

Predicting experimental signatures for the oxidation of magnesia supported palladium clusters by density functional theory

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Abstract. We showed in a recent density functional study that small palladium cluster on a MgO surface with F-centers can be oxidized to epitaxial Pd_xO_y nano-oxides below room temperature [1]. Here, we employ density functional theory in order to explore different methods for an experimental verification of the Pd_xO_y formation. The electronic density of states (DOS) of bare, O_2 -decorated and of oxidized palladium cluster was calculated. For many cluster sizes a clear difference in the DOS could be observed allowing for a detection of the oxidation with surface sensitive spectroscopic methods. In addition, adsorption sites and stretch frequencies of a single CO molecule on bare and oxidized Pd_4 clusters were calculated. While CO prefers hollow sites on Pd_4 , top adsorption sites are found for Pd_4O_2 . Markedly different CO stretch frequencies indicate a possible discrimination of bare clusters and oxides by Fourier transform infrared spectroscopy.

PACS. 68.43.Fg Adsorbate structure (binding sites, geometry) – 68.47.Jn Clusters on oxide surfaces – 73.22.-f Electronic structure of nanoscale materials: clusters, nanoparticles, nanotubes, and nanocrystals

1 Introduction

Oxide-supported transition metal clusters and nanoparticles deserve special attention due to their important role as components of model-catalysts [2–7], sensors [8], solar-cells [9] and magnetic recording devices [10]. Especially, Pd clusters are known to catalyze many important chemical reactions e.g. the oxidation of CO [11] or cyclotrimerization processes in organic chemistry [12]. Interestingly, no lower size limit for this reactivity can be detected. Model-catalytic experiments and ab initio simulations indicated that even a single Pd atom adsorbed at a surface colour center (FC) of the magnesia support can be catalytically active for CO oxidation [13]. In contrast to bulk Pd surfaces, a low-temperature oxidation of CO molecules on small magnesia-supported palladium clusters has been observed [11].

Recently, reaction barriers of only 0.5 eV were detected in our density functional theory (DFT) study of MgO-supported Pd clusters interacting with molecular oxygen [1] suggesting a low-temperature reaction pathway from the O_2 dimer to the dissociated oxygen in the oxide. Figure 1 illustrates this process for the palladium tetramer. Oxygen from the gas phase adsorbs on one of three inequivalent Pd-Pd bridges with adsorption energies

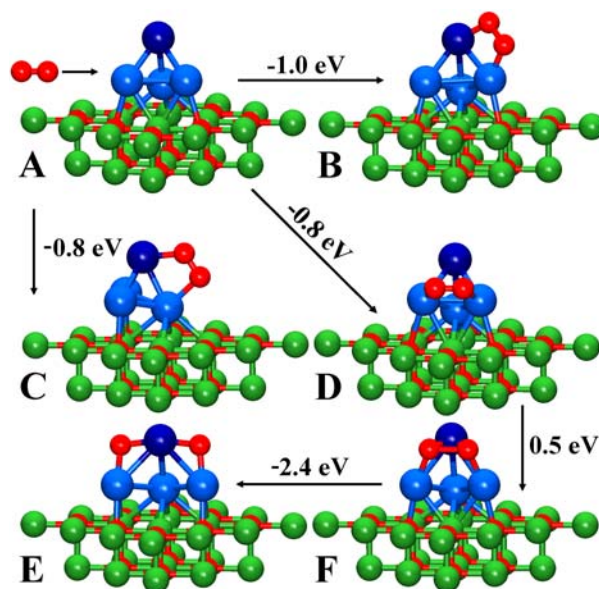


Fig. 1. (Colour online) The oxidation of magnesia-supported Pd_4 . (A) structure of the bare supported Pd_4 ; (B–D) Pd_4 with molecular adsorbed O_2 ; (E) ground state of $\text{Pd}_4\text{O}_2/\text{MgO}(\text{FC})$ with dissociated O_2 ; (F) transition state between D and E. Oxygen atoms are represented by red, Mg by green, Pd atoms in contact with the substrate by light-blue and Pd in the second adlayer by dark-blue spheres. Arrows and numbers indicate transitions and energy differences between states.

