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Trends in the Binding Strength of Surface Species on Nanoparticles: How Does the Adsorption Energy Scale with the Particle Size?**

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How strongly does a molecule or an atom bind to a metal nanoparticle and how does this binding energy change with changing particle size? These questions are at the heart of many fundamental and practical problems, ranging from heterogeneous catalysis to important applied processes connected to materials science. In particular the interaction of oxygen with transition-metal nanoparticles is of pivotal importance for a variety of industrially and environmentally relevant processes such as CO oxidation in exhaust catalytic converters and methane combustion. Understanding the effect of a nanometer-scale confinement of matter on the binding strength of gaseous adsorbates is a current scientific challenge targeting the rational design of new catalytic and functional materials. Studies in this area provide a basis for the fundamental understanding of how the surface binds reactants and guides them through various elementary steps of a reaction to the products.

The interaction of oxygen with palladium surfaces has been the subject of numerous studies, performed both on single-crystal surfaces[1–11] and well-defined model systems consisting of Pd nanoclusters supported on thin oxide films.[12–18] Presently, a very detailed microscopic-level understanding the interaction of oxygen with palladium is available, which proves to be a complex interplay between chemisorption,[1–5,8,9] diffusion of oxygen into the subsurface region and bulk,[2,3,5,10] formation of surface oxide layers,[6,19] refaceting,[2,11] particle reconstruction,[12,13] and bulk oxide formation.[6,18] The processes related to subsurface diffusion, refaceting, reconstruction, and oxidation are typically observed beyond a critical coverage of surface-adsorbed oxygen and temperatures above 300 K. Despite this comprehensive understanding and general agreement on the surface chemistry of the oxygen–palladium system, quantitative information on binding energies of oxygen on Pd nanoparticles is still missing, which is precisely because of the richness of the surface chemistry. When the binding strength is probed by a traditional desorption-based method, such as temperature-programed desorption (TPD), the O–Pd system must be heated to about 900–1000 K to desorb chemisorbed oxygen; this is often accompanied by subsurface O diffusion, surface oxide formation, and particle restructuring. These side processes together with the restrictions imposed by the kinetic modeling of the TPD spectra strongly limit the quantitative determination of binding energies of oxygen on Pd nanoparticles by traditional desorption-based methods, which results in a strong scatter of data available in literature. A strategy to overcome those shortcomings is a direct calorimetric measurement of adsorption enthalpies under isothermal conditions. At present, such fundamental information on the correlation between oxygen binding energies and the exact nature of the adsorption site as well as the size of the metal nanoparticles is not available.

Herein we report on the first direct calorimetric measurement of oxygen binding energies on Pd nanoparticles investigated as a function of particle size and with the reference to a Pd(111) single crystal. The binding energies were obtained on well-defined Pd nanoparticles supported on thin oxide films prepared under ultra-high-vacuum (UHV) conditions. We apply a newly developed UHV single-crystal adsorption calorimeter (SCAC) based on molecular beam techniques[20] in combination with infrared reflection adsorption spectroscopy (IRAS) to investigate the effect that the reduced dimensionality of metallic particles has on the interaction strength with oxygen. Complementary TPD experiments were performed to provide a link between the direct isothermal calorimetric studies and the traditional desorption-based approach. We show that there are two major structural factors determining the oxygen binding energy on Pd: the local configuration of the adsorption site, and the particle size. We provide direct experimental evidence that the change of the local adsorption environment from a multifold-bound position on the extended single-crystal surface to an edge site of Pd nanoparticles results in a strong increase of the oxygen binding energy. On the other hand, if the local environment of the adsorbate is kept

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constant, the reduction of the cluster size leads to a pronounced decrease of the oxygen binding energy. These two counteracting trends were found to give rise to a non-monotonic dependence of the oxygen adsorption energy on particle size.

