle density 5×10^{11}/cm^2). As demonstrated previously by spot profile analysis-low energy electron diffraction [8,9] and atomically resolved scanning tunneling microscopy images of individual particles [10], Pd particles grown at 300 K exhibit the well-faceted shape of a truncated cuboctahedron in (111) orientation (Fig. 1). The particles grow with a (111) facet parallel to the alumina substrate and mainly

expose (111) facets [and to a smaller extent (100) facets], representing one of the equilibrium shapes for a supported fcc metal particle [11]. If the same Pd amount is deposited at 90 K, the particles are less ordered (with more surface defects, edges, steps, etc.) and of smaller size.

SFG vibrational spectra of CO adsorption on alumina supported Pd nanoparticles of 3 nm mean size are presented in Fig. 2. The spectra were taken at 190 K and 10^{-7}, 1, 10, and 200 mbar CO. Although no SFG signal is generated by the gas phase, the absorption of infrared light at high CO pressure must be considered. The SFG intensity critically depends on the intensity of the incident IR pulse, which, in turn, is influenced by gas phase absorption. To compensate for this effect and to normalize our SFG spectra, the energy-dependent absorption of the IR beam in the gas phase was determined using a GaAs reference crystal (GaAs exhibits no inversion symmetry and produces a constant bulk SFG signal). Also, a (nonresonant) SFG signal was obtained from the underlying NiAl substrate, but this signal was energy independent and could be subtracted. The IR frequency was calibrated to an accuracy of ± 2 cm^{-1} by measurements of the atmospheric CO$_2$ absorption bands around 2350 cm^{-1}.

The SFG spectrum of the 3 nm Pd particles at 10^{-7} mbar CO (Fig. 2) is nearly identical to the corresponding infrared reflection absorption spectroscopy (IRAS) data acquired on the same model catalyst at saturation coverage of CO [12]. Two peaks are clearly identified and, according to IRAS results on Pd single
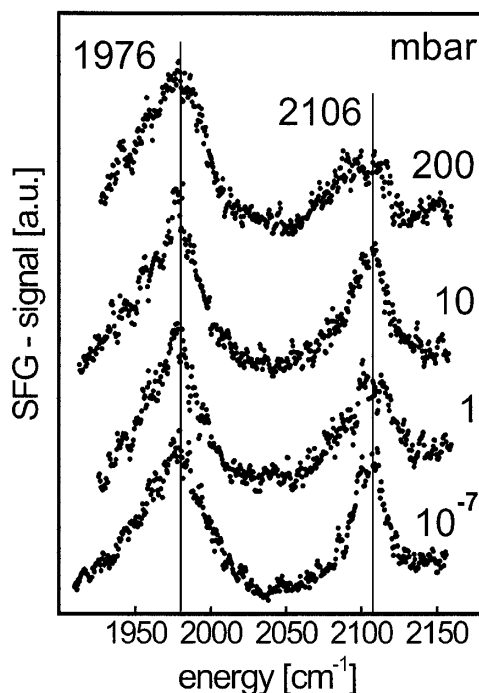

FIG. 2. SFG spectra of CO adsorption on a Pd/Al$_2$O$_3$ model catalyst at 190 K (3 nm Pd particles grown at 90 K). The observed resonances are characteristic of bridge-bonded CO and on-top CO.

