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# Size Dependence of the Adsorption Energy of CO on Metal Nanoparticles: A DFT Search for the Minimum Value

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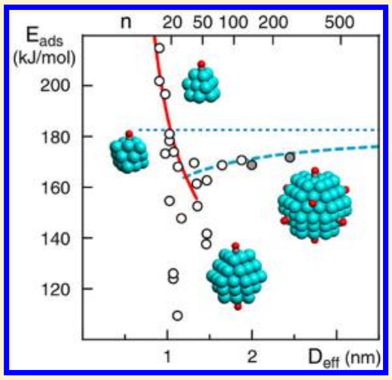
**ABSTRACT:** With a density functional theory method, we studied computationally the size dependence of adsorption properties of metal nanoparticles for CO as a probe on $Pd_n$ clusters with $n = 13-116$ atoms. For large particles, the values slowly decrease with cluster size from the asymptotic value for an (ideal) infinite surface. For clusters of 13−25 atoms, starting well above the asymptotic value, the adsorption energies drop quite steeply with increasing cluster size. These opposite trends meet in an intermediate size range, for clusters of 30−50 atoms, yielding the lowest adsorption energies. These computational results help to resolve a controversy on the size-dependent behavior of adsorption energies of metal nanoparticles.



**KEYWORDS:** *Nanocatalysts, nanoparticles, palladium, density functional calculations*

Metal nanoparticles, dispersed on a solid support of high surface area, form the active component of many modern catalysts.[1] The size of such metal species varies from particles of several thousand[2] to clusters of a few atoms.[3−5] The properties of (large) nanoparticles are size dependent, hence tunable. Therefore, understanding how the reactivity of such nanoparticles scales with size is crucial for the rational design of new catalysts.[1] However, the size dependence of some important properties is still not well understood, even for relatively simple and extensively studied model systems, such as CO adsorption on Pd nanoparticles. A recent direct microcalorimetric measurement of the heat of CO adsorption on Pd nanoclusters of well-defined structure showed that the initial heat of adsorption decreases from 126 kJ $mol^{-1}$ to 106 kJ $mol^{-1}$ for Pd particles ranging from on average 5000 (8 nm diameter) to about 100 atoms (1.8 nm diameter), respectively. The energies measured on Pd nanoparticles were always smaller than the corresponding value for the Pd(111) surface.[6] An earlier computational study of CO adsorption on $Pd_n$ clusters, with $n$ ranging from 260 to 55 atoms, suggested a similar trend of the adsorption energy with decreasing cluster size.[78] In contrast, earlier molecular beam studies[9,10] showed that the adsorption energy on supported particles of 3 nm diameter and smaller rises steeply above the asymptotic value of Pd(111).[9,10] These results are in contrast to those of another temperature programmed desorption study that shows the adsorption energy to decrease compared to the extended single crystal surfaces, by ~10 kJ $mol^{-1}$ on Pd particles of 2.5 nm.[11] Although, recent accurate experimental[6] and theoretical[7] studies strongly suggest that CO interaction becomes weaker as particles become smaller, at least down to sizes of 80−100 atoms with diameters of about 2 nm, an inversion of the trend cannot be excluded for particles smaller than those investigated before.[6,7] In fact, supported (hemispherical) Pd particles with a diameter of 3−3.5 nm are much too large[12] to exhibit a change in trend, which might be expected to occur with the transition from the scalable to the nonscalable region, i.e., for nuclearities $n \approx 100$. (In the nonscalable region particles are small enough for quantum effects to alter properties with the smallest change in size, i.e., "every atom counts",[13] in contrast to the regime of larger particles where scaling relations can be applied to quantify how properties depend on particle size and approach the bulk limit.)[8]

To resolve the controversy among experiments, we present in this letter the results of density functional (DF) calculations of CO adsorption on $Pd_n$ clusters for $n$ ranging from 13 to 116 atoms. The model clusters studied with adsorbed CO molecules are depicted in Figures 1 and 2. We focused on clusters that can be considered as models of catalytic particles grown on thin oxide films (e.g., $Fe_3O_4$) and terminated mainly by (111) facets with a small fraction of (001) facets.[14] Metal nanoparticles may exhibit various types of noncrystallographic