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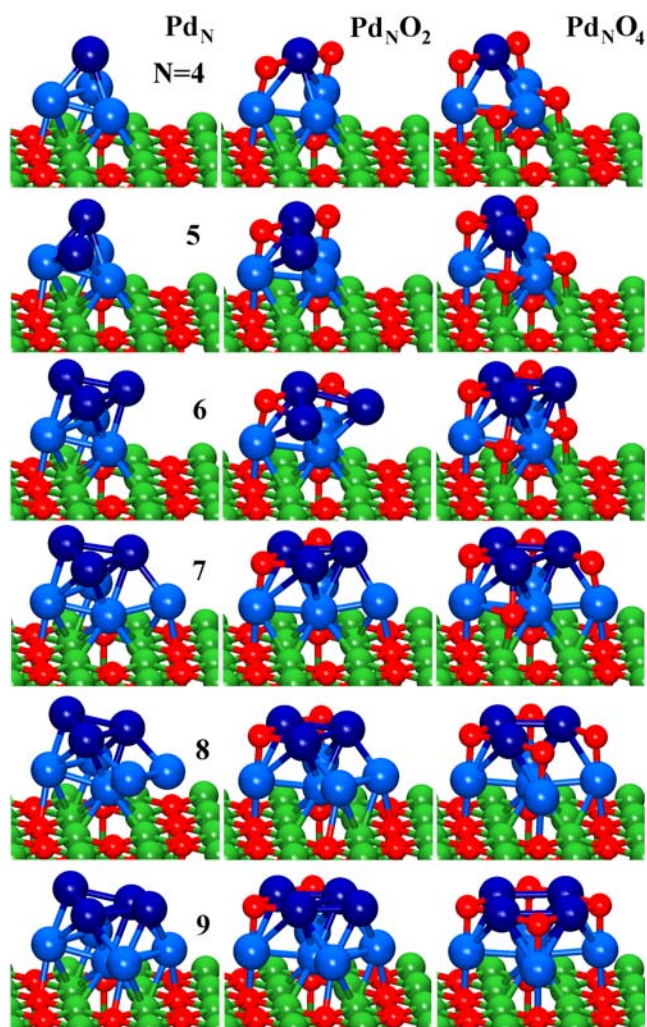


Fig. 2. (Colour online) Structural growth motif of bare and oxidized palladium clusters on MgO(FC).

ranging between 0.8 and 1.0 eV (configurations B–D in Fig. 1). However, Pd₄ with dissociated oxygen (structure E in Fig. 1) has a much higher adsorption energy of 2.7 eV. The dissociation barrier from D to E is only 0.5 eV which is considerably lower than the corresponding 1.0 eV barrier for O₂ dissociation on a Pd(111) surface [14]. The dissociation of O₂ is accompanied by a strong relaxation of the Pd cluster. Pd atoms of the first adlayer are dragged towards surface oxygen top positions creating a registry of Pd₄O₂ with the underlying support. This strong relaxation is responsible for the rather low dissociation barrier of 0.5 eV [1] as suggested by a comparison with the considerably higher barriers in the corresponding gasphase reaction [15].

Calculations for larger Pd_{*n*} clusters (*n* = 5–9) revealed essentially the same results. For *m* = 2, 4, a systematic growth pattern of Pd_{*n*}O_{*m*}/MgO(FC) could be observed (Fig. 2). The first pair of oxygen atoms was always inserted in the second adlayer epitaxially on the oxygen sites of the MgO substrate with an adsorption energy E_{ad} ranging between 2.7 and 3.4 eV. On the other hand, E_{ad} of the

optimum positions of a second pair of O atoms showed a pronounced size dependence. For *n* = 4–6, it occupied ideal MgO sites in the first adlayer with strongly reduced E_{ad} and for *n* = 8, 9 the second adlayer was populated with an E_{ad} similar to the first pair of oxygen atoms. Interestingly, the Pd₉O₄ cluster was found to be in perfect epitaxy with the MgO substrate. Note, that the four oxygen atoms of the second adlayer can serve as Mars-van Krevelen oxygen reservoirs [16] for the oxidation of CO [1].

