Deposition of small Cu, Ag and Au particles on reduced SiO₂


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Abstract

In this work, the adsorption of Mn (M: Cu, Ag, Au; n = 1–3) particles on the ≡Si–O· defect of a SiO₂ surface is studied in the framework of density functional theory. A charge transfer from the metal particle to the support is observed following the sequence: Cu ≡ Ag ≡ Au. This is in agreement with the greater ionization potential of the latter metal. The Mn–OśSi and Mn–OŚi≡ interactions of nucleation and adhesion processes, respectively, were analyzed from an energetic point of view. The strongest interaction is obtained always between two open-shell systems. When the comparison is performed among the metals, the bond strength of the M–M interaction follows the order: Cu ≡ Au ≡ Ag. The deep position of Ag d-levels in the energy scale could explain the relatively weak Ag–Ag interaction. If the M–oxide interaction is considered, this order in the bond strength was observed: Cu ≡ Ag ≡ Au. The strong adhesion for Cu could be ascribed to the greater charge transfer to the support and to a strong Cu(d)–O(p) interaction. On the other hand, for Ag the charge transfer to the support is relatively small, while for Au the Ag(d)–O(p) interaction is relatively weak due to the more localized Ag(d) band.

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Keywords: Cu/SiO₂; Ag/SiO₂; Au/SiO₂; Metal small particles; Metal–support interaction; Density functional theory

1. Introduction

The study of the metal/oxide interface represents a field of wide interest in different industrial areas such as catalysis, gas sensors, electrochemistry and microelectronics. In particular, in heterogeneous catalysis the oxide acts as a support where the metal particles grow. The reactivity of the metal aggregates strongly depends on the cluster size, which in turn depends on the nature of point or extended defects where the particle anchors. Thus, the role of the support material is more important than initially thought.

Cu, Ag and Au-based catalysts have been studied for a wide variety of reactions. For instance, supported Cu catalysts are used for methanol synthesis, oxidation of hydrocarbons and hydrogenation reactions [1–4]. The activity of catalysts based on Ag has been examined for the catalytic reduction of NOx [5,6]. Dispersed ultrafine Au particles on oxides exhibit an extraordinarily high activity for low-temperature catalytic combustion, partial oxidation of hydrocarbons and hydrogenation of unsaturated hydrocarbons [7]. On the other hand, Cu, Ag and Au were used as promoters on the activity and selectivity of Pt and Pd-based catalysts [8,9].

Quantum-chemical studies of the deposition of small metal particles on oxide surfaces are important to get an accurate description of the initial stages of interface formation. For instance, Lopez et al. analyzed the Cu deposition on silica using the DFT formalism [10,11]. They found that the regular sites of the silica surface are unreactive toward metal particles. In contrast, defect sites like the nonbridging oxygen, ≡Si–O·, and the Si dangling bond, ≡Si· (the ≡ symbol indicates the three Si–O bonds), are very reactive and they are probably centers where the nucleation takes place [12,13]. These centers were detected on the surface of dehydroxylated or mechanically activated silica [14]. In a previous work, it was shown that ≡Si–O· sites react more strongly with Cu atoms than the terminal ≡Si· defects [15]. Concerning the chemical reactivity of these Cu particles, it was observed that the support may strongly alter the bonding between the metal and adsorbates such as NCO, H₂ and CO [15–18].

Recently, the deposition of Cu, Ag and Au atoms on different oxides was studied from a theoretical point of view using both cluster and periodic slabs models. For Cu and Ag adsorption on rutile TiO₂(110) surface, Giordano et al. have observed an electron charge transfer from the metal atom to the surface, yielding the formation of Cu⁺ and Ag⁺ ions and a
consequent strong interaction with the bridging oxygens [19]. In the case of Au atoms, the interaction with the surface is weaker in concordance with a less important charge transfer. Here, the bonding was better described as covalent polar. The adsorption energies follow the order Cu > Ag > Au. On the other side, on α-Al2O3(0001) surface the metal atoms also interact preferentially on oxygen sites, following the order Cu > Au > Ag [20]. The metal–oxide interaction was interpreted in terms of two main factors: the charge transfer to the support and the metal polarization. While for Cu and Ag the largest contribution to the interaction energy arises from the charge transfer to the surface, for Au the bonding is dominated by polarization of the metal.

