Theoretical Investigation of the Deposition of Cu, Ag, and Au Atoms on the ZrO$_2$(111) Surface

Ricardo Grau-Crespo,*† Norge Cruz Hernández,‡ Javier F. Sanz,‡ and Nora H. de Leeuw†

Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, U.K., and Departamento de Química Física, Facultad de Química, Universidad de Sevilla, E-41012 Sevilla, Spain

Received: January 17, 2007; In Final Form: April 30, 2007

We have used computer modeling techniques to investigate the interaction of Cu, Ag, and Au atoms (at 0.25 ML coverage) with the (111) surface of zirconia, ZrO$_2$. The surface was simulated by means of periodic slabs, and the calculations were performed using spin-polarized density functional theory (DFT) within the generalized gradient approach. We show that, for the three metals, the most stable adsorption sites are not on top of the outmost oxygen atoms, as previously suggested for the Cu/ZrO$_2$ case, but at less-symmetric bridge sites between oxygen and zirconium. Furthermore, the examination of the charge density and the electronic density of states shows that no full charge transfer takes place between any of the metals and the zirconia surface, as, in all cases, the metal’s unpaired electron remains largely localized on the metal adatom upon adsorption. The origin of the interaction appears to be the polarization of the electronic density of the adsorbed metal atom, together with a modest chemical contribution arising from the mixing of the orbitals of the metal atom and the surface oxygen. The adsorption energies follow the order $|E_{\text{ads}}(\text{Ag})| < |E_{\text{ads}}(\text{Au})| < |E_{\text{ads}}(\text{Cu})|$.

I. Introduction

Oxide-supported metals play a pivotal role in a number of technologically important applications, including sensors, solid oxide fuel cells, and heterogeneous catalysts. Among the supports, zirconia (ZrO$_2$) is of special interest owing to its stability at high temperatures and other convenient mechanical and chemical properties that make it an attractive catalyst support for various reactions.

The catalytic properties of M/ZrO$_2$ interfaces, with M = Cu, Ag, and Au, which are the subject of this work, have been studied experimentally by various authors. For example, Au/ZrO$_2$ and Cu/ZrO$_2$ systems were investigated as low-temperature water—gas shift (WGS) catalysts by Idakiev et al. and by Ko et al., respectively, and copper/zirconia is known to catalyze the production of hydrogen through the steam reformation of methanol. Catalysts consisting of Au, Ag, or Cu supported on zirconia have also been investigated for the synthesis of methanol from carbon dioxide and hydrogen, where it has been shown that both the Cu/ZrO$_2$ and Ag/ZrO$_2$ catalysts exhibit good selectivity for this reaction, although the activity of the silver-containing catalyst is generally lower than that of the copper-containing material. Zirconia-supported gold exhibits the lowest selectivity to methanol synthesis, as it is an active catalyst in the reverse water—gas shift reaction (producing carbon dioxide and water). On the other hand, Au/ZrO$_2$ materials are of significant interest as catalysts for CO oxidation and for the selective hydrogenation of unsaturated compounds. Zhang et al. recently suggested that the most active sites in a Au/ZrO$_2$ catalyst for the latter reaction are isolated Au cations at the surface of zirconia, but in general, the role of isolated gold species in these and other reactions is not clear. For example, whereas some authors describe the mechanism of the gold-catalyzed WGS reaction in terms of active cationic gold sites, others have suggested that the active form of gold comprises small metallic clusters. Many of these experimental studies have been performed using different oxide supports, including zirconia, ceria, and ceria/zirconia, and therefore, the clarification of the role of the support in the formation of the active species is of primary importance.

In recent years, computer modeling techniques have increasingly been applied to the investigation of the geometric and electronic structures of metal/oxide interfaces, in order to provide an atomic-level understanding of their properties. In the case of the zirconia support, the main focus has been on the simulation of interfaces with Pt or Pd and with Ni. Although the adsorption of Cu on ZrO$_2$ has been the subject of some theoretical work, to the best of our knowledge, the deposition of Ag or Au on zirconia has not yet been investigated using modeling techniques.

