Local reactivity of supported metal clusters: Pd_n on Au(111)

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(Dated: October 22, 2003)

The local reactivity of small Pd_n cluster with n=3–10 supported by Au(111) has been studied by calculating atomic hydrogen and CO adsorption energies as a microscopic probe. The calculations are based on density functional theory within the generalized gradient approximation. The Pd clusters turn out to be less reactive than corresponding pseudomorphic Pd overlayers on Au which is a consequence of the reduced atomic distances in the clusters together with the cluster-support interaction. Our results provide a consistent microscopic explanation for the hydrogen evolution rate found in recent STM experiments.

Keywords: Computer simulations, density functional calculations, models of surface chemical reactions, chemisorption, hydrogen,carbaon monoxide, palladium, clusters

I. INTRODUCTION

There is a strong current interest in the study of supported metal clusters, not only from a fundamental point of view but also because of their technological relevance in, e.g., heterogeneous catalysis or the design of nanoscale magnetic storage devices. Systems with reduced dimensions can exhibit surprising properties. Elements that are usually chemically inert can become catalytically active [1, 2]. Non-magnetic bulk materials can show magnetic behavior as nanostructures [3].

Three-dimensional clusters are usually considered to be chemically very reactive due to their large defect-rich surface area [4]. In this letter, we report a theoretical study of the local reactivity of Pd_n clusters with $n \leq 10$ deposited on Au(111) using density functional theory (DFT). The system Pd/Au is of particular interest in the field of electrocatalysis [5–9] because of its catalytic activities in the oxidation reactions of methanol, formic acid and carbon monoxide. We have used atomic hydrogen and CO adsorption energies as a local probe in order to determine the trends in the reactivity. Although care should be taken in identifying adsorption energies with catalytic activity, for many systems there is a strong correlation between these two properties [10].

Recently, we have calculated the hydrogen and CO adsorption energies on pseudomorphic Pd overlayers deposited on Au(111) and Au(100) [11, 12]. According to this study both the substrate interaction as well as the expansion of the Pd overlayers increase the adsorption energies. These results can be rationalized within the d-band model [13, 14]. Both the tensile strain and the relative weak coupling between the Pd and Au atoms lead to an effectively lower coordination of the overlayer atoms. This causes an upshift of the d-band that results in a higher reactivity. For Pt/Ru overlayers, exactly the opposite trend has been found: compressive strain and a strong interaction between overlayer and substrate lead to a reduction in the adsorbate binding energies [15].

Surprisingly, on the Pd_n/Au(111) cluster we find that most adsorption energies are smaller than those on Pd/Au pseudomorphic overlayers [11, 12]. Thus, nano-size supported metal cluster are not necessarily more reactive than thin films. The reduced adsorption energies of the supported clusters are caused by their compressive relaxations together with the support interaction. Based on our results and previous kinetic modeling [16] we propose that flat Pd nano-islands instead of three-dimensional nano-crystals are responsible for the higher hydrogen evolution rate observed in recent STM experiments [9].

II. THEORETICAL METHODS

Self-consistent periodic DFT calculations have been performed using the Vienna *ab initio* simulation package (VASP) [17]. The exchange-correlation effects have been described within the generalized gradient approximation (GGA) using the Perdew-Wang (PW-91) functional [18]. The ionic cores are represented by ultrasoft pseudopotentials [19] as constructed by G. Kresse and J. Hafner [20]. The Kohn-Sham one-electron valence states are expanded in a basis of plane waves with cutoff energies of 200 eV for H adsorption and 400 eV for CO adsorption. The calculated equilibrium lattice constants for bulk Pd and Au, 3.96 Å and 4.18 Å, respectively, are in good agreement with the experiment (3.88 Å and 4.08 Å [21], respectively). The Au(111) substrate has been modeled by a four-layer slab separated by 14.5 and 17.2 Å of vacuum for H and CO adsorption, respectively. The convergence of all results with respect to these technical parameters has been carefully checked.

