Supported Magnetic Nanoclusters: Soft Landing of Pd Clusters on a MgO Surface

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Low-energy deposition of neutral PdN clusters (N = 2–7 and 13) on a MgO(001) surface F center 
(FC) was studied by spin-density-functional molecular dynamics simulations. The incident clusters are 
steered by an attractive “funnel” created by the FC, resulting in adsorption of the cluster, with one of its 
bonds atop of the FC. The deposited Pd2–Pd6 clusters retain their gas-phase structures, while for 
N > 6 surface-commensurate isomers are energetically more favorable. Adsorbed clusters with N > 3 
are found to remain magnetic at the surface.

Deposition of atomic clusters onto solid surfaces is a versatile surface-processing tool, with applications 
ranging from “micromachining” and surface smoothing to thin-film growth and fabrication of model nanocatalysts 
[1–7]. Theoretical investigations, employing most often molecular dynamics (MD) simulations with semiempirical 
interatomic potentials, provided valuable insights into the microscopic mechanisms of the deposition process 
[8–10]. However, when cluster-surface interaction involves surface chemistry (that is, the creation or breaking 
of chemical bonds) [7], spin-dependent (magnetic) processes [2], or surface defects of electronic origin 
(e.g., F center on an ionic surface) [3,11,12], a full quantum description of the cluster deposition process is 
necessary.

Here we report on a first-principles investigation of soft-landing of PdN clusters (N = 2–7 and 13) onto a 
MgO(001) surface containing a surface F center, FC (oxygen vacancy). We show that the interaction between the Pd 
cluster and the FC evolves from an initial long-ranged attractive polarization into chemical bonding involving 
the localized FC electronic state located in the MgO band gap. For N ≤ 6 the cluster retains its gas-phase geometry, 
whereas adsorbed clusters with N = 7 and 13 adapt to the underlying surface rocksalt structure. The interaction 
with the surface quenches the spin for clusters with N ≤ 3, retains the gas-phase triplet state (S = 1) for 4 ≤ N ≤ 7, 
and for N = 13 the gas-phase nonet (S = 4) transforms to a septet (S = 3) state. These results are of importance 
for understanding the activity of Pd/MgO nanocatalysts [13,14], as well as for future investigations of supported 
magnetic nanoclusters.

The PdN/MgO system was treated by the local-spin-density (LSD) functional theory, with scalar-relativistic 
pseudopotentials [15] and self-consistent gradient corrections [16]. For cluster impact energies below the band gap 
of the substrate, the Born-Oppenheimer (BO) approximation describes faithfully the collision dynamics, 
and therefore we employed the BO-LSD-MD method [17] for the calculation of the electronic structure and the 
nuclear motion of the Pd cluster and the substrate.

The MgO substrate with an F center was modeled by a two-layer ab initio cluster Mg13O12, embedded into a 
lattice of point charges [13], with a lattice parameter fixed to the experimental value (4.21 Å) of bulk MgO. 
The PdN cluster and the F center’s four nearest-neighbor Mg atoms and four nearest-neighbor O atoms of the first 
layer were treated dynamically during the deposition. The heat conductivity of the MgO surface was modeled 
via inclusion of a damping term with a damping constant πωD/6 [10], where ωD is the Debye frequency of 
bulk MgO.

The initial spin states (triplet for N = 2–7 and nonet for N = 13) and geometrical structures of the PdN clusters 
were taken from our recent gas-phase study [18]. The clusters were placed with a random orientation 4 Å above 
the FC (measured from the cluster atom closest to the surface) and an initial velocity directed perpendicular to 
the MgO surface, corresponding to a kinetic energy of 0.1 eV per atom to simulate soft-landing conditions [19]. 
The spin of the cluster-substrate system was dynamically evaluated at each MD time step. Subsequent to the dyna-
mal evaluation of the deposition process for about 1 ps the simulation was stopped, and starting from the last 
recorded configuration a corresponding potential energy minimum was located by an energy-gradient optimization 
with variable spin; other spin-isomers (SPIs) were optimized (starting from the aforementioned optimal configura-
tion), in order to explore the thermal stability of the lowest-energy SPI.