The calculations presented in this work are based on the structure of cubic zirconia, which is the stable polymorph of pure ZrO$_2$ only at temperatures above 2650 K and up to the melting point at 2950 K. At lower temperatures, the stable phases are tetragonal (from 1400 to 2650 K) and monoclinic (up to 1400 K). However, the cubic phase can be stabilized by doping with lower-valence cations, and this is, in fact, the phase present in many catalytic applications. It has also been shown that zirconia thin films grown on Pt(111) present a cubic structure. Cubic zirconia adopts the fluorite structure shown in Figure 1, which has a face-centered cubic unit cell (space group Fm$ar{3}$m). In this structure, each zirconium cation is coordinated to eight equivalent nearest-neighbor oxygen anions at the corners of a cube, and each anion is tetrahedrally coordinated to four cations.

We present here a detailed theoretical study of the deposition of isolated Cu, Ag, and Au atoms on different sites at the (111) surface of cubic zirconia, which has been found to be the most stable termination of this structure in a number of theoretical

* Corresponding author. E-mail: r.grau-crespo@ucl.ac.uk.
† University College London.
‡ Universidad de Sevilla.
studies, using both interatomic potentials and quantum-mechanical methods. In addition, the experimental characterization of thin films of zirconia, using low-energy electron diffraction (LEED), shows well-defined (111) surfaces. In the work by Walter et al. on Cu/ZrO₂, the most symmetric surface sites (on top of O₂, O₆, or Zr in Figure 2) were studied for the adsorption of Cu atoms, and the authors concluded that the preferred binding site is atop the terminal oxygen atom, O₆, with charge transfer from the metal atom to that oxygen ion. However, in the present work, we show that Cu, Ag, and Au preferably do not absorb at any of the high-symmetry sites, but at bridging sites between oxygen and zirconium. A detailed examination of the charge density and the electronic density of states suggests that no large charge transfer occurs between the adsorbed metal atoms and the zirconia surface.

II. Models and Computational Methods

To simulate the zirconia (111) surface, we employed the periodic approach, where a repeated slab is used to represent the surface. We considered oxygen-terminated slabs of different thicknesses (see next section) separated from each other by a vacuum gap of ~15 Å, and from the calculated relaxations and surface energies, we concluded that a slab containing nine atomic layers (three O−Zr−O trilayers) in the direction perpendicular to the surface is sufficient to obtain convergence of the surface properties. Parallel to the surface, the supercell consists of a 2 × 2 array of hexagonal surface unit cells. Each unit cell contains one ZrO₂ unit at the surface, and therefore, the three-layer simulation supercell contains 36 atoms in total, with four oxygen ions at each surface. In all of the calculations, the positions of the four atomic layers at the bottom of the slab were kept fixed at the relaxed bulk positions, while the first five layers of the top face, which is the surface under investigation, were fully relaxed. Using this model, we calculated the interaction of the surface with the group IB metal atoms (Cu, Ag, and Au) uniformly deposited at a 0.25 ML coverage. Surface coverage is defined such that 1 ML coverage means that one metal atom is deposited for each surface oxygen site.

All calculations were carried out using the VASP code, which employs a basis set of plane waves to solve the Kohn−Sham equations of density functional theory (DFT) in a periodic system. We used the generalized gradient approximation (GGA), with a spin-polarized density functional built from the Perdew and Zunger local functional, the spin interpolation formula of Vosko et al., and the gradient corrections by Perdew et al. Although, in general, non-spin-polarized approaches can provide valuable insight into the metal−support interaction, explicit consideration of spin-polarization effects might be of importance, and we have therefore included them in our calculations.

The interaction between the valence electrons and the core was described with the projected augmented wave (PAW) method in the implementation of Kresse and Joubert. Scalar relativistic effects are included in these potentials, which is necessary for the correct description of the electronic structure when heavy atomic species (such as Au) are involved.

The number of plane waves in VASP is controlled by a cutoff energy, which in our calculations was set to Eₖₜ₉ = 500 eV (i.e., 100 eV above the recommended value for the set of potentials employed). Structural optimizations were performed using a conjugate gradient technique in which the iterative relaxation of atomic positions at the fixed support, and in each case, we obtained three non-imaginary frequencies, which shows that the geometries obtained via the conjugate gradient method correspond to local minima. For all geometry optimization calculations, a 3 × 3 × 1 mesh of k points was used to sample the reciprocal space, whereas for the final single-point runs for the calculation of the electronic density of states, a denser mesh of 5 × 5 × 1 points was employed.