Bimetallic systems are of interest in heterogeneous catalysis, but they are particularly relevant in electrochemistry [22] since the catalytically active material has to be placed on a conductive electrode. In our calculations, we have not taken into account any electrolyte. However, an additional water adlayer changes the hydrogen adsorption energies by less than 60 meV [23] because water is relatively weakly bound to metal surfaces. Since the presence of water has only little influence on the adsorption energies, the results presented here for the solid-vacuum interface are therefore also relevant for

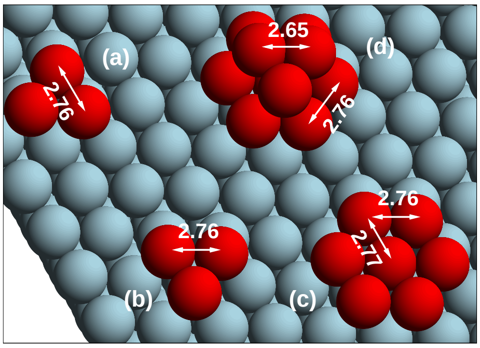

FIG. 1: Calculated nearest-neighbor Pd-Pd distances in Å of Pd_n cluster supported by Au(111).

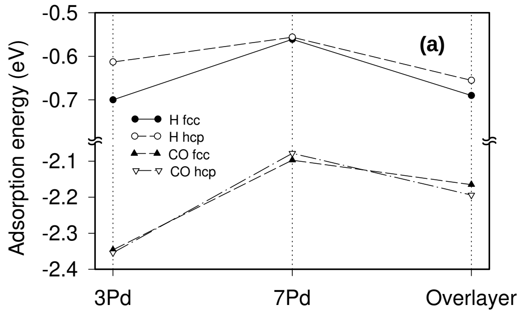

FIG. 2: Calculated CO and hydrogen adsorption energies on planar Pd_3 and Pd_7 clusters deposited on Au(111) compared to the corresponding adsorption energies on the Pd/Au(111) overlayer.

the solid-liquid interface.

III. RESULTS AND DISCUSSION

In a first step, we determined the interaction energy between Pd atoms adsorbed on Au(111). We found that for a separation of about 6 Å there is hardly any interaction. Thus, we have chosen a 3×3 surface unit cell for the supported triangular Pd_3 clusters and a 4×4 surface unit cell for the hexagonal Pd_7 clusters. For these cluster structures we used a Monkhorst-Pack set of 5×5×1 and 3×3×1 **k**-points, respectively. It is well-known that small Pd cluster in the gas phase are magnetic [24]. By performing spin-polarized calculations we checked whether the supported Pd_n cluster show magnetic behavior, but did not find any magnetic polarization, in agreement with previous calculations for metal-supported Pd clusters [3]. Hence all further results presented in this study were obtained by spin-saturated calculations.

In Fig. 1, we have summarized the results for the structural relaxation of the Pd_n/Au(111) clusters. The nearest-neighbor distances in the planar Pd_3 and Pd_7 cluster on Au(111) are 2.76–2.77 Å. This is even smaller than the nearest-neighbor distance in Pd bulk although the Au substrate has a 5% larger lattice constant than Pd. Note that there are two inequivalent triangular cluster on (111) surfaces bounded by {111} and {100}-like microfacets, respectively. The Pd-Pd distance in the top layer of the three-dimensional Pd_{10} cluster is even further reduced to 2.65 Å. The corresponding values for free planar Pd_3 and Pd_7 clusters are 2.50 and 2.64 Å, respectively. Relaxation effects are in fact well-known for clusters; for example, significant compressions for Pd gas-phase cluster with up to 140 atoms have been found in DFT calculations [25].

The H and CO adsorption energies on the planar supported clusters are compared to those on the overlayer in Fig. 2. The hydrogen adsorption energies are taken with respect to the free H_2 molecule. For the hydrogen binding energy E_{H_2} in the gas phase we have taken the calculated GGA value. Note that the energy gain upon adsorption corresponds to a negative adsorption energy. In the following, we will denote by binding energy the negative of the adsorption energy. While on the Pd_3 cluster the binding energies are comparable or even stronger than on the Pd/Au(111) overlayer, on the Pd_7 cluster the binding energies are significantly smaller. Note that on the Pd/Au(111) overlayer the binding energies are already larger than on the Pd(111) surface [12].