The model surfaces employed in the calorimetry study consist of Pd nanoparticles supported on a well-ordered thin Fe_3O_4 film grown on a Pt(111) single crystal (for details of the preparation procedure and structural characterization by scanning tunneling microscopy (STM) see Ref. [18] and Table 1).[21] Four different supported systems with different particles sizes were prepared with nominal Pd deposition thicknesses of 0.6 Å, 1.5 Å, 4 Å, and 7 Å with the average number of Pd atoms per particle of about 220, 430, 720, and 4760, respectively. According to STM data, the particles are crystalline and exhibit a nearly hexagonal shape with a flat top facet, which indicates that Pd particles grow in (111) orientation and their sides are terminated with (111) and (100) facets. All Pd clusters are three-dimensional, as evidenced by the comparison of the average number of Pd atoms per particle and the "footprint" of the clusters obtained by STM. This observation excludes the possibility of strong metal–support interaction in this system. For TPD measurements, Pd nanoparticles (nominal deposition thickness 4 Å) were prepared on a thin (4 nm) amorphous SiO_2 film grown on Si(111)[22] (see the Supporting Information for details). The SiO_2 support was used in these experiments instead of Fe_3O_4 in order to avoid thermal degradation of the samples at elevated temperatures.

Table 1: Structural data of the Pd/Fe_3O_4/Pt(111) model catalyst as determined from STM.[18]

Nominal Pd deposition thickness [Å]	0.6	1.5	4	7
Particle density [particles cm^{-2}]	1.9×10^{12}	2.4×10^{12}	3.8×10^{12}	1×10^{12}
Number of Pd atoms per particle	≈220	≈430	≈720	≈4760
Average Pd particle diameter [nm]	≈2	≈3	≈4	≈7–8
Average number of surface Pd atoms [atoms·cm^{-2}]	2.7×10^{14}	5.3×10^{14}	12×10^{14}	$(9–11)\times10^{14}$
Estimated number of surface Pd atoms per particle	142	220	320	900–1100
Number of O atoms adsorbed in the first pulse per Pd particle, which contribute to the reported initial adsorption energy	7	9	7	26

The calorimetry data in Figure 1 show the dependence of the O binding energy on the coverage of surface-adsorbed oxygen species for Pd(111) (black trace) and 4 nm sized Pd particles (gray trace). The binding energy was determined at 300 K, at which O_2 adsorbs dissociatively, and was combined with a sticking coefficient measurement by the King–Wells method,[23] allowing the quantitative determination of the absolute number of adsorbed oxygen atoms. Complementary, it was verified that O_2 does not adsorb at the oxide support at this temperature. Both model surfaces show a very strong coverage dependence of oxygen binding energies. For Pd(111), the initial adsorption energy on the clean surface amounts to approximately 205 kJ mol^{-1}, which drops to approximately 100 kJ mol^{-1} close to saturation.[24] Two reasons might account for the decreasing adsorption energy with increasing O coverage: interatomic repulsion of neighboring O atoms, and increasing competition for the d electrons of the Pd atoms participating in the O–Pd bonding. A qualitatively similar strong coverage dependence of the adsorption energy was observed for the 4 nm sized Pd nanoparticles and for all other investigated supported systems (not shown). However, there is a very pronounced difference in the initial adsorption energy to the Pd clusters and to Pd(111). While O binds with 205 kJ mol^{-1} on pristine Pd(111), the initial binding energy rises to 275 kJ mol^{-1} on the pristine Pd nanoparticles. It should be noted that on average only about seven O atoms per Pd nanoparticle (exhibiting roughly 320 surface Pd atoms) contribute to the initial adsorption energy, which allows us to consider this energy value as a limiting case for the interaction of an individual O atom with a pristine Pd nanoparticle. Also note that neither subsurface O diffusion nor surface oxide formation can occur at the present low temperature and low oxygen coverages. It is important to take into account that the oxygen adsorption energy exhibits a very strong coverage dependence, especially on Pd nanoparticles, where it spans the range between 275 and 100 kJ mol^{-1}. Thus, when comparing adsorption energies on different Pd surfaces, it is crucial to ensure that the corresponding oxygen surface coverages are equal in order to clearly separate strong coverage-related shifts of the binding energy from those related to the inherent structural and/or electronic properties of the investigated surfaces.