crystals [13–18], can be assigned to bridge-bonded CO at 1976 cm^{-1} and to terminal (on-top) CO at 2106 cm^{-1}. As discussed below, the frequency of the bridge-bonded species points to CO bound to defects and edges of the Pd aggregates. If the integrated SFG signal intensity is taken as a measure of the ratio of on-top to bridged CO, a value of ~0.45 is obtained. Since the SFG intensity cannot be easily correlated with the concentration of a surface species [4], this value is an estimate. The adsorption behavior of the 3 nm Pd nanoparticles is substantially different from single crystal surfaces. Bridge-bonded CO is accompanied by a significant fraction of on-top CO, a situation which is not found on Pd single crystals [14,16,17]. According to an IRAS study on Pd(111) by Tüshaus *et al.* [13,15], the onset of CO adsorption in on-top geometry is at coverages >0.6. At saturation ($\Theta = 0.75$), two strong bands at 2110 and 1895 cm^{-1} were observed and assigned to on-top CO and to CO adsorbed on threefold-hollow sites [13,16]. However, at this high coverage the population of bridge sites on Pd(111) is very small. Conversely, for coverages of about $\Theta = 0.5$–0.65, CO is predominantly bridge bonded (1920–1970 cm^{-1}) while the amount of on-top CO is nearly zero [13,15,16]. For coverages below 0.5, adsorption in threefold-hollow sites dominates on Pd(111) (we could not observe CO adsorption at hollow sites since the frequency range below 1900 cm^{-1} is not accessible by our current SFG setup).

The coexistence of bridge and on-top CO suggests that the 3 nm Pd particles exhibit defects and, in fact, the site occupancy compares best with defect rich Pd(111) or rough Pd thin films [14,15,18]. The peak frequencies also agree well with those observed on 7.5 nm Pd particles supported on silica prepared by impregnation [19], and with alumina [20] and titania [21] supported Pd model catalysts. The difference between supported Pd aggregates and Pd(111) could result from a reduced lateral CO interaction on the nanoparticles or from the presence of additional crystal planes. Taking into account the disordered (surface) structure of Pd particles grown at 90 K, it seems reasonable that the 1976 cm^{-1} peak originates from CO bridge-bonded to defect or edge sites. Bridge-bonded species around 1980 cm^{-1} have previously been assigned to CO on Pd(100) or Pd(110) [20,21]. CO adsorption on Pd(100) yields only the bridging site and the CO frequency shifts from 1895 cm^{-1} at low coverages to 1995 cm^{-1} at $\Theta = 0.8$ [17,22]. Similar frequencies were reported for Pd(110) [23] and Pd(210) [17]. In light of these studies, the disordered, rough Pd surface can also be envisioned as being composed of different microfacets. Increasing the pressure to 1, 10, and 200 mbar CO did not shift the frequency of the peaks and also the ratio of on-top vs bridge CO was nearly unchanged (Fig. 2). The 10^{-7} mbar spectrum could be reproduced after the high gas pressure was pumped out and no evidence for particle disrupture upon CO exposure was evident.

If the same experiment was carried out on larger and well-faceted Pd particles of 6 nm mean size (Fig. 3), a
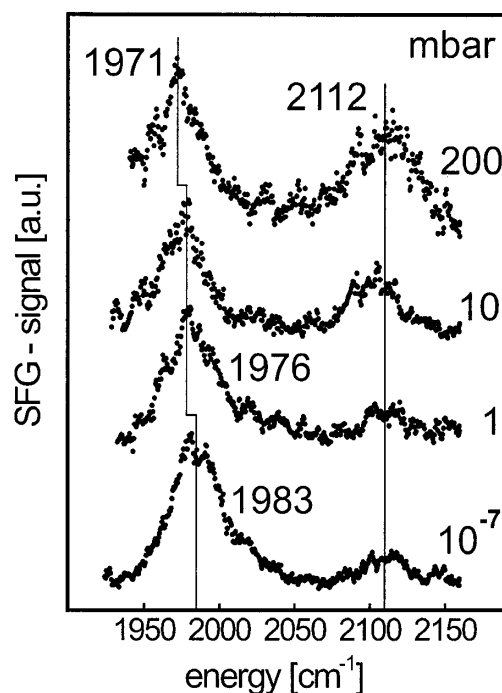

FIG. 3. SFG spectra of CO adsorption on a Pd/Al$_2$O$_3$ model catalyst at 190 K (6 nm Pd particles grown at 300 K). Because of the more ordered structure of the 6 nm Pd particles, at low pressure the fraction of on-top CO is smaller than on the 3 nm Pd particles.