III. Results and Discussion

Bulk and Clean (111) Surface. We first performed a full optimization of the cell parameters and ionic coordinates starting from the perfect cubic structure, and we observed that, even when no symmetry constraints were applied, the structure maintained the cubic symmetry, and no transition to the more stable tetragonal phase took place. The resulting cell parameter was a = 5.130 Å, which is less than 1% above the experimental value of 5.090 Å. (This value is an extrapolation to 0 K using the thermal expansion data in ref 52, as given in ref 29.) The calculated cell parameter corresponds to Zr−O distances of 2.22 Å.

Starting from this relaxed bulk structure, we created slab models representing the stoichiometric (111) surface, using different numbers of layers (6, 9, 12, and 15 atomic layers, which correspond to N₁ = 2, 3, 4, and 5 ZrO₂ layers, respectively). Table 1 shows the relaxation of the interplanar distances for all of the models. In all cases, the relaxation increased the top oxygen−zirconium spacing, which was accompanied by a reduction in the oxygen−oxygen interlayer spacing between the two outermost ZrO₂ trilayers, as can be observed in all but the thinnest slab model. We consider that the model with N₁ = 3 trilayers (nine atomic layers) is sufficient to represent the geometric relaxation of this surface, especially as the calculated surface energy (γ = 1.08 J m⁻²) changes by less than 0.01 J m⁻² when going from N₁ = 3 to N₁ = 5. This value of the surface energy is lower than that obtained by Gennard et al. (1.49 J m⁻²) for the same surface using a similar model and Hartree−Fock calculations, and it is much lower than the value obtained for the (011) surface by these authors with the same technique (2.41 J m⁻²). We also note that the (111) surface energy is typically higher for semicovalent zirconia than...
employed in the present work.

have been calculated using DFT methods similar to those values of 0.39 J m$^{-2}$ for other fluorite-type structures with more ionic character; e.g.,

Models of the ZrO$_2$ (111) Surface with Respect to the Bulk Percentages of the Bulk Values) for the Four Different Slab TABLE 1: Relaxation of the Interplanar Distances (as Percentages of the Bulk Values) for the Four Different Slab Models of the ZrO$_2$(111) Surface with Respect to the Bulk

| layer | $N_l = 2$ | $N_l = 3$ | $N_l = 4$ | $N_l = 5$
|-------|-----------|-----------|-----------|-----------
| O     | +7.9%     | +7.4%     | +7.3%     | +7.4%     |
| Zr    | −5.4%     | −0.4%     | −0.3%     | −0.4%     |
| O     | fixed     | −3.6%     | −4.0%     | −3.9%     |
| O     | fixed     | +1.4%     | +1.2%     | +1.1%     |
| Zr    | fixed     | −1.5%     | −0.3%     | −0.3%     |
| O     | fixed     | fixed     | +1.2%     | +0.8%     |
| O     | fixed     | +0.3%     | 0.0%      |           |
| Zr    | fixed     | fixed     | fixed     | +0.1%     |
| O     | fixed     | fixed     | fixed     | +0.5%     |
| Zr    | fixed     | fixed     |          | −2.0%     |
| O     | fixed     |          |          |           |
| Zr    | fixed     |          |          |           |
| O     | fixed     |          |          |           |

$N_l$ is the number of O–Zr–O trilayers in the slab.

for other fluorite-type structures with more ionic character; e.g., values of 0.39 J m$^{-2}$ for CaF$_2$ and 0.45 J m$^{-2}$ for CeO$_2$ have been calculated using DFT methods similar to those employed in the present work.