These findings are in agreement with earlier pioneering experiments that detected the low-temperature formation of CO₂ on the Pd clusters [4]. Although the simulations in [1] provided deep insights into the reaction mechanisms, only scanning probe experiments were suggested for a possible experimental verification of the Pd_{*x*}O_{*y*} formation. The purpose of the present article is the investigation of additional experimental methods for a corroboration of our earlier results. We present DFT calculations of the electronic density of states of supported Pd_{*x*}O_{*y*} clusters as well as typical CO stretch frequencies and contrast these quantities with corresponding values of the bare clusters. Our calculations predict significant changes in the spectra of surface sensitive spectroscopic methods; for instance metastable impact electron spectroscopy (MIES) [17] or Fourier transform infrared spectroscopy (FTIR) [18]. Consequently, it should be feasible to detect the above mentioned oxidation of the clusters also spectroscopically.

2 Theoretical methods

The calculations were performed using the Born-Oppenheimer local-spin-density molecular dynamics (BO-LSD-MD) method [19] including self-consistent generalized gradient corrections (GGA) [20] with nonlocal normconserving pseudopotentials [21]. The Kohn-Sham orbitals were expanded in a plane-wave basis set, where convergence of the electronic wave functions was achieved by using a energy cutoff of 85 Ry. The BO-LSD-MD method deals with an effectively non-periodic computational cell where the periodic images of the Hartree potential are removed by means of a convolution method [19].

The MgO surface with the F-center is modelled by a two-layer ab initio cluster Mg₁₃O₁₂ [22], embedded in a point-charge lattice to model the long-range Madelung potential [13, 23]. We used 2087 alternating charges of +2 and –2 of Mg and O ions, respectively. In addition, those positive point charges that would be nearest neighbours to the periphery O atoms of the Mg₁₃O₁₂ cluster have been replaced by ‘empty’ Mg pseudopotentials to prevent unphysical polarization of O ions. The lattice parameter of the embedding part is fixed to the experimental lattice constant (4.21 Å) of bulk MgO. For each cluster system Pd_{*n*}/MgO(FC) the Mg and O ions of the substrate are kept fixed to the ideal bulk positions. The Pd clusters and reactant molecules are fully dynamical during steepest-descent-like optimizations. For each structure, spin-restricted optimizations were performed covering all energetically important spin multiplicities.