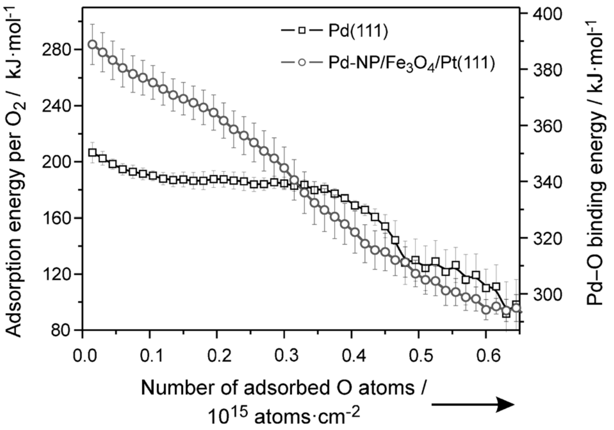

Figure 1. Differential adsorption heat per mole of O_2 (left axis) and Pd–O binding energy (right axis) plotted as a function of the number of adsorbed O atoms. The data are shown for Pd(111) and for 4 nm sized Pd nanoparticles (nominal deposition thickness 4 Å) supported on Fe_3O_4/Pt(111) film. The adsorption heats were obtained at 300 K and are shown as an average of four to six independent measurements on freshly prepared surfaces. The error bars correspond to the error of the mean.

A qualitatively similar trend for the O_2 adsorption energy on Pd(111) versus Pd nanoparticles of similar size (nominal deposition thicknesses of 4 Å, corresponding to the average particles size of about 4.5 nm) was also deduced from the TPD experiments. Figure 2 shows O_2 desorption traces from Pd(111) and Pd nanoparticles following O_2 exposure at 300 K.

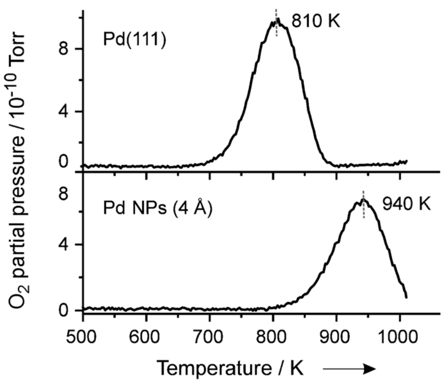

Figure 2. O_2 TPD spectra from Pd(111) and Pd nanoparticles supported on SiO_2/Si(111) with a nominal Pd deposition thickness of 4 Å (average particle size ca. 4.5 nm). The signals correspond to desorption of roughly 0.1×10^{15} O atoms cm^{-2}.

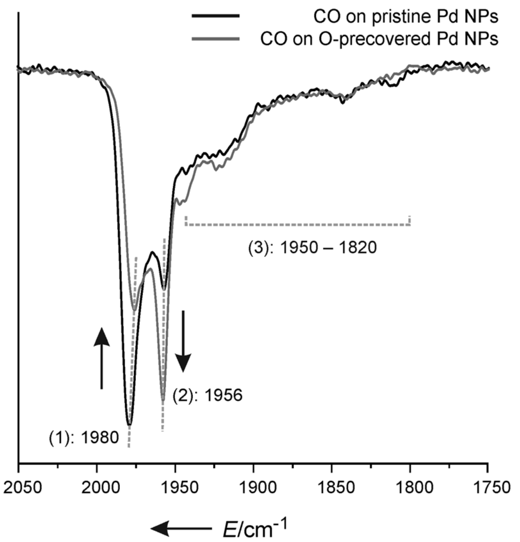

Figure 3. IRAS spectra for CO adsorbed on Pd nanoparticles (nominal deposition thickness 4 Å) supported on Fe_3O_4/Pt(111). The black curve corresponds to the pristine sample, the gray curve to the sample pre-exposed to approximately 1×10^{14} O atoms cm^{-2}.

The increase of the desorption temperature from 810 K on Pd(111) to 940 K on 4 Å Pd nanoparticles corresponds to an adsorption energy difference of about 40 kJ mol^{-1} as estimated by the second-order Redhead analysis with a pre-exponential factor of ca. 2.6×10^{13} ML^{-1} s^{-1} (ML = monolayer).[25] This calculated energy difference is somewhat lower than the energy difference of roughly 60 kJ mol^{-1} observed in coverage-resolved SCAC measurements for this particular O coverage (0.1×10^{15} O atoms cm^{-2}), which might be related both to the structural differences of the Pd nanoparticles supported on different oxides and to the details of kinetic modeling of the desorption process applied for TPD analysis.