These results can all be understood within the d-band model. Tensile strain and substrate interaction effects lead to an upshift of the d-band center from $\varepsilon_d = -1.64$ eV for Pd(111) to $\varepsilon_d = -1.27$ eV for the Pd/Au(111) overlayer [12] with respect to the Fermi energy. For the supported clusters, there are two opposing effects. On the one hand, the lower coordination of the cluster atoms should lead to a further upshift of the d-band center. On the other hand, the reduction of the Pd-Pd distances has the opposite effect. As for the Pd_3 clusters, both effects almost cancel each other. The d-band center is located at -1.21 eV close to the value for the overlayer; consequently, the adsorption energies are comparable to the Pd/Au(111) overlayer. The local d-band centers of the Pd_7 cluster are at -1.26 eV and -1.48 eV at the corner and the center atoms, respectively. The low-lying d-band center of the center atom reflects the high coordination of this atom, $N = 9$, where N is the coordination number. At the three-fold hollow sites, the adsorbate binds to two corner atoms and the center atom. The higher coordination of the center atom in the Pd_7 cluster together with its compression lead to the smaller binding energies.

We have analysed the electronic structure in even more detail. In Fig. 3, we present the orbital resolved d-band local density of states (LDOS) for Pd_3 clusters deposited on Au(111) and on Pd(111). In addition, we compare the LDOS of the supported clusters with those of the free Pd_3 cluster. The free cluster exhibits a discrete structure of electronic levels, as is expected for a finite system. Interestingly, for the Pd_3/Au(111) cluster the d-band orbitals that are confined within the cluster layer, i.e., within the xy-plane, namely the d_{xy} and the $d_{x^2-y^2}$ orbitals, also

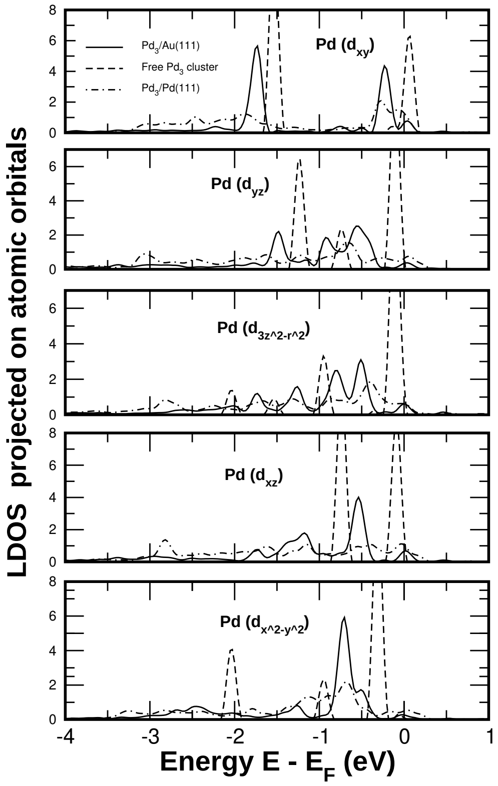

FIG. 3: Orbital resolved d-band local density of states (LDOS) of the $Pd_3/Au(111)$, $Pd_3/Pd(111)$ and the free Pd_3 clusters.