In this work, a comparative theoretical analysis of the Cu_n, Ag_n and Au_n (n = 1–3) particles deposition on reduced SiO_2 is performed in the framework of density functional theory (DFT). In our model, only the =Si–O– surface defect site was considered as a possible center where the metal particle grows. The goal is to attain a qualitative description of both the metal–metal and metal–oxide interactions.

2. Computational details

Calculations were carried out in a system consisting of a metal particle, M_n (with M = Cu, Ag, Au and n = 1–3), adsorbed on the =Si–O– surface defect of silica represented by a cluster model approach. In the past, it was established that the bond formed between Cu and defect sites of the silica surface is very local and even small clusters describe properly the nature of this chemical interaction [11].

Density Functional Theory (DFT) quantum-mechanical calculations were carried out using the gradient corrected Becke’s three parameters hybrid exchange functional in combination with the correlation functional of Lee, Yang and Parr (B3LYP) [21]. This method has been widely used to study adsorption processes yielding reliable results both on oxides and metal clusters. The 6-31G(d) basis set was applied on all the atoms belonging to the central tetrahedron, and the 6-31G basis set on those of the peripheral tetrahedrons. For Cu, Ag and Au the LANL2DZ basis set was used.

The SiO_2 surfaces were represented using SiO_4(OH)_9 clusters. The terminal oxygen atoms were saturated with hydrogen atoms. We started with the ideal β-cristobalite structure as initial geometry. The position of surface oxygen defect and the orientation of the peripheral tetrahedrons were fully relaxed (see Fig. 1). For the M_n/SiO_2 systems the metal aggregates were also fully optimized. Geometry optimizations have been performed by means of analytical gradients with no symmetry constraints.

In order to analyze the direct interaction between the metal particles and the surface oxygen defect, the adhesion energy was calculated. Furthermore, the strength of the metal–metal bonding was investigated by means of the nucleation energy. These energies are defined as follows: E_{adhs} = [E(M_n/SiO_2)−E(M_1)−E(SiO_2)], with n = 1, 2 or 3, and E_{nuc1} = [E(M_n/SiO_2)−E(M_1)−E(M_{n-1}/SiO_2)], with n = 2 or 3, and where M = Cu, Ag or Au. The adhesion energies for supported M_3 were calculated considering the isolated M_3 molecule at its triangular structure. Our calculations indicate that the quasi-linear and the triangular structures are very close in energy for the three metals (they differ at most by 0.15 eV).

The interaction energies were corrected by the basis set superposition error (BSSE) using the counter-poission correction [22]. The atomic charges were computed according to the NBO (Natural Bond Orbital) population analysis which is based on quantum perturbation theory [23]. The spin density (SD) is expressed in terms of the Mulliken population analysis [24]. This quantity has demonstrated its usefulness for the characterization of the bond at the interface of similar systems [19]. The calculations have been performed using the Gaussian 03 program package [25].

3. Results and discussion

3.1. Optimized structures and charge transfer

In Fig. 2, the optimized geometries of individual metal atoms interacting with the oxide surface are pictured. The metal atoms adsorb on the =Si–O– site forming a Si–O–M angle of nearly 115°. In all the cases, an electron charge transfer from the metal to the support occurs (see Table 1). The values are of 0.7e for Cu and Ag, and of 0.5e for Au in agreement with its poor capability to be oxidized. The charge taken by the support resides mainly on the O of the =Si–O group, changing from −0.6e in the defective bare surface to about −1.2e (for Cu and Ag) and −1.0e (for Au) when the metal atoms interact with it.

The optimized geometries of the deposited dimers are represented in Fig. 3. For Cu, an electrostatic interaction takes place between the terminal atom (Cu_b in Fig. 3) and a regular bridging O atom [10,15]. The interaction of Ag_2 with the support produces a different structure with both atoms directly linked with the surface O atom. In contrast, the Au dimer is the only case for which the interaction with the surface is accomplished by means of one metal atom. Similar results were recently found by Antonietti et al. for the adsorption of Au_2 on α-SiO_2 cluster models [26]. The amount of charge transferred to the support is similar to that obtained for the monomer (Table 2). However, the atomic charge distribution is
different for the three cases. For Cu, the atom directly linked to the support has a higher positive charge than the terminal one. In spite of that, the terminal atom (Cu₉₉) has enough positive charge to establish the above-mentioned electrostatic interaction with a regular O atom of the support. In case of Ag₂, the atomic net charges are similar for both silver atoms owing to its symmetric structure. For Au₂, while the positive charge of the atom directly attached to the support is as high as that obtained for Cu₂, the terminal one is hardly negatively charged.