The adsorption of a single Pd atom on top of the FC 
(rFC site) is characterized by a strong binding energy 
(3.31 eV) and a short equilibrium adsorption distance 
(1.65 Å), compared to adsorption on top of an oxygen 
(rO) atom at the ideal MgO surface (1.16 eV and 2.17 Å). 
The bonding between the Pd atom and the FC involves the localized FC electronic orbital, located in the band gap of 
MgO (separated from the top of the valence band by 2.3 eV), and (mainly) the d(m = 0) orbital of the Pd atom. The attractive interaction to the F center is rather long-ranged extending up to about 5 Å above the surface; 
e.g., the interaction energy of a Pd atom placed 5.2 Å

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above the FC is 0.1 eV. This weak attraction is due to
polarization of the $d(m = 0)$ valence orbital of Pd by the
FC. None of the other adsorption sites for the Pd atom,
lying in the vicinity of the F center [e.g., on top of the
neighboring oxygen (O)], on top of the neighboring Mg
atom (tMg), the Mg-Mg bridge (bMgMg), the Mg-O
bridge (bMgO), and the Mg-Mg-O hollow site
(hMgMgO), are stable; i.e., optimization starting from
any of these sites leads to a spontaneous (barrierless)
transition to the aforementioned tFC configuration. We
conclude that the FC center acts as a rather wide attractive
funnel for the Pd atom, extending several Å both laterally and vertically [20]. Such funneling steers the incident
crystal and dominates the dynamics of the initial phases
of the deposition process, as illustrated below for the
representative case of Pd$_3$.

When the Pd$_3$ cluster is placed 4 Å above the oxygen
vacancy, the FC electronic state (located just below $E_F$)
combines with $d$ orbitals of the closest Pd atom to form
two bonding molecular orbitals [see the up-spin highest
occupied molecular orbital (HOMO)-1 and the down-spin
HOMO in Fig. 1(a)]. All other orbitals [e.g., the lowest
unoccupied orbital (LUMO) of Pd$_3$ shown in Fig. 1(a)]
remain essentially eigenstates of the separated systems,
and consequently the corresponding density of states
[DOS in Fig. 1(b)] may be represented as a superposition
of those of the bare surface and the free cluster.

The long-range attraction between the cluster and the
FC accelerates the lowermost Pd atom towards the tFC
site [note the strong deformation of the Pd$_3$ cluster at
0.2 ps in Fig. 1(c) and the increase of the kinetic energy
in Fig. 1(d)]. Subsequently, other Pd atoms are attracted to
neighboring bMgO positions [Fig. 1(c), $t = 0.5$ ps] accom-
panied by additional release of kinetic energy. Consequently, the center of mass (CM) velocity toward
the surface increases to almost twice its initial value
[Fig. 1(d)] leading to a strong flattening of the cluster at
$t = 0.5$ ps [see the minimum in the $z$ component of the
cluster CM in Fig. 1(e)]. The cluster shape deformation
causes a transient reordering of the molecular orbitals;
i.e., it raises the energy of the up-spin HOMO-1 level
[marked 75 $\uparrow$ in Fig. 1(a)] and turns it into a HOMO
at $t = 0.32$ ps, and even into a LUMO at $t = 0.36$ ps;
this sequence is portrayed in Fig. 1(e) by closing of
the HOMO-LUMO gap (black curve) and the minimum in
the eigenvalue energy difference $\epsilon_{75\uparrow} - \epsilon_{34\downarrow}$ (red
curve). Since the down-spin LUMO [74 $\downarrow$ in Fig. 1(a)]
temporarily becomes the HOMO state, the total spin flips
temporarily from $S = 1$ to $S = 0$ [Fig. 1(e)]. After 0.5 ps
the cluster recoils and the reverse process drives the cluster back into the triplet spin state at $t = 0.63$ ps
[Fig. 1(e)].

Optimization of the adsorbed cluster after a 1.2 ps
simulation [see Fig. 1(c) for the last MD configuration],
resulted in a trigonal bipyramide structure (coinciding
with the gas-phase optimal configuration) with a triangu-
lar facet against a tFC-bMgO-bMgO surface triangle
[Fig. 1(f)]. The spin polarization of the triplet ground
state [$S = 1$ isosurface in Fig. 1(f)] resembles that of the
free cluster with a minor additional contribution
from four surface oxygens closest to the FC. As expected
from our gas-phase calculations [18] the slightly high-
lying singlet state ($\Delta E = 24$ meV) consists of an anti-
ferromagnetic ordering of the local magnetic moments
[$S = 0$ isosurface in Fig. 1(f)]. The spatial character of
the orbitals close to $E_F$ and the surface and cluster
corrections to the DOS of the triplet ground state
of Pd$_3$/MgO(FC) are shown in Figs. 1(f) and 1(h), respectively.

Using the above methodology, we have determined the
ground states for the other deposited Pd$_N$ clusters [21]. For
$3 \leq N \leq 6$ we observed a regular size evolution
[Fig. 2(a)] where the gas-phase GS structures are anch-
ored to the MgO surface with one Pd atom on the tFC,
another Pd on the bMgMgO site (for $N = 2$), or two
additional Pd atoms on bMgO sites close to the rO posi-
tion (for $3 \leq N \leq 6$). For Pd$_7$ and Pd$_{13}$ the free clusters
transform to structures with a higher commensurability
to the underlying surface, incorporating a Pd$_6$ and Pd$_7$
subunit, respectively [Fig. 2(a)]. Here the loss in the intra-
cluster cohesion is counterbalanced by a considerable gain
of adhesion energy $E_{ad}$ [defined as $E_{ad} = E(MgO(FC)) + E(Pd_N) - E(Pd_N/MgO(FC))$; see the red curve in
Fig. 2(b)]. Consequently, the cohesive energy $E_c$ per Pd
atom [defined as $E_c = (E(MgO(FC)) + NE(Pd) - E(Pd_N/MgO(FC)))/N$; see the blue curve in Fig. 2(b)]
continues to increase after Pd$_6$ and remains well above
the gas-phase $E_c$ values.