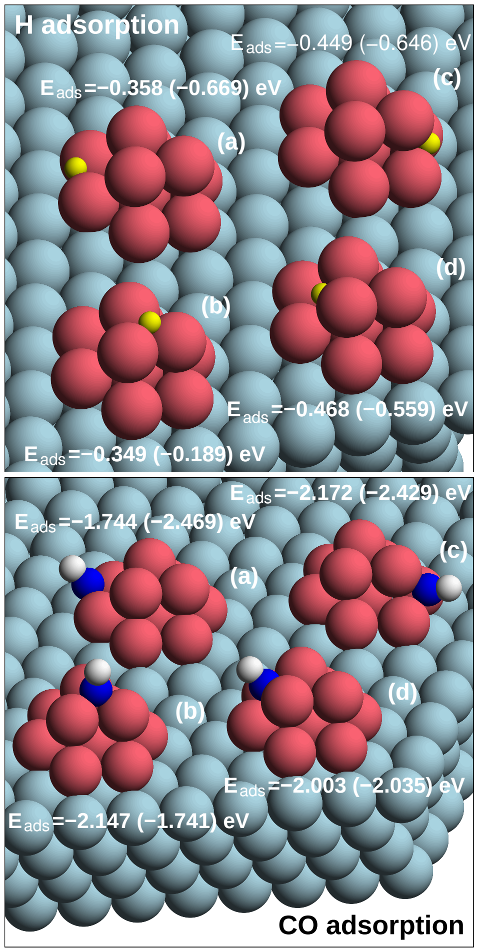

FIG. 4: Calculated H and CO adsorption positions and energies on the $Pd_{10}/Au(111)$ cluster. The numbers in parentheses correspond to the adsorption energies on free Pd_{10} clusters in exactly the same configuration as the supported clusters.

show a rather discrete structure. This means that these orbitals are indeed confined within the cluster. The other three orbitals, however, that have a component along the vertical z-direction are already rather broad, indicating the significant coupling to the Au(111) substrate.

The Pd_3 cluster is even more strongly coupled to an underlying Pd(111) substrate, as the LDOS in Fig. 3 demonstrates. In that case, *all* d orbitals in the cluster are considerably broadened. The stronger coupling is also reflected by a deeper lying d-band center at $\varepsilon_d = -1.39$ eV compared to $\varepsilon_d = -1.21$ eV for the $Pd_3/Au(111)$ cluster. This deeper lying d-band center also leads to smaller binding energies of the adsorbates. For example, the adsorption energies of atomic hydrogen are only -0.45 eV and -0.60 eV on the hcp and fcc sites, respectively, on the Pd_3 cluster supported by Pd(111) compared to -0.61 eV and -0.70 eV at the corresponding sites of the cluster on the Au(111) support.

It has been speculated that the unsual electrochemical stability of nanofabricated supported metal clusters [26] could be caused by quantum confinement effects [27] that would lead to a discrete electronic spectrum in the clusters. Our calculations show that already small supported Pd_3 clusters exhibit a continuous spectrum. The strong coupling to the substrate leads to the metallic nature of these clusters. For larger clusters quantum confinement effects are even less likely; hence our calculations do not support the speculation of Ref. [27].

The H and CO adsorption positions and energies on the three-dimensional $Pd_{10}/Au(111)$ cluster are collected in Fig. 4. We first note that, surprinsingly, all calculated hydrogen binding energies on the supported Pd_{10} clusters are smaller than those on the planar clusters and on the overlayers. As for CO, the binding energies on the Pd_{10} cluster are about the the same as on the overlayer and the planar Pd_7 cluster, but they are considerably smaller than on the Pd_3 cluster. There are three symmetrically distinct atomic positions, the center and the corner positions in the first or lower layer and the second or upper layer position. The local d-band centers at these three positions are located at -1.83 eV, -1.41 eV and -1.39 eV, respectively. Although the coordination of the corner atom in the first layer, $N = 7$, is larger than the one of the second layer atom, $N = 5$, still the local d band centers are almost at the same position. Again, this can be understood by the reduced distance of the topmost Pd atoms which increases their effective coordination. Consequently, the adsorption energies on top of the Pd_{10} clusters are rather similar to the ones at the sides. The only exception is the site labeled (a) for CO where the binding energy is reduced by about 0.4 eV with respect to the top site. This is caused by the CO-support interaction: CO binding on Au is very weak, its binding energy is about 1.5 eV smaller on Au than on Pd [11, 12].

