Adsorption of isolated Cu, Ni and Pd atoms on various sites of MgO(001): Density functional studies (*)

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Summary. — Results of gradient-corrected density functional calculations are presented for the adsorption of single Cu, Ni and Pd atoms on a regular MgO(001) surface. The surface has been represented by stoichiometric clusters embedded in large arrays of point charges to simulate the Madelung potential. Three adsorption sites have been compared: on-top adsorption on the oxide anion and on the magnesium cation as well as bridge adsorption over two adjacent oxide anions. The weakly adsorbed Cu atom is slightly more stabilized atop magnesium cations than in the alternative positions; however, the energy differences are small and an easy diffusion of Cu on the surface is predicted. For the significantly stronger adsorbed Ni and Pd atoms the calculations yield a clear preference to occupy the place atop oxygen anions. This finding does not support previous experimental assignments that atoms of small palladium clusters deposited on MgO(001) occupy positions on top of Mg cations.

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1. – Introduction

Adsorption of isolated metal atoms on a surface represents the initial step of forming a supported metallic film. On oxide substrates this interaction preferentially takes place with defect sites than with regular sites on terraces [1]. Nevertheless, knowledge on interactions of individual metal atoms with a regular substrate is important for understanding the microscopic mechanism of nucleation and growth of deposited metal particles and films.

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Recently, a high-level density functional (DF) study has been carried out to analyze the bonding of nine transition-metal atomic species adsorbed on top of oxide anions of a regular MgO(001) surface [2]. It has been shown that some of the adsorbates investigated, Cu, Ag, Au, Cr and Mo, exhibit weak or very weak bonding of the order of one-third of an eV. The interaction is due to polarization and dispersion, little mixing occurs with substrate orbitals. On the other hand, another group of the adsorbed atoms, Ni, Pd, Pt and W, forms rather strong bonds of about one eV with the oxide anions; this bond has a covalent polar nature. The adsorption site on top of oxide anions has been suggested as the most probable one based on the results of other DF calculations [3-5]. For Cu and Ni atoms, adsorption in other conceivable position, bridge place over two adjacent oxide anions, was also considered and found energetically less favorable than that on top of oxygen [2]. Theoretical studies on metal deposition at oxide surfaces have been the subject of two recent reviews [6, 7].

The goal of the present gradient-corrected DF calculations is to compare various adsorption sites of isolated Cu, Ni and Pd atoms on a regular MgO(001) surface and to discriminate between the positions on top of O anions, on top of Mg cations and the bridge place over two adjacent O anions. Cu represents atoms weakly interacting with MgO, while Ni and Pd exemplify the group of stronger adsorbed atoms. Experimental findings for Pd clusters deposited on MgO(001) are in line with preferential adsorption of Pd atoms on top of Mg^{2+} rather than on top of O^{2-} ions. This apparent discrepancy to our previous computational results [2] provided additional important motivation for this communication.

2. – Method and computational details

All-electron calculations have been carried out using the linear combination of Gaussian-type orbital DF (LCGTO-DF) code [9, 10]. The local density exchange-correlation potential [11] was employed to self-consistently determine the electron density which then was used to evaluate the total energy by applying the gradient-corrected BLYP functional [12, 13]. Scalar-relativistic calculations [14, 15] were performed for Pd adsorption complexes.

The MgO(001) surface was modeled by three two-layer molecular clusters (fig. 1). The clusters O_9Mg_9 (fig. 1A) and Mg_9O_9 (fig. 1C) belonging to the C_{4v} point group were

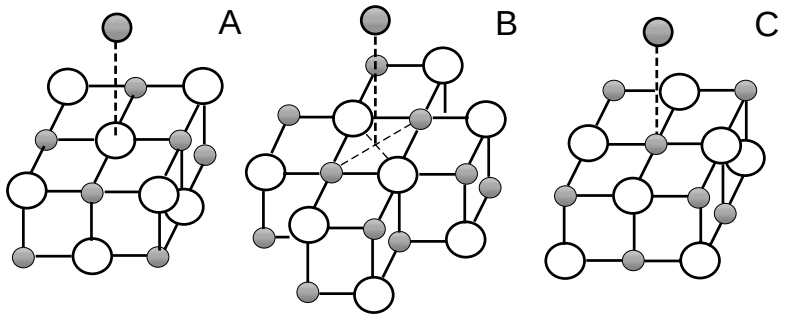

Fig. 1. – Cluster models of isolated metal atoms M adsorbed in two on top and one bridge sites of MgO(001) surface: A) M-O_9Mg_9, B) M-$Mg_{12}O_{12}$, C) M-Mg_9O_9. Empty and small shaded circles represent O and Mg ions, respectively; M atoms are identified by large shaded circles.