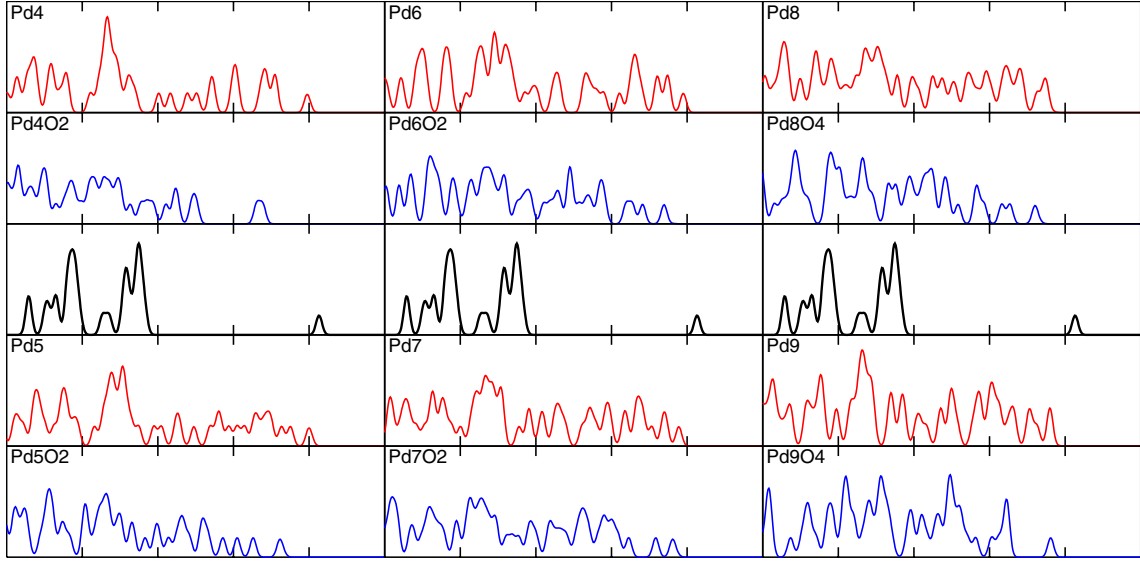


Fig. 3. (Colour online) DOS for the bare Pd_n (red line) and the oxidized Pd_nO_m (blue line) supported on $\text{MgO}(\text{FC})$. In the middle row the DOS of the pure $\text{MgO}(\text{FC})$ substrate is shown.

In our earlier spin-polarized calculations of gasphase sodium clusters spin splittings of the Kohn-Sham energies could be observed which were not present in the experimental photoelectron spectra [24]. Since the corresponding spin-unpolarized calculations were in much better agreement with the spectra of the sodium cluster, we also present in this work the spin-unpolarized electronic density of states of the palladium clusters in the geometry of the spin-polarized energetic optimum.

3 Results

In Figure 3 the DOS of supported Pd_n clusters (red lines) and oxidized Pd_nO_m clusters (blue lines) are shown. In addition, the DOS of the pure magnesia surface with an F-center is depicted in the middle row (black lines). Following the observation of reference [1] that the adsorption energy of the second O_2 dimer is significantly lower than the first one for $n < 8$, we present in Figure 3 the DOS of Pd_nO_2 for $n \leq 7$ and the DOS of Pd_nO_4 for $n \geq 8$. For each cluster the DOS was shifted to align the binding energy of the highest occupied molecular orbital (HOMO) with the calculated ionisation potential.

Both the bare and the oxidized Pd clusters have in common that they close the 2 eV gap between the HOMO and HOMO-1 of the $\text{MgO}(\text{FC})$ substrate. On the other hand, the detailed structure of the DOS shows considerable differences for the bare and oxidized Pd_x . The largest deviation occurs for Pd_4O_2 and Pd_9O_4 . For these two nano-oxides the DOS exhibits large gaps which are not present in the DOS of the corresponding bare clusters. However, also for the other sizes a measurement of the DOS (e.g. by MIES experiments) should allow a validation of the oxide formation. Particularly, the different values for the ionisation potential (IP) can be used to distinguish the oxidized from the bare state (see Tab. 1 showing

Table 1. Ionisation potential IP and its difference ΔIP for Pd_n and Pd_nO_m .

	$IP \text{ Pd}_n$ (eV)	$IP \text{ Pd}_n\text{O}_m$ (eV)	ΔIP (eV)
$n = 4, m = 2$	5.03	5.60	0.57
$n = 5, m = 2$	5.01	5.39	0.38
$n = 6, m = 2$	5.06	5.31	0.25
$n = 7, m = 2$	5.11	5.19	0.08
$n = 8, m = 4$	5.24	5.40	0.16
$n = 9, m = 4$	5.20	5.20	0.00

Table 2. Ionisation potential IP for different adsorption sites on Pd_4O_2 .