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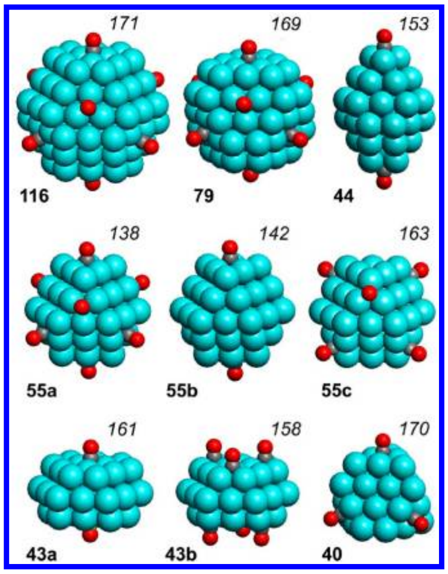

**Figure 1.** Nanoclusters with CO adsorbates: Pd$_{116}$ ($O_h$ symmetry), Pd$_{79}$, Pd$_{55}$ ($O_h$ for **55a** and $D_{3d}$ for **55b** and **55c**), Pd$_{43}$ ($D_{3d}$), Pd$_{44}$, and Pd$_{40}$ ($T_d$). Calculated adsorption energies (italic) in kJ mol$^{-1}$. Eight, six/two, and four adsorbed CO molecules per cluster for models with $O_h$, $D_{3d}$, and $T_d$ symmetry, respectively.

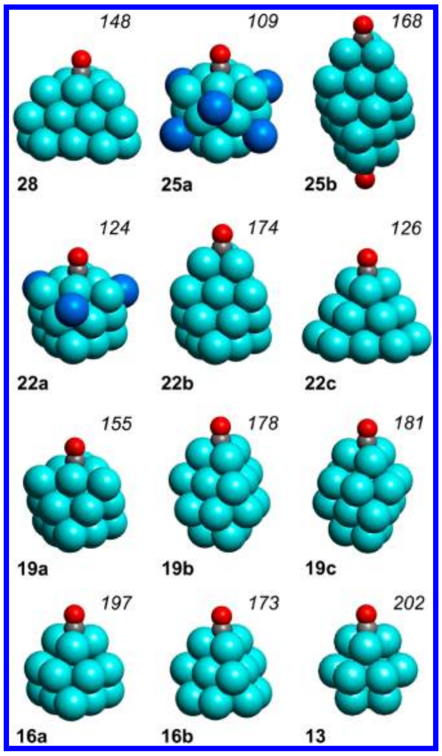

**Figure 2.** Subnanometer Pd clusters with CO adsorbates: Pd$_{13}$, Pd$_{16}$, Pd$_{19}$, Pd$_{22}$, and Pd$_{25}$, Pd$_{28}$; all with $C_{3v}$ symmetry, except **25b** ($D_{3d}$). Calculated adsorption energies (italic) in kJ mol$^{-1}$. Pd centers of models **22a** and **25a** deposited in non-fcc growth mode are shown in dark blue.

atomic packing.[15,16] Yet, a recent computational search for global minimum structures of small Pd clusters showed a rather early preference for bulk-like fcc structures based on the octahedron Pd$_{19}$.[17] Moreover, an oxide support with appropriately chosen structure can serve as a template for growing well-ordered nanocrystallites of bulk-like structures.[2,18] Therefore, we considered mainly clusters of fcc-like structure (Figures 1 and 2) with the exception of models **22a** and **25a** (Figure 2), where additional atoms on the facets of the octahedron Pd$_{19}$ induce deviations from fcc packing.

We examined the adsorption properties of Pd clusters by depositing CO molecules at three-fold hollow sites of closed-packed nanofacets of (111) orientation. At low coverage on the single crystal Pd(111) surface, three-fold sites are most favorable for CO adsorption.[19] These types of sites also dominate larger nanoparticles, terminated mainly by (111) facets. However, a variety of adsorption modes, including bridge, top, and hollow, were detected for small Pd clusters with up to 25 atoms.[20] Smaller clusters obviously feature a higher fraction of edge and vertex atoms which may bind CO ligands in bridge or top mode.[19] We focused the present study on the question of how the adsorption strength of hollow sites on (111) facets varies with cluster size. We addressed effects related to other adsorption modes only in one case, model **22a**.