To study the deposited M₃ particles, the optimization was started positioning the third atom over the optimal dimer structure. This possibility was the only explored, not excluding the existence of other minima on the potential energy surface. The resulting geometries are depicted in Fig. 4. In all the cases quasi-equilateral triangles are formed, which are bonded to the surface similarly than the corresponding dimers. In particular, for the Cu trimer the electrostatic bonding between one Cu atom and a regular O is also present. Interestingly, this bonding is absent when the geometrical structure of SiO₂ is settled to that of the ideal β-cristobalite [17]. The charge transfer from M₃ to the oxide shows similar trends than that of M₂ (Table 3). Although the trimer orientation for Cu and Ag are different, the charge distribution is similar for both metals.

As a measure of the ability of Mₙ particles to release electronic charge to the silica surface, the vertical ionization potentials (IP) for the isolated metal particles were evaluated and summarized in Table 4. Looking at the corresponding IP values, we observe that the charge transfer to the oxide follows the order Cu ≻ Ag ≻ Au, which is in line with the higher IP for the latter metal. Moreover, for the sake of comparison, the experimental values have also been reported in the same table [27–29]. It is noteworthy the very good agreement between both series of data.

### 3.2. Study of the metal–metal interaction: nucleation energies

The metal–metal interaction was analyzed by means of the nucleation energy concept defined above, i.e. the energy associated with the dimer formation when an isolated metal atom interacts with a preadsorbed atom, and with the trimer formation when an isolated metal atom interacts with a preadsorbed M₂ particle. The values are listed in Tables 2 and 3 and shown as a diagram in Fig. 5. Such a study is relevant to understand the initial stages of a metal particle formation.

Looking at Fig. 5, we observe that the interaction of two open-shell systems is a more favorable situation than the interaction of one open-shell system with a closed-shell one. The former case corresponds to M₃–O–Si≡ and to free M₂. Here, a direct coupling with two unpaired electrons is produced (M₁⁺ + M₂–O–Si≡ and M₁⁺ + M₁⁺, respectively). Conversely, the latter case corresponds to M₂–O–Si≡ and to free M₃. A closed-shell system has to ‘open’ its configuration in order to form a bond [10]. This seems to be the phenomenon which rules the interaction of fragments if the comparison is based on the type of interacting system, independently of the metal component.

Thus, the noticeable differences between the $E_{\text{nuc}}$ values for particles at gas phase and for supported ones in the case of M₁–M₂ and M₂–M₁ interactions are mainly due to the fact that the support ‘changes’ the electronic structure of one of the interacting fragments, from a closed-shell at gas phase to an open-shell when the cluster is supported, or vice versa.

Recently, Wang et al. have studied the electronic structures of isolated Cu₂, Ag₂, and Au₂ using the DFT theory [30]. For Cu₂ and Au₂, they found that the energy gaps between d- and s-type molecular orbitals are small and close, which accounts for their similar spectroscopic properties. Conversely, for Ag₂ a small contribution of d electrons to the frontier molecular orbitals was observed owing to the large separation between s- and d-type molecular orbitals. Our results for these molecules follow the same trend (see Fig. 6). In particular, the calculated dissociation energy values follow the order Cu ≻ Au > Ag (in magnitude), in line with the experimental results [27] (Table 2). This behaviour could be ascribed to the relatively stronger interaction between d orbitals of Cu and Au, and a relatively weaker interaction between the more localized d orbitals of Ag.

