

Particle-size dependent heats of adsorption of CO on supported Pd nanoparticles as measured with a single-crystal microcalorimeter

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We present calorimetric measurements of the effect of cluster size on the adsorption enthalpy of carbon monoxide on Pd nanoclusters sized from 120 to 4900 Pd atoms per particle, which were grown *in situ* on a well-ordered Fe₃O₄/Pt(111) film. A substantial decrease in the initial heat of adsorption amounting to about 20–40 kJ mol⁻¹ was observed on the smallest Pd nanoparticles as compared to the larger Pd clusters and the extended Pd(111) single-crystal surface. We discuss this effect in terms of the size-dependent properties of the Pd nanoparticles.

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This Rapid Communication addresses the question: how does the heat of chemisorption of a molecule change when comparing a metal single-crystal surface with a supported metal nanoparticle, and how does it depend on particle size? This is an exceptionally important question that lies at the very heart of understanding particle size effects in catalysis.¹

The energetics of interaction of gaseous molecules, particularly carbon monoxide, with well-defined metal nanoparticles were previously addressed indirectly in nonisothermal temperature-programmed desorption (TPD) experiments² and in isothermal modulated molecular-beam studies,³ where the adsorption energies were obtained by modeling the desorption process and analyzing the lifetimes of the adsorbate on the surface. However, these indirect methods did not provide a clear trend in the changes in the adsorption energy with the particles size: whereas the TPD studies found a decrease in the adsorption energy by about 10 kJ mol⁻¹ on the 2.5 nm sized Pd particles as compared to the extended single-crystal surfaces, the kinetic model used for analysis of the molecular-beam experiments predicted a pronounced increase in the adsorption energy by about 35 kJ mol⁻¹ on the particles smaller than 1.5 nm.

A strategy to overcome the shortcomings of such indirect methods based on the model assumptions is direct calorimetric measurement of adsorption enthalpies. Recently, two types of calorimeters were developed that allow direct adsorption energy measurements on single-crystal surfaces.^{4,5} However, many phenomena inherent to dispersed supported catalysts and technically relevant nanoparticle-based materials cannot be addressed on such simplified model systems since they do not reproduce some properties of realistic surfaces such as different particles sizes or interactions between nanoparticles and their support material. Only a limited amount of calorimetric data is available today on dispersed supported metal powder catalysts,^{6,7} suffering, however, from a high degree of inhomogeneity in metal particle size distribution and low support homogeneity. A strategy to surmount this shortcoming was the development of well-defined, single-crystal-based model surfaces, consisting of

metal nanoparticles deposited on flat thin oxide films.⁸ The structural properties of these model systems such as particle size and shape can be controlled and characterized in great detail. Up to date, there is no direct calorimetric data available on the interaction of gaseous molecules with such well-defined model surfaces.

In order to directly address the energetics of the gas-surface interaction and link it to a detailed knowledge on the structure of the particles, a new microcalorimeter has been built and integrated into an ultrahigh vacuum apparatus.⁹ This setup allows for the preparation of a single-crystal oxide film on an ultrathin (1 μm) metal single crystal and preparation of metal nanoparticles with a narrow size distribution. Measurement of adsorption heats is realized by use of a pyroelectric heat detector and requires an elaborate calibration procedure, which will be described in a forthcoming publication but is similar to Ref. 5.

In this Rapid Communication, we report the heats of adsorption of CO measured in a direct way by single-crystal adsorption microcalorimetry as a function of particle size. The model surfaces employed in this study consist of Pd nanoparticles supported on a well-ordered thin Fe₃O₄ film grown on a Pt(111) single crystal (for details of the preparation procedure, see Ref. 10). Additionally, CO adsorption on Pd(111) was studied as a reference for the majority of the facets present on nanoparticles.