The calculated CO adsorption energies are summarized in Figure 3, plotted as function of $n^{-1/3}$ (which scales as the inverse of the cluster diameters). In contrast to large clusters like Pd$_{79}$ and Pd$_{116}$, facets of smaller particles (Figures 1 and 2) mainly comprise Pd centers with coordination numbers less than 9, the value for atoms on (111) facets. One can distinguish several subseries of clusters with hollow sites formed by (i) five-coordinated atoms, e.g., models **44**, **25b**, **22b**,**c**, **19b**,**c**, **16a**,**b**, and **13** ($E_{\mathrm{ads}} \approx 170$ kJ mol$^{-1}$); (ii) seven-coordinated atoms in **55a**,**b**, **40**, **28**, and **19a** ($E_{\mathrm{ads}} \approx 145$ kJ mol$^{-1}$); and (iii) eight-coordinated atoms in **22a** and **25a** ($E_{\mathrm{ads}}$ = 109, 124 kJ mol$^{-1}$).[19] This variety of structures is reflected in strong variations of $E_{\mathrm{ads}}$ for smaller clusters, with a rather sharp increase of $E_{\mathrm{ads}}$ for the smallest clusters (Figures 2 and 3). The trend for the adsorption energies of CO on (111) facets of large particles Pd$_n$ with nuclearities $n$ from 79 to 260 and extrapolated to the limit of an infinite (111) surface is shown in Figure 3 as a dashed line.[7]

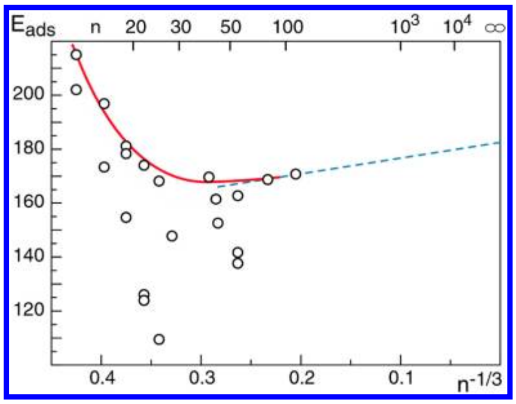

**Figure 3.** DF calculated energies of CO adsorption, $E_{\mathrm{ads}}$ (open circles, kJ mol$^{-1}$), on Pd$_n$ clusters with $n$ from 13 to 116 (see Figures 1 and 2) as function of $n^{-1/3}$. The values for the most stable adsorption complexes (for a given nuclearity $n$) are approximated by the solid line. The scaling trend extrapolated to the limit of an infinite (111) surface is shown as a dashed line (ref 7).

Figure 3 obviously displays two opposite trends for the values of $E_{\mathrm{ads}}$ for both small and large clusters. In the scalable region, for large particles, the observed growth of CO binding strength with cluster size, in the spirit of bonding competition, is associated with an elongation of the average Pd−Pd distance and a change in the van der Waals attraction.[6,7] To rationalize the size dependence of adsorption energies in the nonscalable region, we invoke the concept of orbital interactions between CO and a transition-metal cluster. The most important effect is due to back bonding from (localized) d-type valence orbitals of the metal moiety to the $2\pi^*$ lowest unoccupied molecular orbital (LUMO) of the adsorbate.[21,22] Perturbation theory suggests this interaction $E_{\mathrm{ads}}$ to be characterized roughly by

$$E_{\mathrm{ads}} = V^2/\Delta \tag{1}$$

where we assume a local interaction $V$, essentially independent of the particle size, in contrast to the energy gap $\Delta$. As the energy of the $2\pi^*$ level of CO in the gas phase is fixed, size-dependent effects are mainly determined by the energies of the d levels. We approximate these energies by the center $\varepsilon_d$ of the $d$-band,[23] which shifts to larger binding energies with increasing cluster size (Figure 4). This downward shift of $\varepsilon_d$ is due to the decreasing fraction of low-coordinated atoms on the surface as the cluster size increases.[24,25] Similarly to several other size-dependent properties of metal clusters, this trend can be well represented as linear function of the surface-to-volume ratio of the clusters $\mathrm{Pd}_n$, measured by $n^{-1/3}$ (Figure 4):[26,27]