### Table 1

<table>
<thead>
<tr>
<th>Mₙ/SiO₂</th>
<th>Cu/SiO₂</th>
<th>Ag/SiO₂</th>
<th>Au/SiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{\text{ad}}$ (eV)</td>
<td>−2.92</td>
<td>−2.13</td>
<td>−1.90</td>
</tr>
<tr>
<td>$Q(M)$ (a.u.)</td>
<td>0.71</td>
<td>0.70</td>
<td>0.49</td>
</tr>
<tr>
<td>$Q(O_{\text{sup}})$ (a.u.)</td>
<td>−1.22</td>
<td>−1.20</td>
<td>−1.05</td>
</tr>
</tbody>
</table>

Fig. 2. Structural models of Cu, Ag and Au monomers on the $=$Si–O–$\equiv$ adsorption site (distances in Å). (a) Cu/SiO₂; (b) Ag/SiO₂; (c) Au/SiO₂.
Fig. 3. Structural models of Cu, Ag and Au dimers on the $\equiv$Si–O• adsorption site (distances in Å). (a) Cu$_2$/SiO$_2$; (b) Ag$_2$/SiO$_2$; (c) Au$_2$/SiO$_2$.

Table 2

<table>
<thead>
<tr>
<th>M$_2$/SiO$_2$</th>
<th>Cu</th>
<th>Ag</th>
<th>Au</th>
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</thead>
<tbody>
<tr>
<td>$E_{\text{nucl}}$ (eV)</td>
<td>−0.99 (−1.81)$^a$</td>
<td>−0.85 (−1.49)$^a$</td>
<td>−1.08 (−1.80)$^a$</td>
</tr>
<tr>
<td>$E_{\text{adh}}$ (eV)</td>
<td>−2.17</td>
<td>−1.54</td>
<td>−1.20</td>
</tr>
<tr>
<td>$Q$(M$_A$) (a.u.)</td>
<td>0.46</td>
<td>0.39</td>
<td>0.45</td>
</tr>
<tr>
<td>$Q$(M$_B$) (a.u.)</td>
<td>0.25</td>
<td>0.35</td>
<td>−0.07</td>
</tr>
<tr>
<td>$Q$(M$_C$) (a.u.)</td>
<td>0.71</td>
<td>0.74</td>
<td>0.38</td>
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<tr>
<td>$Q$(O$_{\text{supp}}$) (a.u.)</td>
<td>−1.25</td>
<td>−1.25</td>
<td>−0.98</td>
</tr>
<tr>
<td>SD on M$_A$</td>
<td>0.41</td>
<td>0.41</td>
<td>0.24</td>
</tr>
<tr>
<td>SD on M$_B$</td>
<td>0.43</td>
<td>0.43</td>
<td>0.34</td>
</tr>
<tr>
<td>SD on O$_{\text{supp}}$</td>
<td>0.14</td>
<td>0.14</td>
<td>0.40</td>
</tr>
</tbody>
</table>

$^a$ In parentheses, the $E_{\text{nucl}}$ of free metal dimers: $E_{\text{nucl}} = E(M_2) - E(M_1)$.  
$^b$ SD stands for spin density.

Fig. 4. Structural models of Cu, Ag and Au trimers on the $\equiv$Si–O• adsorption site (distances in Å). (a) Cu$_3$/SiO$_2$; (b) Ag$_3$/SiO$_2$; (c) Au$_3$/SiO$_2$.

Table 3

<table>
<thead>
<tr>
<th>M$_3$/SiO$_2$</th>
<th>Cu</th>
<th>Ag</th>
<th>Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{\text{nucl}}$ (eV)</td>
<td>−2.49 (−0.72)$^a$</td>
<td>−1.96 (−0.48)$^a$</td>
<td>−2.00 (−0.61)$^a$</td>
</tr>
<tr>
<td>$E_{\text{adh}}$ (eV)</td>
<td>−3.94</td>
<td>−3.04</td>
<td>−2.59</td>
</tr>
<tr>
<td>$Q$(M$_A$) (a.u.)</td>
<td>0.53</td>
<td>0.52</td>
<td>0.41</td>
</tr>
<tr>
<td>$Q$(M$_B$) (a.u.)</td>
<td>0.39</td>
<td>0.51</td>
<td>0.09</td>
</tr>
<tr>
<td>$Q$(M$_C$) (a.u.)</td>
<td>−0.17</td>
<td>−0.24</td>
<td>0.08</td>
</tr>
<tr>
<td>$Q$(M$_D$) (a.u.)</td>
<td>0.75</td>
<td>0.79</td>
<td>0.58</td>
</tr>
<tr>
<td>$Q$(O$_{\text{supp}}$) (a.u.)</td>
<td>−1.29</td>
<td>−1.30</td>
<td>−1.14</td>
</tr>
</tbody>
</table>

$^a$ In parentheses, the $E_{\text{nucl}}$ of free metal trimers: $E_{\text{nucl}} = E(M_3) - E(M_1) - E(M_2)$.  