The HOMO-LUMO gap [Fig. 2(b)] of the combined
Pd$_N$/MgO(FC) system is governed mainly by the metal
cluster since the top part of its density of states lies in the
MgO band gap. Most interestingly, the deposited Pd$_N$
clusters with $N \geq 4$ remain magnetic: $S = 1$ for $4 \leq N \leq 7$ and $S = 3$ for $N = 13$. The crossover from nonmag-
netic to magnetic states between Pd$_3$ and Pd$_4$ correlates
with an increased “thickness” of the cluster [Fig. 2(c)],
corroborating our finding that flattening of the cluster on
the surface tends to be accompanied by quenching of the
spin [see discussion in the context of Fig. 1(e)].

In general, the deposition of the cluster reduces the
energy separation between SPIs, thus lowering the thresh-
old temperature for their coexistence. For instance, the
triplet-singlet energy difference of supported Pd$_4$
is $\Delta E = 65$ meV compared to the gas-phase values of
$\Delta E = 136$ meV; for Pd$_{13}$ five SPIs can be found within
a 0.5 eV range, which expressed in terms of temperature
corresponds to about 350 K [Fig. 2(c), inset]. This result
indicates that experiments aiming at distinguishing mag-
netic states of the adsorbed clusters could be carried out at
room temperature.

In summary, our soft-landing first-principles simula-
tions show that an F center creates an attractive funnel
for the approaching metal cluster, resulting in preferred binding configurations with one Pd atom atop the F center. For adsorbed Pd$_2$-Pd$_6$ the gas-phase geometry is retained, while Pd$_7$ and Pd$_{13}$ adapt to the underlying MgO structure. Although the surface tends to reduce the spin of the adsorbed cluster, clusters larger than Pd$_3$ remain magnetic at the surface, exhibiting several low-lying structural and spin isomers. These results provide the
impetus for further investigations regarding the interplay of structural and magnetic states of supported metal clusters and their catalytic properties.

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[3] See U. Heiz and W-D. Schneider, in Metal Clusters at Surfaces [1].
[15] N. Troullier and J.L. Martins, Phys. Rev. B 43, 1993 (1991). The core radii (in $a_0$) are the following: Pd (2.45) local, $p(2.6)$, $d(2.45)$; Mg $s(2.5)$, $p(2.75)$ local; O $s(1.45)$, $p(1.45)$ local. A plane-wave basis with a 62 Ry cutoff was used.
[19] A few (uncorrelated) initial starting configurations with random orientations were used, and the results did not depend on the starting configuration.
[20] Experimentally, nanocatalysts are prepared [3] by soft-landing metal clusters on thin MgO films containing typically a few % ML coverage of FCs. In this case, an average FC-FC distance is a few lattice constants. Therefore, most metal clusters either experience directly the “funnel effect” of the nearest FCs while approaching the MgO surface or become trapped rapidly at FCs.
[21] For Pd$_N$ clusters, with $N \leq 7$, other structural/spin isomers were optimized (to a local minimum), and except for Pd$_6$ (where the dynamical deposition yielded a higher-energy cluster, $\Delta E = 0.18$ eV) this resulted in isomers with higher energy compared to those determined via the dynamical deposition.

FIG. 2 (color). Structural and magnetic size evolution of supported Pd$_N$ clusters. (a) GS structures of Pd$_N$ ($N = 2$, 3, 4, 6, 7, and 13). Color coding as in Fig. 1 except for Pd$_{13}$ where a subset of the Pd atoms is colored in yellow in order to highlight the Pd$_5$ subunit (blue). (b) Size evolution of the adhesion energy $E_{ad}$ (red filled squares), the binding energy per atom $E_b$ for the supported (blue solid dots) and free (blue circles) clusters, and the HOMO-LUMO gap of the supported (green solid diamonds) and free (green open diamonds) clusters. (c) Size evolution of GS spin $S$ (red diamonds) and the distance of the highest cluster atom to the surface (blue solid dots). The inset of (c) shows the SPI energies $\Delta E$ (with reference to the GS configuration, $S = 3$ for the adsorbed cluster and $S = 4$ for the free one) and corresponding activation temperatures $T = 2\Delta E/k/(3N - 6)$ of supported (green solid dots) and free Pd$_{13}$ (green circles) clusters.