Figure 1 shows a series of scanning tunneling microscopy (STM) images for different nominal coverages of deposited Pd; Table I summarizes the structural data derived from the STM images. At the lowest investigated Pd coverage [0.3 Å, Fig. 1(a)], nucleation of the Pd particles occurs in a well-distributed fashion over the Fe₃O₄ terraces. The inset shows a closeup of a few individual particles, which appear round. However, it should be kept in mind that due to convolution with the tip shape, the precise identification of the particle shape and size is difficult in the low particle size limit.⁸ The average number of Pd atoms per particle is estimated to be about 120 as calculated from the total number of deposited Pd atoms and the average island density. Increasing Pd cov-

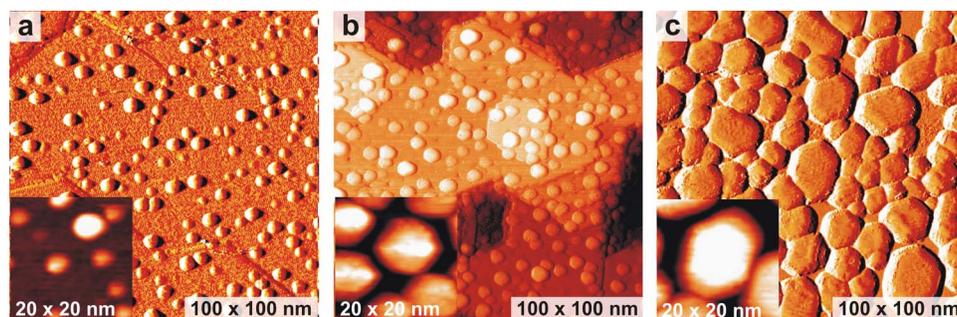


FIG. 1. (Color online) STM images of the Pd/Fe₃O₄/Pt(111) model catalyst as a function of Pd coverage after preparation and annealing at 600 K for nominal Pd coverage of (a) 0.3 Å, (b) 4 Å, and (c) 7 Å. (From Ref. 10.)

erage [4.0 Å, Fig. 1(b)] results in increased particle nucleation density and formation of crystalline aggregates with a rather flat top of near hexagonal shape, which indicates that Pd particles grow in (111) orientation and their sides are terminated either with (111) or (100) facets. An average number of Pd atoms in an individual aggregate is about an order of magnitude higher than for the deposition thickness 0.3 Å. Pronouncedly larger aggregates (~ 4900 Pd atoms/island) are formed for 7.0 Å coverage, which retain a hexagonal form and a high degree of crystallinity. From these structural data the number of the surface Pd atoms have been estimated from the number of atoms per particle assuming a semispherical particle shape (see Table I).

A typical microcalorimetric data set is shown in Fig. 2. Plotted is the heat of CO adsorption measured at 300 K as a function of CO coverage for the smallest (~ 120 Pd atoms/particle, ~ 1.8 nm particles, the lowest trace), the highest (~ 4900 Pd atoms/particle, ~ 8 nm particles, the intermediate trace) Pd coverage and for the Pd(111) single crystal (the uppermost trace). The absolute CO surface coverage was determined by integrated sticking coefficient measurements via the King-Wells method.¹¹ The data sets for the Pd particles were obtained by averaging over four to six independent experimental runs, each carried out on a freshly prepared model surface. Note that CO diffusion on Pd is fast on the time scale of heat measurement, resulting in fast equilibration of adsorbed species at the energetically most favorable positions.¹² On the smallest Pd particles (~ 120 Pd atoms/particle), the heat of CO adsorption initially amounts to 106 ± 2 kJ mol⁻¹. After adsorption of about 0.07×10^{15} CO molecules cm⁻² the surface of the particles reaches saturation (with the corresponding CO surface coverage of 0.6 ML with respect to the number of surface Pd atoms) and the adsorption heat levels out at 75 ± 9 kJ mol⁻¹. Two reasons account for the decreasing adsorption enthalpy with growing CO coverage: intermolecular repulsion of neighboring CO molecules and increasing competition for the *d* electrons of Pd nanoclusters participating in the CO-Pd bonding.