If now the analysis of $E_{\text{nucl}}$ values is performed taking into account the nature of the metal, the same trend is observed for isolated and supported dimers: Cu $\equiv$ Au $\approx$ Ag (in magnitude). Similarly as for free dimers, the deep position of Ag d-levels in the energy scale could explain the relatively weak Ag–Ag interaction.

However, for supported M$_3$ the sequence in the M–M strength is slightly different: Cu $\equiv$ Ag $\approx$ Au. This behaviour could be interpreted as follows. Two main factors take place in the M$_1$–M$_2$O–Si$_h$ bonding: (i) the interaction between two d-type orbitals and (ii) the reactivity of the ·M$_2$–O–Si$_h$ site due to its open-shell electronic structure to bind another M atom. For Cu, both factors are important. The spin density (SD) is mainly localized on the dimer (SD$_Z$ 0.84; see Table 2) yielding a strong interaction with the isolated Cu atom during the nucleation process. For Ag, the contribution (i) is relatively weak, nevertheless (ii) should be important due the high reactivity of the supported Ag$_2$; in fact, the SD values are the same as for copper. Finally, for Au the factor (i) contributes strongly to the bonding but the factor (ii) is relatively weak because the supported Au$_2$ has a SD value of 0.54, making this site less reactive towards the Au atom. Thus, while for Cu both factors are important, for Ag and Au only one of them contributes greatly.

3.3. Study of the metal–oxide interaction: adhesion energies

The adhesion energy is defined as the energy associated with the metal particle adsorption as a unit. The calculated values are shown as a diagram in Fig. 7. Comparing individually the M$_n$–O$\equiv$ interactions we observe that, as before, the coupling of two open-shell systems (M$_1$ · or M$_3$ + ·O–Si$_h$) produces very strong bonds.

If the comparison is performed among the metals, a clear trend in the M$_n$–O$\equiv$ bond strength is observed: Cu $\approx$ Ag $\approx$ Au. If we consider that the main component of the bonding is the M–oxide charge transfer, we would expect the sequence: Cu $\approx$ Ag $\approx$ Au, according to the atomic charge and IP values. However, due to the more localized Ag(d) band, the Ag(d)–O(p) interaction should be relatively weak, making this interaction less strong than expected. Analogous arguments were employed by Grönbeck and Broqvist to explain the weak adsorption of atomic Ag on a regular O site of MgO(100) [31]. They ascribed this phenomenon to a closed d shell and a large s–d splitting for Ag. Hence, for Cu both the covalent component and the Cu–oxide charge transfer contribute to the bonding. For Ag, the charge transfer is predominant, while for Au, the Au(d)–O(p) mixing is relevant.

If the present results for M$_1$/SiO$_2$ are compared with those reported previously for TiO$_2$ [19] and Al$_2$O$_3$ [20], we can conclude that the charge transfer to the surface takes place according to the sequence Cu $\approx$ Ag $\approx$ Au for the three oxides. On the other hand, the magnitude of adhesion energies follow the order Cu $\approx$ Ag $\approx$ Au on SiO$_2$ and TiO$_2$, and Cu $\approx$ Au $\approx$ Ag

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**Table 4**

<table>
<thead>
<tr>
<th></th>
<th>Cu</th>
<th>Ag</th>
<th>Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_1$</td>
<td>7.83 (7.72)$^a$</td>
<td>7.75 (7.57)$^a$</td>
<td>9.42 (9.22)$^a$</td>
</tr>
<tr>
<td>$M_2$</td>
<td>7.99 (7.89)$^a$</td>
<td>7.80 (7.56)$^a$</td>
<td>9.49 (9.16)$^c$</td>
</tr>
<tr>
<td>$M_3$</td>
<td>5.76 (5.78)$^a$</td>
<td>5.77 (~6)$^b$</td>
<td>7.22 (7.27)$^c$</td>
</tr>
</tbody>
</table>

Experimental IP values between brackets.

$^a$ From ref. [27].

$^b$ From ref. [28].