Structure of Figure 1	IP (eV)
A	5.03
B	5.24
C	5.40
D	5.32
E	5.60

the IP for both situations). Especially, for the smaller clusters a significant difference of the ionisation potential can be observed. For Pd_4 , Pd_5 and Pd_6 the IP of the nano-oxide exceeds the IP of the bare Pd_x by 0.57, 0.38 and 0.25 eV, respectively. Unfortunately, the difference in the IP s reduces for the following sizes and vanishes completely for the nonamer (Tab. 1). Consequently, the existence of Pd_9O_4 can only be corroborated by observing the 0.5 eV gap below the HOMO in the DOS.

In summary, the gap structure of the DOS and the ionisation potential allows to distinguish between the bare Pd_x clusters and the oxidized ones. However, in order to verify the formation of Pd_xO_y nano-oxides on $\text{MgO}(\text{FC})$ spectroscopically one has also to ensure that the DOS of the Pd_x system with molecular adsorbed O_2 differs from the oxidized one. Therefore, we studied the DOS for

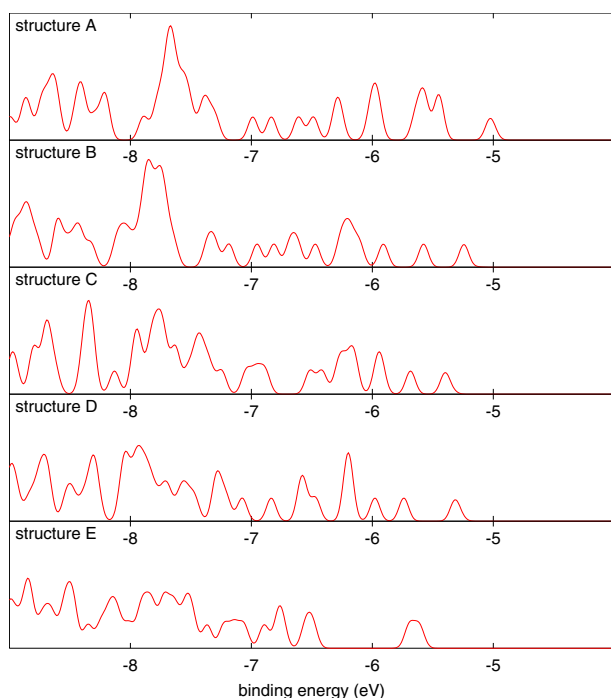


Fig. 4. DOS for the bare Pd₄ (A) and the different molecular (B, C and D) and dissociative (E) adsorption sites of Pd₄O₂ from Figure 1.

Pd₄O₂ with molecular oxygen on different possible adsorption sites. Figure 4 compares the DOS for the bare cluster (Fig. 1A), the different molecular adsorption sites (Figs. 1B–1D) and the nano-oxide state (Fig. 1E). The Pd₄O₂ with molecular oxygen at the sites B, C and D displays an ionisation potential which is 0.2–0.4 eV higher than the *IP* of the bare cluster and 0.2–0.4 eV lower than that of the structure E with the dissociated O₂ (see Tab. 2). Furthermore, a clear difference in the shape of the DOS between molecular and dissociative adsorption can be found. While the cluster with dissociated oxygen shows a large gap of 0.8 eV between the second and third highest Kohn-Sham orbital all O₂-decorated clusters have a more uniformly distributed DOS (rather resembling the DOS of the bare cluster).

Experimentally, the oxidation could therefore be detected in the following way. After measuring the *IP* of the bare clusters, the O₂ is added at low temperatures. This should result in an measurable increase of the *IP* (from the bare Pd₄ value to that of the O₂-decorated system). An additional rise in *IP* after a heating to room temperature will finally indicate the formation of the oxide.

In order to provide the experimentalists with an alternative method to detect the formation of Pd-nano-oxides, the adsorption sites of CO molecules on the bare Pd₄ and the oxidized Pd₄O₂ were determined (see Fig. 5). On the bare Pd tetramer the CO adsorbs preferentially on hollow positions with adsorption energies of 2.3 eV and 1.7 eV. Carbon monoxide on bridge positions is weaker bound ($E_{ad} = 1.8$ eV and 1.2 eV) while the most unfavourable adsorption sites are on top of Pd atoms ($E_{ad} = 1.1$ eV).