small shift in frequency occurred but a much smaller fraction of on-top CO (ca. 0.15) was detected at 10^{-7} mbar. It was assumed that the relation between the SFG intensity and the surface concentration of CO is comparable on 3 and 6 nm Pd particles. Apparently, the on-top adsorption site is strongly preferred on small defective aggregates while Pd nanoparticles grown at 300 K are dominated by bridged CO. This effect presumably originates from the bigger size and the more ordered surface of the 6 nm Pd particles which facilitate the formation of bridge bonds, in agreement with our IRAS study on the same system [12] and NMR [24] and infrared spectroscopic [20,21,25] studies on supported Pd clusters. Taking into account the particle morphology (Fig. 1), it seems unlikely that CO adsorption on Pd(100) contributes to the spectrum since these facets are present only in a minor fraction. In our previous IRAS study [12], different frequency regimes were assigned to bridge-bonded CO on terraces (1930–1970 cm^{-1}) and to bridge-bonded CO on the edges of the aggregates (1970–2000 cm^{-1}), but the smaller resolution of our SFG setup (~20 cm^{-1} compared to <5 cm^{-1} for IRAS) prevents a clear discrimination between these species. With increasing pressure the relative ratio of on-top CO increased to about the same value (0.5) as observed for the 3 nm Pd particles (1 mbar: 0.15; 10 mbar: 0.4; 200 mbar: 0.5).

If the sample temperature is raised to 300 K, which is above the desorption temperature of on-top CO on Pd clusters [9], bridge-bonded CO is the only species that
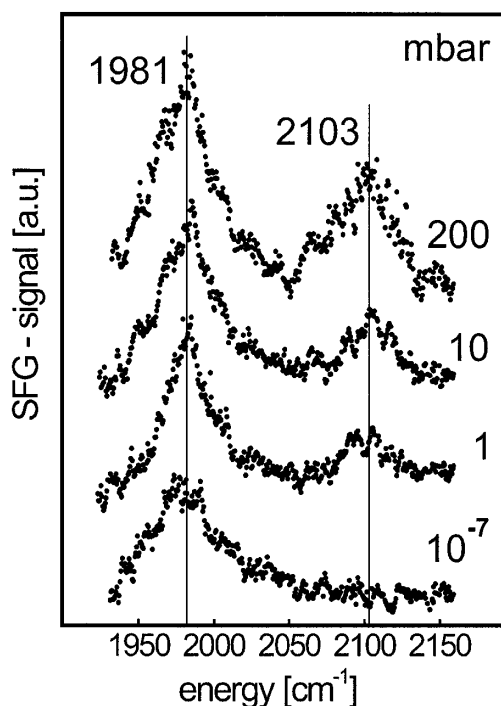
FIG. 4. SFG spectra of CO adsorption on a Pd/Al_2O_3 model catalyst at 300 K (6 nm Pd particles grown at 300 K). On-top CO can be repopulated at ≥ 1 mbar.

can be observed at 10^{-7} mbar for both 3 and 6 nm Pd particles (Fig. 4; the corresponding spectra for 3 nm Pd particles are nearly identical). With increasing pressure, the on-top adsorption sites can be repopulated and the ratio of on-top CO can be raised up to ~ 0.5, i.e., to a value that was also obtained at 190 K (1 mbar: 0.15; 10 mbar: 0.25; 200 mbar: 0.5). This indicates that the adsorption site occupancy of CO on Pd/Al_2O_3 is mainly governed by the CO pressure and that the influence of particle size, structure, and temperature is less important.