A qualitatively similar dependence of the adsorption heat on the CO coverage was observed for all larger Pd particles and for the single-crystal surface. Figure 2 shows the results of CO adsorption on the largest Pd particles (~ 4900 Pd atoms/particle, ~ 8 nm) and the Pd(111) single crystal. On both surfaces, the initially high adsorption heat continuously decreases with growing CO coverage and reaches a lower steady-state value in the quasisaturation regime. However, higher initial CO adsorption energies were measured on the large Pd nanoparticles ($+20$ kJ mol⁻¹) and the Pd(111) sur-

face ($+40$ kJ mol⁻¹), with respect to the initial adsorption energy measured on the smallest particles. For the Pd(111) single-crystal surface, both the initial heat of adsorption (149 ± 4 kJ mol⁻¹) as well as the saturation coverage at 300 K ($\sim 0.75 \times 10^{15}$ CO molecules cm⁻² or 0.5 per Pd surface atom) were found to be in a very good quantitative agreement with the data reported in the literature.¹³⁻¹⁵

To address the dependence of the initial heats of CO adsorption on the particle size in more detail, five different supported model systems with nominal Pd deposition thicknesses of 0.3, 0.6, 1.5, 4, and 7 Å were investigated in a way identical to the one described above. These Pd coverages correspond to particle sizes between 120 and 4900 Pd atoms per particle or between 1.8 and 8 nm assuming a hemispherical particle shape. The initial heat of adsorption on all supported model systems are displayed in Fig. 3 as a function of nominal Pd coverage together with data measured on Pd(111). Each point in this curve is an average of four to six independent measurements on freshly prepared model systems.

The dependence of initial CO adsorption heats on the particle size shows a pronounced trend: the initial heat of adsorption decreases with the nominal Pd deposition thickness, i.e., with decreasing particle size, from 126 ± 7 kJ mol⁻¹ on 8 nm sized Pd particles to 106 ± 2 kJ mol⁻¹ on the smallest 1.8 nm clusters. Additionally, all investigated particles showed smaller initial adsorption enthalpy as compared to the single-crystal surface (149 kJ mol⁻¹). It has to be noted that two experimental problems can principally affect the

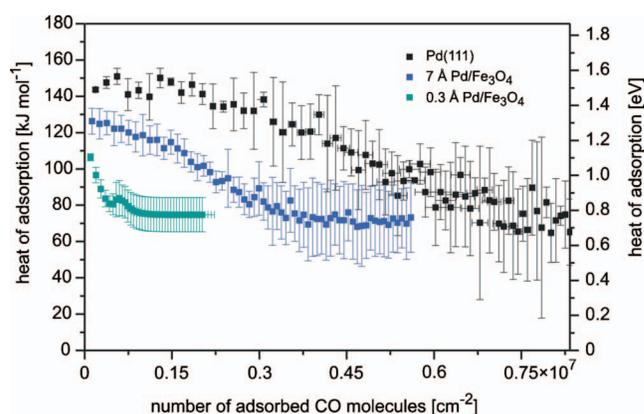


FIG. 2. (Color) Adsorption heat of CO on Pd(111) and on Pd/Fe₃O₄/Pt(111) model catalyst plotted as a function of CO surface coverage. Each curve is an average of four to six experimental runs measured on freshly prepared samples.

TABLE I. Structural data of the Pd/Fe₃O₄ model catalyst as determined from STM (see Fig. 1).