Adsorption of Metal Atoms on the (111) Surface. Different sites on the O-terminated ZrO$_2$(111) surface were considered for the adsorption of the metal atoms. Figure 2 shows side and top views of the surface and the positions of the high-symmetry surface sites for adsorption: the surface Zr atoms and two different types of oxygen sites. Specifically, O$_u$ (up) is the outmost oxygen, and O$_d$ (down) is the subsurface oxygen atom in the top ZrO$_2$ trilayer. Not only did we consider these sites, but we also deposited the metal atoms in less-symmetric initial positions in the surface plane, including the center of the Zr–O$_u$–O$_d$ “triangle” and the region between each pair of sites (O$_u$–Zr, O$_u$–O$_d$, Zr–O$_d$). For each site, the adsorption energy was calculated as the difference between the energy of the slab with the metal atom adsorbed and the sum of the energies of the clean oxide surface and the isolated metal atom.

The influence of surface relaxation on the adsorption energies was analyzed by performing two series of calculations. In the first series (fixed surface), the surface atoms were kept frozen at the positions obtained from the clean surface optimization, and only the metal atom positions were fully optimized. In the second series of calculations (relaxed surface), the positions of all of the atoms in the outermost slab layers were fully optimized.

TABLE 2: Calculated Adsorption Energies (in eV) of Cu, Ag, and Au Atoms on the (111) Surface of Cubic Zirconia

<table>
<thead>
<tr>
<th></th>
<th>O$_d$</th>
<th>O$_u$</th>
<th>Zr</th>
<th>O$_u$–Zr</th>
<th>O$_d$–O$_u$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu fixed</td>
<td>−0.556</td>
<td>−0.608</td>
<td>−0.427</td>
<td>−0.694</td>
<td>−0.664</td>
</tr>
<tr>
<td>Cu relaxed</td>
<td>−O$_u$–Zr</td>
<td>−O$_d$–Zr</td>
<td>−0.476</td>
<td>−1.038</td>
<td>−0.809</td>
</tr>
<tr>
<td>Ag fixed</td>
<td>−0.219</td>
<td>−0.160</td>
<td>−0.247</td>
<td>−0.253</td>
<td>−0.214</td>
</tr>
<tr>
<td>Ag relaxed</td>
<td>−O$_u$–Zr</td>
<td>−O$_d$–Zr</td>
<td>−0.249</td>
<td>−0.178</td>
<td>−0.276</td>
</tr>
<tr>
<td>Au fixed</td>
<td>−0.418</td>
<td>−0.370</td>
<td>−0.469</td>
<td>−0.532</td>
<td>−0.469</td>
</tr>
<tr>
<td>Au relaxed</td>
<td>−O$_u$–O$_d$</td>
<td>−0.419</td>
<td>−0.546</td>
<td>−0.807</td>
<td>−0.595</td>
</tr>
</tbody>
</table>

* Values in italics mark the most stable adsorption site in each case.

The adsorption energies for the two series of calculations are reported in Table 2. Only those sites for which a local minimum was found in the first series of calculations, i.e., adsorption at fixed surface sites, are included in the table, as, in all other cases, the structure converged to one of these sites (O$_d$, O$_u$, Zr, O$_u$–Zr, O$_u$–O$_d$). In addition, not all of these initial sites were found to remain stable after the simultaneous optimization of both the surface species and the metal adatom, and we show in the table the site to which the adsorbed atom moved upon relaxation. It is worth stressing that no symmetry restrictions were applied in our calculations, and therefore, the metal atoms were free to move to stable positions.

In all cases, we identified that the most stable site for the metal adatom is a bridge position between the topmost oxygen atom and the zirconium atom (O$_u$–Zr). The fact that the most stable site is not one of the high-symmetry sites (Zr, O$_u$, or O$_d$) is interesting, as, in some earlier studies, only these sites had been considered. For example, a previous investigation of the adsorption of Cu on ZrO$_2$ concluded, after a series of symmetry-constrained optimizations, that the preferred binding site is atop the terminal oxygen atom (O$_u$). However, our calculations show that, although this position is indeed the most stable one among the three highest-symmetry sites when the atom is deposited on the fixed surface, it is less stable than either bridge position. In addition, during full relaxation of the surface–adsorbate system without symmetry constraints, no local minimum could be found for the Cu atom adsorbed directly on top of the oxygen site, and the O$_u$–Zr site is the preferred adsorption site in all cases.