The present study has clearly demonstrated the potential of SFG spectroscopy to monitor adsorbates on alumina supported Pd nanoparticles over a wide pressure (10^{-7} to 200 mbar) and temperature (190–300 K) range. At low pressure (cf. spectra at 10^{-7} mbar), the adsorption site distribution (on-top vs bridged CO) depends on particle size, structure, and temperature. With increasing particle size and order the fraction of on-top CO decreases. At 190 K, bridge-bonded and on-top CO were observed with their ratio depending on pressure. At 300 K, only bridge-bonded CO was detected at 10^{-7} mbar, but the on-top sites could be repopulated at ≥ 1 mbar. At high pressure (cf. spectra at 200 mbar), an adsorption site occupancy is obtained that is nearly independent of the structural properties and the temperature of the Pd particles (at least under the conditions studied). The high gas pressure may lead to surface coverages that exceed the "saturation coverage" of UHV studies and, hence, adsorbate structures may form that cannot be observed at the fairly low exposures gener-

ally applied in UHV. We could not monitor adsorption in threefold hollow sites due to limitations of our current SFG setup. The hollow site is particularly important on Pd(111) at low coverage [13–16] and additional information about its population at high pressure would help to complete the picture. At present, we are setting up a new OPG/OPA system to improve our resolution and to explore the range below 1900 cm^{-1}. By combining SFG spectroscopy with a well-defined nanocluster model catalyst the pressure and materials gaps between surface science and applied catalysis can be bridged simultaneously. The pressure dependent site occupation of Pd particles at 300 K illustrates the limitation of low pressure studies. The high pressure capability of SFG, combined with improved frequency and time resolution, will make sum frequency generation spectroscopy an indispensable *in situ* diagnostic tool to study supported metals and should significantly contribute to our understanding of catalytic processes.

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[1] J. Miragliotta *et al.,* Appl. Phys. A **51**, 221 (1990).
[2] C. Klünker *et al.,* Surf. Sci. **360**, 104 (1996).
[3] X. Su *et al.,* J. Am. Chem. Soc. **119**, 3994 (1997).
[4] G. A. Somorjai and G. Rupprechter, J. Phys. Chem. B **103**, 1623 (1999).
[5] A. Bandara *et al.,* Surf. Sci. **387**, 312 (1997).
[6] H. Härle *et al.,* Chem. Phys. Lett. **293**, 26 (1998).
[7] Y. R. Shen, Surf. Sci. **299/300**, 551 (1994).
[8] M. Bäumer *et al.,* Ber. Bunsen-Ges. Phys. Chem. **99**, 1381 (1995).
[9] M. Bäumer and H.-J. Freund, Prog. Surf. Sci. **61**, 127 (1999).
[10] K. H. Hansen *et al.,* Phys. Rev. Lett. **83**, 4120 (1999).
[11] C. R. Henry, Surf. Sci. Rep. **31**, 235 (1998).
[12] K. Wolter *et al.,* Surf. Sci. **399**, 190 (1998).
[13] M. Tüshaus *et al.,* Appl. Phys. A **51**, 91 (1990).
[14] F. M. Hoffmann, Surf. Sci. Rep. **3**, 103 (1983).
[15] M. Tüshaus, Ph.D. thesis, Free University Berlin, 1990.
[16] W. K. Kuhn, J. Szanyi, and D. W. Goodman, Surf. Sci. Lett. **274**, L611 (1992).
[17] A. M. Bradshaw and F. M. Hoffmann, Surf. Sci. **72**, 513 (1978).
[18] A. M. Bradshaw and F. M. Hoffmann, Surf. Sci. **52**, 449 (1975).
[19] P. Gelin, A. Siedle, and J. Yates, J. Phys. Chem. **88**, 2978 (1984).
[20] D. R. Rainer *et al.,* J. Vac. Sci. Technol. A **14**, 1184 (1996).
[21] J. Evans, B. E. Hayden, and G. Lu, Surf. Sci. **360**, 61 (1996).
[22] A. Ortega, F. M. Hoffmann, and A. M. Bradshaw, Surf. Sci. **119**, 79 (1982).
[23] R. Raval *et al.,* Chem. Phys. Lett. **167**, 391 (1990).
[24] L. R. Becerra, C. T. Slichter, and J. H. Sinfelt, J. Phys. Chem. **97**, 10 (1993).
[25] L. Sheu, Z. Karpinski, and W. M. H. Sachtler, J. Phys. Chem. **93**, 4890 (1989).