$$\Delta(n) = \Delta_\infty(1 - cn^{-1/3}) \tag{2}$$

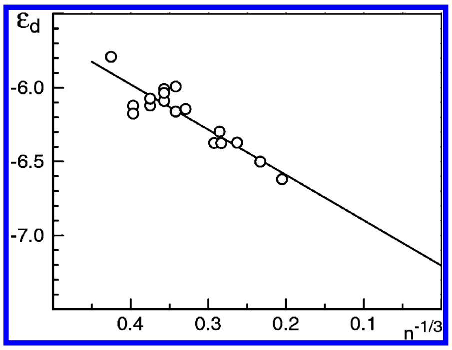

**Figure 4.** Energies $\varepsilon_d$ (eV) of the center of the $d$-band of $\mathrm{Pd}_n$ clusters, with $n$ ranging from 13 to 116 as function of $n^{-1/3}$.

$\Delta_\infty$ is the energy gap of infinitely large particles. From eq 1 one obtains the dependence of $E_{\mathrm{ads}}$ on the nuclearity $n$ of (small) particles as

$$E_{\mathrm{ads}}(n) = E_\infty/(1 - cn^{-1/3}) \tag{3}$$

Alternatively, one can determine $E_\infty$ and $c$ by fitting to the results calculated for smaller model clusters. The latter procedure yields the solid (red) trend line in Figure 5, where $E_{\mathrm{ads}}$ is plotted as function of particle diameter $D_{\mathrm{eff}} = 0.384\, n^{1/3}$, assuming hemispherical particles for an improved correspondence to the experiment. In this way we can fit the strongest adsorption energies on hollow sites in the nonscalable regime for nuclearities 13−43 by a linear regression according to eq 3 with a regression coefficient $R^2 = 0.65$. It is remarkable how well this trend line fits the data points, keeping in mind that one describes a supposedly "irregular" regime where "every atom counts".[13] Despite the simplicity of our model, this curve very well describes the behavior of calculated $E_{\mathrm{ads}}$ values of small clusters and intersects the trend line defined for extended (111) facets near $n \sim 40$.[7]

Thus, as function of particle size, the interaction of CO follows opposite trends for small (decreasing with $D_{\mathrm{eff}}$) and large nuclearities $n$ (increasing with $D_{\mathrm{eff}}$, Figure 5), forming an inverted "volcano" curve that implies a change of mechanism. For nuclearities above 100 atoms (scalable size regime), both theoretical[7] and microcalorimetrical[6] data agree that the strength $E_{\mathrm{ads}}$ of the CO interaction with (111)-faceted nanoparticles decreases with the particle size. This qualitative agreement between experiment and theory is remarkable because the experiment measured the heat of adsorption, averaged over different adsorption sites, while only one kind of adsorption sites, though obviously the most representative one, was considered in the computational modeling. Thus the degree of coordination of surface atoms on stepped surfaces does not seem to be as important in determining CO adsorption energies on Pd as on other metals, e.g., on Pt.[6] Therefore, the increasing fraction of low-coordinated atoms with decreasing particle size, normally expected to lead to higher adsorption energies, does not seem to be the dominant effect in determining how CO adsorption energies vary with the size of Pd clusters. A direct experimental study of CO adsorption on particles smaller than ∼120 atoms, where low-coordinated sites will affect the overall activity, was not possible for technical reasons.[6]