The energy value obtained by SCAC for Pd(111) in the lowest coverage limit (205 kJ mol^{-1} at the surface coverage of 0.01×10^{15} O atoms cm^{-2}) is in good agreement with literature values of O adsorption energies at low coverages situated in the range of 210 to 230 kJ mol^{-1}.[3,5,8] In contrast, the very high initial energy value obtained for Pd nanoparticles (275 kJ mol^{-1} at 0.01×10^{15} O atoms cm^{-2}) cannot be compared to any value reported in TPD studies neither for low Miller index Pd surfaces, nor for stepped Pd crystals, which typically span the range between 190 and 230 kJ mol^{-1}.[1,3,5,10] Thus, this high initial adsorption energy must be related to some structural feature inherent to Pd nanoparticles, which cannot be reproduced even by the steps of the high Miller index Pd surfaces. Such adsorption sites on Pd nanoparticles might be the low coordinated surface sites (edges, corners). In previous STM studies on supported Pd nanoparticles, oxygen was shown to modify such sites first, indicating that they are the strongest adsorption sites on Pd nanoparticles.[16]

To check the feasibility of this explanation, we carried out CO titration experiments to identify the preferential adsorption sites of oxygen on Pd nanoparticles. In previous IRAS studies, the CO molecule was shown to be a suitable probe molecule for probing different adsorption sites on Pd nanoparticles, allowing independent identification of the regular adsorption sites on the (111) terraces and the low-coordinated adsorption sites such as edges and corners.[26] Figure 3 shows a comparison of IRAS spectra obtained at 120 K after dosing $\approx 8\times10^{14}$ CO molecules cm^{-2} at 300 K on the clean Pd nanoparticles (black curve) and on the same sample, at which ca. 1×10^{14} O atoms cm^{-2} were pre-adsorbed at 300 K to produce a sub-monolayer coverage of oxygen, and then the same amount of CO was dosed under identical conditions (gray curve). The spectrum of CO on pristine Pd nanoparticles is dominated by a sharp adsorption feature at 1980 cm^{-1} [(1) in Figure 3]. Additionally, a peak of lower intensity at 1956 cm^{-1} (2) is observed alongside with a broad low-frequency shoulder at 1950–1820 cm^{-1} (3). Previously, for Pd particles of similar size, the low-frequency features (between 1820 cm^{-1} and 1970 cm^{-1}) were assigned to CO adsorbed on bridge and hollow sites predominantly on Pd(111). The prominent absorption band at 1980 cm^{-1} (1) originates from a superposition of bridge-bonded CO adsorbed at low-coordinated surface sites (edges/corners) and on (100) facets.[26] The contribution from the (100) facets, however, is expected to be small since they are strongly tilted and thus the corresponding vibrational features are strongly attenuated according to the metal surface selection rule.[27] Note that the relative intensities of the vibrational features do not directly reflect the relative abundance of the corresponding sites due to dipole-coupling effects.[28] After adsorption of oxygen, drastic changes are observed in the CO spectrum. The edge-related peak at 1980 cm^{-1} (1) is strongly attenuated, whereas the feature at 1956 cm^{-1} gains in intensity, indicating that CO adsorption at particle edge/corner sites is blocked by pre-adsorbed oxygen species. The concomitant gain of intensity at 1956 cm^{-1} arises from the reduced intensity transfer to high-frequency features. From these observations we conclude that oxygen preferentially accumulates at the low-coordinated sites (particle edges and corners). Furthermore, we can unambiguously attribute the unexpectedly high initial adsorption energy (275 kJ mol^{-1}), measured in a calorimetric experiment on supported Pd nanoparticles, to oxygen adsorption at edge and corner sites. It remains, however, an open question as to why the edge sites of Pd nanoclusters interact so strongly with adsorbed oxygen. Further theoretical work is needed in order to rationalize the microscopic nature of this phenomenon, which can presumably originate from the previously reported reconstruction or refaceting of the particles edges.[13,16,17]