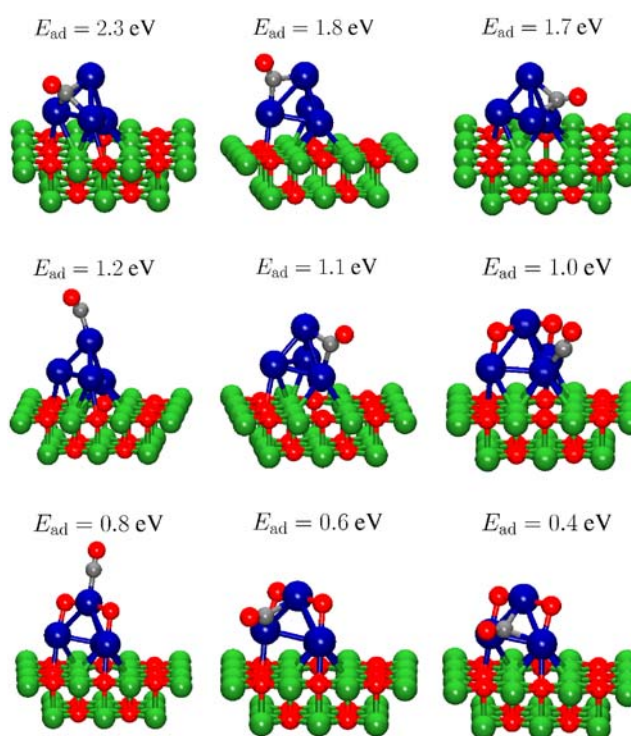


Fig. 5. (Colour online) Stable CO adsorption sites on bare and oxidized Pd₄ with corresponding adsorption energy.

Table 3. CO stretch frequencies ω_e for different adsorption sites on bare and oxidized Pd₄.

Cluster	Binding type	ω_e (cm ⁻¹)	E_{ad} (eV)
Pd ₄	hollow	1758	2.3
Pd ₄	bridge	1867	1.8
Pd ₄	top	2011	1.2
Pd ₄ O ₂	top	2001	1.0
Pd ₄ O ₂	top	2050	0.8

Note, that the same cluster with molecularly adsorbed oxygen exhibits essentially a similar energetic ordering of the CO adsorption sites. On the other hand, the ordering changes completely if the cluster is oxidized. In this case, the Pd top positions become the preferred adsorption sites with adsorption energies ranging between 0.8 and 1.0 eV while CO adsorbs on the best bridge site with $E_{ad} = 0.6$ eV and on the best hollow position with $E_{ad} = 0.4$ eV.

The different preferred adsorption sites on the bare and oxidized cluster can be used to verify the oxidation of the Pd cluster since different coordinated sites possess a significant different CO stretch frequency. Table 3 displays the calculated CO stretch frequencies for the adsorptions sites in Figure 5. For both types of clusters the CO stretch frequency for single coordinated top positions range between 2000–2050 cm⁻¹. This is in marked contrast to the threefold coordinated positions. For instance, we calculated a stretch frequency of only 1758 cm⁻¹ for CO on the most favourable hollow site of the bare Pd₄ cluster. Twofold coordinated positions (Pd-Pd bridges) possess intermediate CO stretch frequencies (e.g. 1867 cm⁻¹ for the

configuration on the bare Pd₄ in Fig. 5). These results suggest that the oxidation of Pd clusters could also be detected experimentally with Fourier transform infrared spectroscopy.