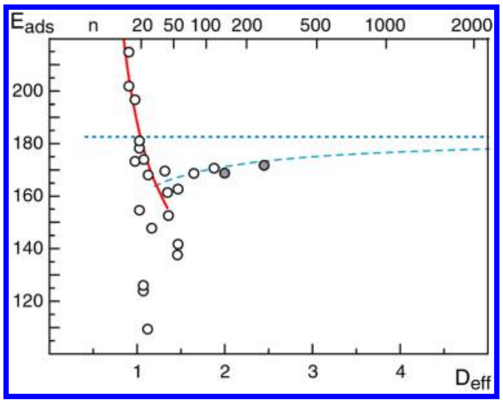

**Figure 5.** DF calculated energies of CO adsorption, $E_{\mathrm{ads}}$ (open circles, kJ mol$^{-1}$), on $\mathrm{Pd}_n$ clusters as function of the effective particle diameter $D_{\mathrm{eff}}$ (nm). (Data for $\mathrm{Pd}_{140}$ and $\mathrm{Pd}_{260}$ from ref 7 shown as filled circles). The trend in the nonscalable size regime according to eq 3 is shown by the solid line. The trend in the scalable size regime is shown as the dashed line (ref 7); the dotted line represents the extrapolated value for an infinite (111) surface.

In contrast, in the nonscalable regime, the size-dependent behavior shown in Figure 5 exhibits a striking similarity to the trend found by Henry et al. based on a kinetic analysis of molecular beam experiments.[9,10] The latter studies implied a change in the trend (increase) of $E_{\mathrm{ads}}$ values for particles from ∼3.5 nm diameter and below, while according to our calculations, this change in trend occurs for clusters as small as 1−1.5 nm. These latter clusters with nuclearities of ∼50 mark the critical size range where the dominant mechanism for the interaction of CO with the metal species changes from decreasing to increasing (with growing nuclearity). This size range is somewhat below that where one normally expects the transition from the nonscalable to the scalable regime, ∼100,[13] but agrees with the estimated onset for quantum effects becoming essential.[28] In their microcalorimetric study,[6] Campbell et al. proposed that Pd particles of 1.8 nm almost reach the large-size limit, based on the weakness with which they bind adsorbates.[29] Remarkably, the trend to increased activity of small clusters was found here while neglecting many other effects that can enhance the catalytic activity, e.g., the influence of the support or the role of defects. Thus, the change in trend identified results purely from effects related to the size of the particles. Note that experimental references[6,9] considered here use different oxide supports for Pd particles; $Fe_2O_4$ support evidently binds metal particles stronger than MgO and, hence, affects properties more strongly.[29] Therefore, on different supports, size effects of the same nature may occur at different particle sizes.[29]

It is instructive to compare the size dependence of adsorption properties of Pd nanoparticles with properties of other metal particles. A recent DFT study on a series of cuboctahedral Au clusters with nuclearities from 13 to 1415 atoms determined the adsorption energies of CO at top sites to increase with decreasing cluster size, below nuclearities of about 100.[30] Note that the electronic structure of gold differs notably from that of palladium and many other transition metals; recall the inactivity of bulk gold for CO adsorption.[31] Clusters with 309 and more Au atoms were calculated to yield essentially the same adsorption energy of CO or O probe adsorbates as infinitely large surfaces,[30] while for Pd in the same size range experimental measurements, supported by theoretical predictions, provide evidence for weaker interaction of CO than on a single crystal surface.[6] Although only a monotonous increase of $E_{ads}$ with decreasing cluster size was reported,[30] the computational results on Au clusters hint at a nonmonotonous size-dependent behavior in the adsorption energies of oxygen atoms (at fcc hollow sites), as the value calculated for $Au_{55}$ is significantly smaller than for other clusters and an extended gold surface. Recall that in the present study the lowest activity of Pd clusters in CO adsorption was also detected in the size range of 40−50 atoms. The highest CO binding energy, calculated for $Au_{13}$,[30] suggests a similar trend for small Au clusters as reported in the present study for Pd clusters. The study of Au clusters is limited to magic numbers determined by cuboctahedral shape.[30] Therefore, additional calculations on models with nuclearities the range between 13 and 147 would be of interest to quantify in more detail the size dependence of CO adsorption properties. One may also refer to the nonmonotonous activity in CO oxidation of Au nanoparticles, supported on titania, which showed a maximum for particles of ∼3 nm.[32]