Note that there are two different side facets of the Pd_{10} clusters corresponding to {111} and {100} microfacets. The different adsorption energies at these facets roughly reflect the ordering of H and CO adsorption on the hollow adsorption sites on Pd(111) and Pd(100) [12]. It is obvious that CO adsorbs in a configuration that is locally perpendicular to the microfacets. The adsorption sites labeled (a) in Fig. 4 correspond to the local minima that one finds if one tries to put H and CO into the fourfold hollow position made from two Pd and two Au atoms at the edge of the cluster. The noble metal substrate Au is so inert that the adsorbates relax towards the Pd cluster atoms and end up in a quasi twofold bridge position.

In order to estimate the cluster-support interaction, we have also determined the adsorption energies on free Pd_{10} clusters in exactly the same geometry as the supported clusters. As far as the adsorbates are concerned that mainly bind to the first layer Pd atoms, their binding binding energies on the free clusters are significantly larger, in particular for CO, than on the supported clusters and also on flat [28] and stepped Pd surfaces [29, 30], This confirms that in spite of their compression free clusters are much more reactive than surfaces because of their low coordination. Thus it is the strong interaction of the three-dimensional Pd clusters with the Au support that contributes to the low adsorption energies on the metal-supported clusters. On oxide-supported clusters, on the other hand, the substrate-cluster interaction is much smaller so that the adsorption energies should be larger. Interestingly enough, at the top layer adsorption site the adsorbate binding energies on the free cluster are smaller than on the supported cluster. This surprising result is caused by the reactivity of the unsaturated hexagonal bottom layer of the free Pd_{10} cluster. It binds the three topmost Pd atoms so strongly that the top layer becomes less reactive, as an analysis of the energetics and the electronic structure of the free cluster confirms.

Just recently, a high hydrogen evolution rate has been found experimentally on Pd nanoparticles deposited on Au(111) using an electrochemical STM set-up [9]. The nanoparticles were, however, rather flat with a diameter to height ratio of about 5 - 10. The thinnest Pd particles with a height corresponding to two to three layers showed a hydrogen evolution rate that was about three orders of magnitude larger than the largest particles studied with a height of more than 10 monolayers. In a subsequent kinetic modeling the high hydrogen evolution rate could be explained under the assumption of a small desorption rate of hydrogen from the Pd particles [16]. Then the hdyrogen atoms will spillover from the Pd particles to the Au substrate from where they will be released. The Pd particles thus represent an efficient hydrogen source.

We have found relatively small hydrogen binding energies on the three-dimensional Pd_{10} cluster. This would rather lead to a large desorption rate. On the other hand, pseudomorphic Pd overlayer on Au(111) show a maximum hydrogen binding energy for two overlayers [12] that is 0.2 eV larger than on flat Pd(111) and 0.3 eV larger than on the three-dimensional Pd_{10} clusters. At room temperature, these higher atomic binding energies lead to *associative* desorption rates that are reduced by at least six orders of magnitude. These findings suggest that the experiment has not probed properties of three-dimensional nanoparticles but rather of small islands that are locally pseudomorphic with the Au substrate, i.e. expanded by 5%. We have checked that larger Pd islands will grow pseudomorphically on Au(111) by performing Pd/Au(111) overlayer calculations in a $\sqrt{7} \times \sqrt{7}$ surface unit cell. In such a setup, contracted hexagonal Pd_7 cluster could form. However, we found that they were not stable with respect to the pseudomorphic overlayer.

IV. CONCLUSIONS

In conclusion, we have calculated the adsorption energies of hydrogen atoms and CO on small supported Pd_n/Au(111) clusters as a probe of the local reactivity. We find that the reactivity of the supported clusters is determined by a combination of coordination, relaxation and support interaction effects. Due to the reduced interatomic distances and the strong interaction with the Au substrate, the three-dimensional supported Pd cluster are less reactive than corresponding pseudomorphic Pd overlayers.

Acknowledgments

Financial support by the Deutsche Forschungsgemeinschaft through the priority programm SPP 1030 is gratefully acknowledged. We would like to thank J. Meier, M. Eikerling and U. Stimming for stimulating discussions and for sharing their results with us prior to publication.

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