4 Summary

We showed that the oxidation of Pd clusters on a MgO substrate results in a substantial change of the electronic density of states. In combination with spectroscopic experiments this effect should allow for a verification of the formation of Pd_xO_y nano-oxides. An increase of the ionisation potential or the opening of a gap between the HOMO and HOMO-1 states are likely fingerprints of the occurrence of the nano-oxides. We also presented an alternative detection route using Fourier transform infrared spectroscopy. Here, the CO stretch frequencies should increase upon dissociation of the O₂.

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References

1. B. Huber, P. Koskinen, H. Häkkinen, M. Moseler, *Nature Materials* **5**, 44 (2006)
2. R.M. Lambert, G. Pacchioni, in *Chemisorption and Reactivity on Supported Clusters and Thin Films* (Kluwer, Dordrecht, 1997), pp. 395–424
3. H. Grönbeck, *Top. Catalys.* **28**, 59 (2004)
4. U. Heiz, W.D. Schneider, in *Metal Clusters at Surfaces* (Springer, Berlin, 2000), pp. 237–273
5. C. Becker, C.R. Henry, *Surf. Sci.* **352**, 457 (1996)
6. H.J. Freund, *Adv. Catal.* **45**, 333 (2000)
7. S.H. Shaikhutdinov et al., *Surf. Sci.* **501**, 270 (2002)
8. J. Mizei, J. Voutilainen, S. Saukko, V. Lantto, *Thin Solid Films* **391**, 209 (2001)
9. M. Westphalen, U. Kreibig, J. Rostalski, H. Luth, D. Meissner, *Sol. Ener. Mater. Sol. Cells.* **61**, 97 (2000)
10. S. Fukami, A. Ohno, A. Tanaka, *Mater. Trans.* **45**, 2012 (2004)
11. U. Heiz, A. Sanchez, S. Abbet, W.D. Schneider, *Chem. Phys.* **262**, 189 (2000)
12. S. Abbet, A. Sanchez, U. Heiz, W.D. Schneider, A.M. Ferrari, G. Pacchioni, N. Rösch, *J. Am. Chem. Soc.* **122**, 3453 (2000)
13. S. Abbet, U. Heiz, H. Häkkinen, U. Landman, *Phys. Rev. Lett.* **86**, 5950 (2001)
14. A. Eichler, F. Mittendorfer, J. Hafner, *Phys. Rev. B* **62**, 4744 (2000)
15. B. Huber, H. Häkkinen, U. Landman, M. Moseler, *Comp. Mat. Sci.* **35**, 371 (2006)
16. P. Mars, D.W. van Krevelen, *Chem. Eng. Sci.* **3**, 41 (1954)
17. L.N. Kantorovich, A.L. Shluger, P.V. Sushko, J. Günster, P. Stracke, D.W. Goodman, V. Kempter, *Faraday Discuss.* **114**, 173 (1999)
18. A.S. Wörz, K. Judai, S. Abbet, U. Heiz, *J. Am. Chem. Soc.* **125**, 7964 (2003)
19. R.N. Barnett, U. Landman, *Phys. Rev. B* **48**, 2081 (1993)
20. J.P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996)
21. N. Troullier, J.L. Martins, *Phys. Rev. B* **43**, 1993 (1991)
22. The error caused by the finiteness of the Mg₁₃O₁₂ cluster was estimated by calculating the structure and binding energy of a Pd atom on the relevant O top positions of a defect-free Mg₁₃O₁₃ and Mg₂₅O₂₅ cluster. Neither the distance of the adsorption site from the centre nor the size of the substrate had a remarkable influence on the binding position of the Pd atom. Furthermore, the variation of binding energies was less than 5% indicating that finite size errors can be safely neglected
23. S. Abbet, E. Riedo, H. Brune, U. Heiz, A.M. Ferrari, L. Giordano, G. Pacchioni, *J. Am. Chem. Soc.* **123**, 6172 (2001)
24. M. Moseler, B. Huber, H. Häkkinen, U. Landman, G. Wrigge, M.A. Hoffmann, B. von Issendorff, *Phys. Rev. B* **68**, 165413 (2003)