$^c$ From ref. [29].
on \( \text{Al}_2\text{O}_3 \). The interaction with the surface is strong for Cu and Ag on both \( \text{SiO}_2 \) and \( \text{TiO}_2 \) with adsorption energies in the range \(-2.1 \) to \(-2.9 \) eV. For these metal atoms, a mainly covalent bond is formed on \( \text{SiO}_2 \) with a charge delocalization on the oxide surface. Conversely, Cu and Ag atoms interact mainly with the bridging oxygens of \( \text{TiO}_2 \) with formation of \( \text{Cu}^+ \) and \( \text{Ag}^+ \) ions due to a nearly full electron transfer to the oxide [19]. The adsorption of Au atom is stronger on \( \text{SiO}_2 \) (\( E_{\text{adh}} \sim -1.9 \) eV) than on \( \text{TiO}_2 \) (\( E_{\text{adh}} \sim -0.7 \) eV). On the other hand, on \( \text{Al}_2\text{O}_3 \) the metal–surface interaction is weaker than on \( \text{SiO}_2 \) and \( \text{TiO}_2 \), with adsorption energies in the range \(-0.7 \) to \(-1.1 \) eV. On this surface, the oxygen anions become competitive with the aluminum cations for adsorbing the metal atoms. While for Cu and Ag atoms the more favored sites are the threefold hollow O sites, Au atom prefers to bind on top of the O atoms.

If the adhesion and nucleation energies are compared, a larger variation for adhesion values is observed by going from metal to metal. Thus, they can change up to 1.3 eV for \( \text{M}_3 \), and larger variation for adhesion values is observed by going from \( \text{O} \) atoms.

As a consequence, whereas the metal–oxide interaction clearly presents a variation interval of 0.2 eV for \( \text{M}_2 \) and 0.5 eV for \( \text{M}_3 \). The nucleation energies for the \( \text{Cu} \)–metal–metal interaction show a less important variation by changing the metal.

4. Conclusions

(i) An electronic charge transfer from the metal particle to the support occurs following the sequence: \( \text{Cu} \approx \text{Ag} > \text{Au} \). The charge taken by the support resides mainly on the O of the \( \equiv \text{Si}–\text{O} \) group.

(ii) For supported \( \text{Cu}_2 \) and \( \text{Cu}_3 \), an electrostatic interaction takes place between the terminal atom and a regular bridging O atom. For supported \( \text{Ag}_2 \) and \( \text{Ag}_3 \), two metal atoms are directly linked with the surface O atom. In contrast, \( \text{Au}_2 \) and \( \text{Au}_3 \) interact with the surface by means of only one metal atom.

(iii) The metal–metal (\( \text{M}_1–\text{M}_1 \) and \( \text{M}_2–\text{M}_1 \)) interactions were analyzed from an energetic point of view. The interaction of two open-shell systems is always stronger than the interaction of a closed-shell system with a closed-shell one. Particularly, for \( \text{M}–\text{M} \) interactions, the noticeable differences observed between the isolated and supported situations are mainly due to the fact that the support 'changes' the electronic structure of one of the interacting fragments.

(iv) If a comparative study among the metals were performed, the bond strength of \( \text{M}–\text{M} \) interaction follows the order: \( \text{Cu} \approx \text{Au} > \text{Ag} \). The deeper Ag d-type orbitals could explain the relatively weak Ag–Ag interaction. On the other hand, if the same analysis is made for the \( \text{M}–\text{oxide} \) interaction, a clear trend in the bond strength was observed: \( \text{Cu} > \text{Ag} > \text{Au} \). Whereas for Au the charge transfer to the support is relatively small, for Ag the Ag(d)–O(p) interaction should be relatively weak due to the more localized Ag(d) band.

(v) By comparing the present results on \( \text{SiO}_2 \) with those reported for \( \text{TiO}_2 \) and \( \text{Al}_2\text{O}_3 \), only considering the atomic adsorption, we can conclude that the charge transfer to the surface takes place according to the sequence \( \text{Cu} \approx \text{Ag} > \text{Au} \) for the three oxides. The adhesion energies follow the same order \( \text{Cu} > \text{Ag} > \text{Au} \) (in magnitude) only for \( \text{SiO}_2 \) and \( \text{TiO}_2 \).

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References