used to represent on top adsorption of metal atoms on the central O (site A) or Mg (site C) ions, respectively. The cluster $Mg_{12}O_{12}$ (fig. 1B, C_{2v}) was employed for modeling adsorption at the bridge position (site B). The clusters were embedded into arrays of point charges (± 2.0 au) with the dimensions $17 \times 17 \times 6$ and $16 \times 16 \times 6$ for the C_{4v} and C_{2v} clusters, respectively.

Several energy points at different heights from the surface were calculated. The resulting BLYP potential curve, not corrected for the basis set superposition error (BSSE), was fitted by a polynomial to calculate the equilibrium height as well as the corresponding force constant and vibrational frequency. The final adsorption energy has been corrected by the BSSE.

Further computational details, including a description of the basis sets employed, can be found elsewhere [2].

3. – Results and discussion

In case of weak adsorption one expects rather small energy differences for various adsorption places. Results for Cu on MgO (table I) agree with this assumption. The calculated binding energies for complexes A and C differ by only 0.06 eV, slightly favoring the interaction with Mg cations. However, one should keep in mind the model character of this study and possible inaccuracies due to the relatively large BSSE; thus, the calculated energy difference does not rule out the structure with Cu on top of O anions. The sizeable change of the adsorbate-substrate distance is not surprising as the potential curves are very flat. Almost equal small values of the dynamic dipole moment manifest that the bonding in all three complexes is similar without a substantial charge transfer from Cu to MgO, as has already been pointed out [2, 3].

TABLE I. – *Calculated adsorption properties of* Cu, Ni *and* Pd *atoms on* MgO(001).

System	Cu/MgO ([a])			Ni/MgO ([b])			Pd/MgO ([c])		
Adsorption site	A	B	C	A	B	C	A	B	C
h(MgO-M) ([d]) (Å)	2.18	2.42	2.76	1.87 (2.22)	1.97	2.50 (2.72)	2.15	2.19	2.52
ω_e(MgO-M) ([e]) (cm^{-1})	98	76	81	249 (107)	136	124 (82)	134	109	108
f(MgO-M) ([f]) (mdyn/Å)	0.36	0.22	0.24	2.12 (0.39)	0.61	0.52 (0.23)	1.14	0.75	0.73
D_e(BSSE) ([g]) (eV)	0.30	0.21	0.36	0.88 (0.41)	0.02	−0.14 (0.54)	0.81	0.58	0.59
$(d\mu/dh)$ ([h]) (au)	0.24	0.22	0.22	0.48 (0.16)	0.23	0.49 (0.23)	0.09	0.23	0.28

([a]) State $^2A_1$.
([b]) States $^1A_1$ and $^3B_2$ (in parentheses); for structure B the fractional occupation number technique [9] has been employed.
([c]) State $^1A_1$.
([d]) Height of the atom M above the surface plane.
([e]) Frequency of the MgO-M stretching mode.
([f]) Force constant of the MgO-M stretching mode.
([g]) BSSE corrected adsorption energy.
([h]) Dynamic dipole moment of the MgO-M motion at equilibrium geometry.

The stronger adsorption of Ni atoms on MgO(001) surface has also been analyzed in our previous study [2]. For the present discussion it is important that Ni clearly prefers the position on top of O compared to that on top of Mg for the $^1A_1$ state (MgO + Ni d^{10}), exhibiting a deeper energy minimum of 0.88 eV (table I). The interaction of Ni atop Mg (site C, $^1A_1$) leads to a structure which is unbound compared to the separated fragments. Interestingly, for the first excited state $^3B_2$ which correlates with MgO + Ni d^9s^1, no such preference to adsorb on top of O has been computed. On the contrary, we found a bound system, by 0.54 eV, when adsorption occurs on Mg ($^3B_2$). This site is 0.13 eV more stable than adsorption on top of oxygen, see table I. Therefore, the energy difference between the more stable O adsorption site ($^1A_1$ state) and the Mg one ($^3B_2$ state) is of about 0.3 eV. For the bridge position, we found almost no binding, table I. This is in part due to the fact that the covalent polar bond between Ni and the oxide anion is broken , but is also due to the crossing of the $^1A_1$ and $^3B_2$ states as the atom goes from site A to site C.