Nominal thickness of deposited Pd layer	0.3 Å	4.0 Å	7.0 Å
Nominal Pd coverage (atoms cm ⁻²)	2.1×10^{14}	2.8×10^{15}	4.9×10^{15}
Island density (cm ⁻²)	1.7×10^{12}	3.8×10^{12}	1.0×10^{12}
Average number of Pd atoms per island	~120	~740	~4900
Estimated number of surface Pd atoms per island	~65	~240	~870
Number of CO molecules per Pd island adsorbed in the first MB pulse	~4	~3	~14
Average size (nm)	1.8	4	8

measured value of the initial adsorption heat. First, different amounts of CO molecules per Pd particle could be adsorbed in the first pulse, giving rise to a probability distribution of initial CO coverages. To lessen the effect of this problem, our experimental conditions were chosen in such a way that only a few molecules (0.01–0.06 CO molecules per surface Pd atom as estimated from the number of adsorbed molecules and the number of surface Pd atoms) are adsorbed after the first CO pulse (see Table I for more details). Therefore it can safely be assumed that the initial heats of adsorption were obtained in the low-coverage limit and governed predominantly by the interaction of a CO molecule with a Pd cluster and not by the repulsive interaction between the adsorbates. Second, a variety of contaminating species can be adsorbed from the background and affect the measured initial heats of adsorption. We checked for possible contaminants by TPD after a typical waiting time of 30 min after cleaning the sample and found neither water nor CO₂; only negligible amounts of CO (~1% of saturation coverage). Note that CO does not dissociate on the Pd clusters at this temperature.¹⁶

The surface of the Pd particles investigated in this work exposes mainly (111) terraces alongside with a smaller frac-

tion of (100) facets and low-coordinated defect sites such as edges and corners.¹⁰ According to theoretical calculations, such irregular sites exhibit higher CO adsorption energies than Pd(111).¹⁷ Experimentally, there is a general agreement that the CO adsorption energy on the (100) plane is by about 10 to 15 kJ mol⁻¹ higher than on the (111) plane.¹³ However, the dramatic effect of low-coordination defect sites (like step edges) on CO adsorption energy, such as observed for Pt(111),¹⁸ is *not* seen on Pd(111).^{13,14} This suggests that the degree of coordination of the surface atoms on stepped surfaces is not as important in determining CO adsorption energies on Pd as on other metals such as Pt. Therefore, the increasing fraction of low-coordination Pd atoms with decreasing particle size, which normally would be expected to lead to higher adsorption energies for CO, might not be the dominant effect in determining how CO adsorption energies vary with particle size for Pd. Instead, other size-dependent properties of a Pd nanocluster must be responsible for the observed decrease in the initial adsorption enthalpy of carbon monoxide with decreasing the particle size.

Two alternative microscopic effects, for example, may contribute to the observed decrease in the initial CO adsorption heat with decreasing particle size: (i) weakening of the chemisorptive interaction and (ii) reduction in the van der Waals attraction. First, the decrease in the chemisorption energy can result from the contraction of the lattice parameter of a small metal nanoparticle. Previously, it has been demonstrated experimentally^{19,20} that the interatomic bond length in small metal particles decreases with decreasing particle size. It is now well established also by computational studies of various metals including Pd (Refs. 21–23) that relaxed structures of metal clusters exhibit shorter interatomic distances than bulk crystals. This phenomenon has been rationalized as a result of decreasing average coordination number of the atoms with the higher surface-to-volume ratio of the cluster.^{21–23} Particularly for Pd, it was shown that the average calculated Pd-Pd nearest-neighbor distance decreases linearly with decreasing linear dimension of a nanoparticle in the range of 55–260 atoms per cluster.²⁴ This lattice contraction in the small metal clusters was theoretically shown to result in a reduction in the adsorbate binding energy. Particularly for CO adsorption on the Pd clusters consisting of 55–260 atoms (in the size regime corresponding to or lower than our smallest investigated nanoparticles), it was demonstrated that the clusters with optimized structures show systematically lower adsorption energies by about 10–15 kJ mol⁻¹ than the clusters with a bulk terminated ge-