To address the dependence of the initial O adsorption energies on particle size in more detail, four different supported model systems with different nominal Pd deposition thicknesses ranging from 0.6 to 7 Å were investigated by SCAC. The coverage dependence of the oxygen adsorption energy was found to exhibit very similar qualitative behavior for all particles sizes. The initial heats of adsorption on all supported systems are displayed in Figure 4a as a function of the nominal Pd deposition thickness together with data measured on Pd(111). The dependence of the O adsorption energy on the particle size shows a clear trend: it strongly rises from about 205 kJ mol^{-1} to 250–275 kJ mol^{-1} when changing from Pd(111), where oxygen adsorbs at threefold-hollow sites, to large Pd nanoclusters, where oxygen first occupies particles edges, as evidenced by the IRAS data. However, when the local adsorption site (the edge/corner site) was preserved, and only the particles size was reduced, the initial oxygen adsorption energy was observed to strongly decrease, reaching a value of 205 kJ mol^{-1} on the smallest Pd nanoparticles. Thus, the reduction of the Pd cluster size results in an opposite trend—decrease of the adsorption energy—with a magnitude that is comparable with the effect of the change of the local adsorption environment. Note that the total number of oxygen atoms, contributing to the initial adsorption energies (on the pristine Pd nanoparticles) reported in Figure 4a, amounts typically to only a few O atoms per particle or less than 0.04 O atmos per surface Pd atom (see Table 1). Since the number of surface Pd atoms on each particle is much larger (from 140 to 1100) than the number of adsorbed O atoms, we can safely assume that the repulsive interactions between adsorbed O atoms do not play any significant role for these low oxygen surface coverages.

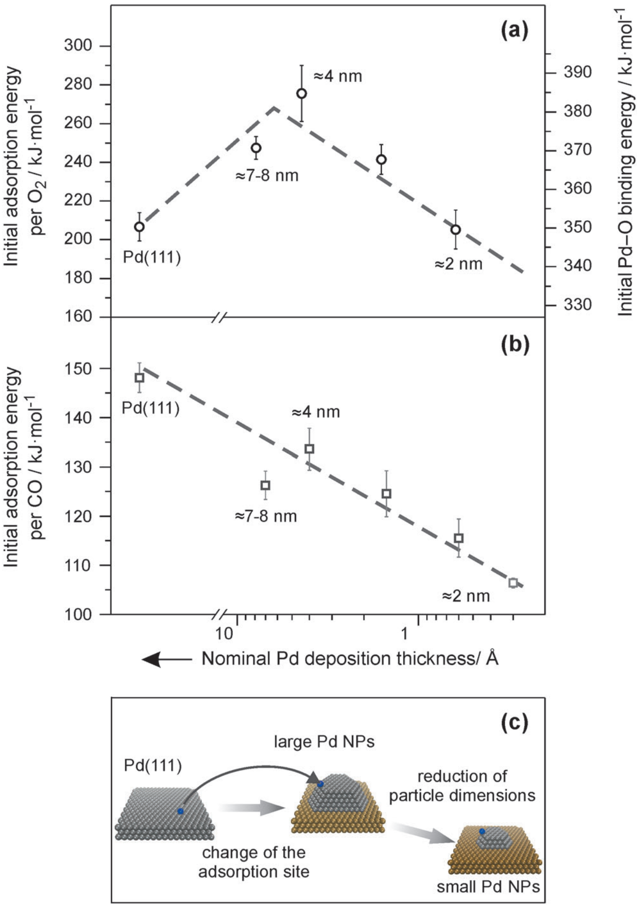

Figure 4. Initial adsorption energy for O$_2$ (a) and CO (b) molecules plotted as a function of the nominal Pd coverage on the Fe$_3$O$_4$/Pt(111) samples with the nominal deposition thickness of 0.3 (only for CO), 0.6, 1.5, 4, and 7 Å and on the Pd(111) single-crystal surface. Next to the data points, the average diameters of the Pd particles are given. Error bars show the standard error of the mean. The dashed lines are given to guide the eye. c) A model describing two microscopic trends affecting the binding energy: the local configuration of the adsorption site, and the particle size.