An important question is to what extent different types of adsorption sites are involved in experimentally monitored binding of CO, especially on small clusters where most surface atoms exhibit a very low coordination number (<7 for clusters with $n < 30$). We explored this issue in model **22a** where the central hollow site features a rather small adsorption energy, only 124 kJ $mol^{-1}$. A stronger interaction activity may be expected for three-coordinated sites on the side facets (Figure 2). However, our calculations suggest other modes of CO bonding than three-fold hollow adsorption. When CO is deposited in the vicinity of these three-coordinated Pd atoms, the most stable position is atop, with $E_{ads}$ = 127 kJ $mol^{-1}$; bridge sites are slightly less stable, $E_{ads}$ = 121 kJ $mol^{-1}$. Such small energy differences may imply that various types of sites coexist in experimental probes. Differences between sites of the same cluster seem to be smaller than energy differences between small clusters. In an earlier study we have shown that atoms at edges of extended close-packed facets also bind CO rather strongly.[19] In agreement with experimental evidence[5,20] these latter results show that a top adsorption can play a role on small particles, rich in low-coordinated atoms. Evidently, the properties and the relative importance of various adsorption sites deserve a special study for each given configuration and nuclearity for those (molecule-like) clusters which comprise only few atoms because quantum effects can entail significant activity differences for clusters that differ slightly in size or shape. In that size range, strong variations of activity are known also from experiments.[33,34]

In summary, calculated CO adsorption energies on $Pd_n$ nanoparticles were found to exhibit two trends regarding the particle size $n$: (i) When the surface structure is dominated by extended close-packed facets, adsorption bonds formed by CO molecules become weaker with decreasing particle size.[6,7] This trend, valid for $n$ from infinity down to about 50−100,[6] results from a contraction of the lattice caused by surface stress.[7] (ii) In metal clusters of less than about 100 atoms, the fraction of low-coordinated atoms is higher and grows with decreasing value of $n$. At some critical size below $n \sim 50$, the concomitant upward shift of the metal d-levels induces a higher activity for CO adsorption. Such effects of increased activity of small Pd particles were previously found in molecular beam studies.[9,10] However, the present results together with recent experimental[6] and theoretical[7] studies of particles of nuclearities $n$ beyond 100−200 suggest a reassessment of the critical cluster size, where the adsorption activity starts to grow as clusters become smaller. Our computational results imply a change in trend of the CO adsorption energy at nuclearities of about 40−50 atoms with linear dimensions of 1 nm diameter or slightly larger. Taking into account that only three-fold adsorption sites for CO were examined computationally and support effects were neglected, this result is in fair agreement with the experimental findings. In addition, it provides a rationalization for the change in the trend of adsorption energies, including the existence of a size region of minimum values.

**Computational Methods.** Relativistic all-electron calculations were carried out using the linear combination of Gaussian-type orbitals fitting functions DF (LCGTO-FF-DF) method[35] as implemented in the parallel code ParaGauss.[36,37] The scalar relativistic variant of the LCGTO-FF-DF method employs a second-order Douglas−Kroll transformation of the Dirac−Kohn−Sham equation.[38,39] The geometries of $Pd_n$ clusters, bare as well as with adsorbed CO species, and the CO binding energies were calculated with the generalized gradient approximation (GGA) using the revised PBE[40] exchange−correlation functional. We used GGA-optimized geometries to model consistently the adsorbate-induced relaxation of surface sites which may have a notable influence on adsorption energies at smaller clusters. (In previous studies of large clusters,[7,19,33] adsorption energies were determined for fixed LDA-optimized geometries of the bare metal species.) The resulting $E_{ads}$ values were corrected for the basis set superposition error, invoking the counterpoise technique.[41] The scaling relation for $E_{ads}(n)$ in the scalable size regime yielding a limiting $E_{ads}$ value of 183 kJ $mol^{-1}$ for Pd(111) surface was determined as in previous work; experimentally 147 kJ $mol^{-1}$ is measured for the (111) surface.[6,7] Spin-restricted calculations were carried out, except for $Pd_{13}$.[42] To exploit symmetry in case of larger cluster models, we assumed several CO molecules to be deposited; comparison of models **55a** and **55b** (Figure 1) shows that such increase of CO coverage has only a minor effect on the adsorption energy. Other technical details, in particular the Gaussian-type orbital and auxiliary basis sets, have been described elsewhere.[33]

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### Notes

The authors declare no competing financial interest.

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