Let us now turn to Pd adsorption on MgO(001) which is the most interesting case because it has been studied in detail experimentally [8, 16] (and references therein).

All data presented so far have been calculated assuming that cluster effects on properties of adsorption complexes can be neglected, at least, as far as trends are concerned. It is known, however, that computed parameters of adsorption complexes on MgO may be affected by the cluster size [17], in particular when the strategy of embedding in point charges is employed [18]. Special care has been taken to render cluster effect for three types of complexes under consideration as similar as possible. Even for the A and C sites described by the substrate clusters of the same stoichiometry, O_9Mg_9 and Mg_9O_9, respectively, cluster effects are slightly different because of the surrounding point changes. An oxide cluster model with only two layers of point charges reduces these differences, yet is suitable to mimic adsorption both on top of O and on top of Mg. For Pd/MgO(001), the results of this model differ only insignificantly from those displayed in table I. For instance, the adsorption energy increases for site A from 0.81 to 0.89 eV and decreases for site C from 0.59 to 0.56 eV. Thus, the energy variation for these two sites is slightly larger compared to the other cluster models used, 0.22 *vs.* 0.33 eV, when some of the cluster artifacts (*i.e.* differing references) are removed. This latter finding corroborates the model cluster results of table I.

The calculated results for Pd/MgO (see table I and fig. 2) show similarities with

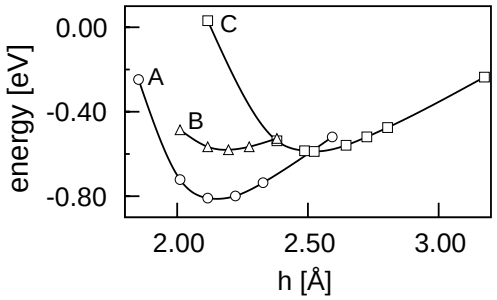

Fig. 2. – Ground state ($^1A_1$) potential energy curves for Pd atoms adsorbed in three different positions of MgO surface: A) Pd-O_9Mg_9, B) Pd-$Mg_{12}O_{12}$, C) Pd-Mg_9O_9 (see fig. 1). The curves were shifted vertically to adjust the adsorption energies for the BSSE correction at equilibrium.

those for Ni/MgO (table I). The values of the binding energies for Ni and Pd differ by less than 0.1 eV for both adsorption on O and Mg and are large compared to Cu/MgO. The preference of Pd to occupy a position on top of O is noticeable, about 0.2 eV, and similar to Ni, 0.3 eV, table I. Taking into account the above discussion of cluster effects, the energy difference of 0.2–0.3 eV between the sites A and C seems reliable. Also, the shorter Pd-MgO distance and the corresponding higher vibrational frequency computed for the complex A than for C are in line with the conclusion that adsorption of Pd on top of O anions is advantageous. For Pd the adsorption energy on the bridge site B, 0.58 eV, is much larger than for Ni, see table I. We believe that this is related to the fact that for Pd the electronic state does not change as the atom moves from O to Mg, at variance with the Ni case.

The bonding of Ni and Pd atoms on top of oxide anions of MgO has been analyzed in detail in ref. [2], and it was shown to be due to the formation of a covalent polar bond between the metal and oxygen. Cu, on the other hand, is bound mainly through polarization forces. The relatively strong bond of Ni and Pd with the surface Mg^{2+} ions, about 0.5 eV, comes in part from the polarization of the atoms, but also from some mixing of the metal orbitals with the 2*p* levels of the neighboring surface oxide anions. We intend to perform a decomposition of the interaction energy in order to evaluate the relative importance of these two contributions.

Of course, all these results refer to single metal atoms and changes in the preferred adsorption site may occur as clusters or thin films are deposited on the surface.

The calculated adsorption energy of 0.81 eV can be compared to the value of 0.48 eV per Pd atom, estimated experimentally for the deposition of palladium clusters on MgO(001) [16], although higher values, 0.7–1.0 eV have also been suggested [19]. The experimental conclusion that palladium clusters are accommodated on the MgO(001) surface with *the Pd atoms on top of the Mg cations* is not in line with our results as well as with other theoretical studies of metal deposition [3-5]. The experiments on deposited clusters [16] do not exactly correspond to the process of adsorption of isolated Pd atoms considered here and the experimentally preferred site may very well be influenced by interactions involving surface defects.

DF calculations of palladium clusters on a MgO(001) surface are under way to clarify the preferential adsorption site during the initial phase of the nucleation process.

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