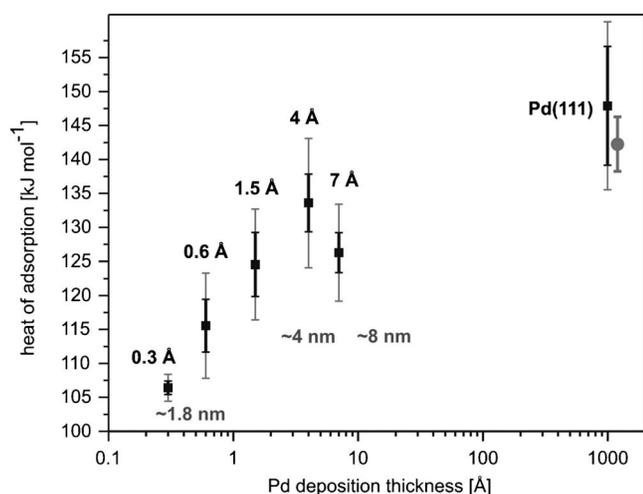


FIG. 3. Initial heat of adsorption of CO as a function of Pd coverage measured on the Fe₃O₄/Pt(111) samples with the nominal deposition thickness of 0.3, 0.6, 1.5, 4, and 7 Å and on the Pd(111) single-crystal surface. The gray circle corresponds to the value of the CO adsorption heat on Pd (111) reported by Ertl and co-workers (Ref. 13). Error bars: gray corresponds to the standard deviation and black to the standard error of the mean.

ometry, i.e., with all interatomic distances $d(\text{Pd-Pd}) = 275$ pm.²⁵ This finding agrees with the principle of bond order conservation:²⁶ 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. The decrease in the adsorbate binding energy with the lattice constant can be also rationalized in terms of the strain effect, which is associated with a downward shift of the valence d band with decreasing lattice parameter.^{25,27} Such effects were found not to be restricted to threefold hollow sites on (111) facets but reflect a general trend that also holds for adsorption at other sites of the particles such as bridge sites and edges.²⁵

A second reason for the decrease in adsorption heat of a gas-phase molecule on the small metal clusters is a feasible weakening of the dispersion force (van der Waals interaction) that is induced by dynamic response of bulk electrons of the metal to charge-density fluctuations in an adsorbed molecule. Previously, it has been shown that the electron population at the Fermi edge, which is mainly relevant for this interaction, drastically changes with the cluster size in the range of a few nanometers.²⁸ The gradual decrease in the initial adsorption heat with the decreasing cluster size can be reasonably understood since smaller clusters contain less electrons available for dynamic response. Similar behavior has been previously observed in TPD studies for methane on Pd (Ref. 29) and NO on Ag nanoclusters³⁰ and was also attributed to the reduced polarizability of the small metal nanoparticles.

The large magnitude of the effect obtained in our study [about 40 kJ mol⁻¹ relative to the Pd(111) surface] allows us to suggest that most likely reduction in both van der Waals interaction and chemisorption strength contributes to the

overall decrease in the adsorption heat. In order to judge the relevant magnitude of each contribution one would have to resort to calculations that treat both interactions on the same footing for bigger clusters. Those are not available at present.

In conclusion, we investigated the particle size dependence of the adsorption heat of carbon monoxide on well-defined Pd nanoclusters ranging from 120 to 4900 atoms per particle or from 1.8 to 8 nm and on the extended Pd(111) surface by single-crystal adsorption microcalorimetry. We provide a direct experimental proof that the CO binding energy decreases with decreasing particle size. The obtained initial adsorption enthalpy of carbon monoxide on the 1.8 nm-sized Pd clusters is reduced by about ~ 20 kJ mol⁻¹ as compared to the largest 8 nm particles and by ~ 40 kJ mol⁻¹ relative to the extended Pd(111) single-crystal surface. Two phenomena were suggested to contribute to the observed reduction in CO binding strength on the small nanoparticles: (i) weakening of chemisorptive interaction due to the contraction of the lattice parameter of the Pd cluster and (ii) reduction in van der Waals attraction due to the reduced polarizability of the small particles.

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