The latter trend—decreasing adsorption energy with decreasing particle size[29]—coincides with the trend previously observed in our studies for CO adsorption in direct calorimetric experiments.[30] The initial CO adsorption energy on the same Pd nanoparticles (Figure 4b) shows a pronounced decrease of the adsorption energy for small clusters. In contrast, the change of the adsorption site from a threefold-hollow site on Pd(111) to the strongest binding site on Pd nanoparticles obviously does not result in an increase of the adsorption energy as observed for oxygen. This observation agrees well with literature data, suggesting that the degree of coordination of the surface Pd atoms both on low Miller index surfaces and on stepped Pd surfaces does not significantly affect the CO binding energy.[30]

Two alternative microscopic effects, for example, can be put forward to rationalize the observed decrease of the initial adsorption energy on Pd nanoparticles both for oxygen and CO adsorption: weakening of the chemisorptive interaction and reduction of the van der Waals attraction. The decrease of the chemisorption energy has been predicted in a recent theoretical study for Pd clusters.[31] These computational results showed that interatomic Pd–Pd bond length in small metal particles decreases with decreasing particle size and this effect results in systematically lower adsorption energies than that on clusters with a bulk terminated geometry.[31] This finding agrees well with the principle of bond order conservation:[32] in the contracted clusters, one expects weaker adsorption bonds and stronger binding within the adsorbate as a result of better saturated valences of the substrate atoms. A second reason for the decrease of adsorption energy of a gas-phase molecule on the small metal clusters is a feasible weakening of the van der Waals interaction strength. This type of interaction is induced by the dynamic response of bulk electrons of the metal to charge density fluctuations in an adsorbed molecule, and since smaller clusters contain fewer electrons available for the dynamic response, the dispersive interaction strength weakens. This effect is expected to play a more important role for the interaction of CO with Pd clusters and be of minor importance in case of oxygen.

In summary, we investigated, for the first time, the particle size dependence of the oxygen adsorption energy on well-defined Pd nanoparticles ranging from 220 to 4800 atoms per particle and on an extended Pd(111) single-crystal surface in a direct calorimetric study complemented by temperature-programmed desorption investigations. Two microscopic structural parameters were identified to critically control the oxygen binding energy on Pd nanoparticles: the local configuration of the adsorption site and the particle size. The change of the local adsorption environment from a threefold hollow position on an extended Pd (111) single-crystal surface to an edge site of Pd nanoparticles results in a strong increase of oxygen binding energy by about 70 kJ mol^{-1}. The preferential adsorption site of oxygen atoms was investigated spectroscopically by IRAS, using CO as a probe molecule for different adsorption sites, and was found to be at the edges/corners of the Pd clusters. The unexpectedly strong binding energy of oxygen at the particles edges exceeds all literature values of oxygen adsorption energies at stepped single-crystal surfaces. On the other hand, if the local configuration of the adsorption site is kept constant (O adsorption at the edges/corners of Pd nanoparticles), the reduction of the cluster size leads to a pronounced decrease of oxygen binding energy from 275 kJ mol^{-1} observed on the large clusters to 205 kJ mol^{-1} measured for the smallest investigated nanoparticles. This latter trend coincides with the particle size dependence of CO adsorption energy on Pd particles obtained earlier. The decreasing adsorption energy with decreasing particle size observed in our studies for both CO and oxygen adsorption is indicative of the general nature of this phenomenon, which might be connected to the theoretically predicted weakening of chemisorptive interaction due to the contraction of the lattice parameter of the Pd cluster. The effects, which both of these structural parameters exert on the oxygen adsorption energy, result in counteracting trends—the increase of the binding strength due to adsorption at the low-coordinated surface sites, and the decrease of the adsorption energy due to reduced particle dimensions. In total, the oxygen binding energy turns out to be a convolution of these two trends resulting in a non-monotonic dependence of the oxygen adsorption energy on particle size.

These observations highlight the complexity of the effects that the nanometer-scale confinement of matter has on the binding strength of gaseous adsorbates. Related effects are expected to play a key role in controlling the binding strength of adsorbates on a broad range of transition-metal nanoparticles, and have direct implications for the performance of the corresponding heterogeneous catalysts.

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