By definition, a full relaxation of the system decreases the energy, and therefore, the adsorption energy increases in all cases. For the most stable adsorption site, the main structural
relaxation effect is the displacement of the O_u atom away from the Zr atom in the O_u-Zr bridge, as shown in Figure 3 for the adsorption of gold. The same surface relaxation pattern is found for the adsorption of all of the metals, with the largest increase of the O_u-Zr distance in the case of Cu and the smallest deviation for Ag (see last column in Table 3). The variation in the adsorption energy induced by the relaxation of the support is also largest in the case of Cu (ΔE_ads = −0.34 eV), whereas it is significant in the case of Au (ΔE_ads = −0.28 eV) and relatively small in the case of Ag (ΔE_ads = −0.08 eV). Thus, these contributions represent 33%, 24%, and 35% of the total interaction energies for Cu, Ag, and Au, respectively. However, in all cases, the preferred sites of adsorption remain the same, regardless of the metal or the relaxation status of the oxide surface.

The variation in the adsorption energy from metal to metal (|E_ads(Cu)| > |E_ads(Au)| > |E_ads(Ag)|) is also independent of the surface relaxation. Similar trends for the adsorption energies of these metals have been found for other “nonreducible” oxides, e.g., α-Al2O3 (ref 55) and MgO (ref 56). We note that, in the case of MgO, a more recent study27 showed that the adsorption energies of Au and Cu are actually very similar, whereas in our case, the difference is also small (0.15 eV) but still significant.

In Figure 4, we show a plot of a positive and negative contour surface of the electron-density difference Δρ = ρ(M/ZrO2) − ρ(ZrO2) − ρ(M) for each substrate/metal system. The electron density around the metal atoms is polarized, increasing in the direction of the positive Zr ion. An interesting aspect here is whether the interaction reflected in this polarization is mainly physical, involving only electrostatic and dispersion forces, or whether it contains significant chemical contributions. The strong reorganization of the electron density around the metal atoms, shown in the contour maps in Figure 4, and the relatively large values of the adsorption energies suggest that more than just physical interactions are involved.

To clarify this point, we plotted the electronic density of states (DOS) of the system projected on the orbitals of the metal adatoms and of the surface oxygen ions (Figure 5). This analysis was performed for adsorption at the most favorable sites only and in the relaxed system. The first observation is that, in all cases, valence peaks of mainly s character are distinguishable just below the Fermi energy in the DOS projected on the metal adatom orbitals, suggesting that the adsorbed species retain their d10 s1 electronic configurations. However, because similar peaks are found in the O p-orbital projected DOS, we should examine the possibility of charge transfer from the metal atom to the surface. Figure 6 shows the decomposition of the valence peaks below the Fermi energy into contributions from the orbitals in the atoms forming the O_u-M-Zr bridges. In all cases, the main contribution comes from the metal adatom s level, but the strength of the contributions from the other levels changes from metal to metal. For example, the participation of the metal d

![Figure 3](image1.png)

**Figure 3.** Top view of the relaxed ZrO2(111) surface with 0.25 ML of Au adsorbed at the most stable site (bridging between O_u and Zr). Upon adsorption, the O_u atom moves away from the Zr atom at the other side of the bridge. Similar relaxations take place upon the adsorption of Cu or Ag, but with different variations of the O_u-Zr distances (see Table 3).

**TABLE 3: Optimized Distances (Å) from the Metal Atoms (in Their Most Stable Adsorption Sites) to the Atoms in the ZrO2(111) Surface and Variation of the O_u-Zr Distance at the Surface upon Adsorption of the Metal Atom**

<table>
<thead>
<tr>
<th>M</th>
<th>d(M–Zr)</th>
<th>d(M–O_u)</th>
<th>d(M–O_d)</th>
<th>d(O_u–Zr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>2.74</td>
<td>1.89</td>
<td>3.45</td>
<td>+0.81</td>
</tr>
<tr>
<td>Ag</td>
<td>3.02</td>
<td>2.36</td>
<td>3.89</td>
<td>+0.55</td>
</tr>
<tr>
<td>Au</td>
<td>2.81</td>
<td>2.21</td>
<td>3.63</td>
<td>+0.79</td>
</tr>
</tbody>
</table>

a d(O_u–Zr) = 2.23 Å at the clean surface.

![Figure 4](image2.png)

**Figure 4.** Calculated electron-density differences for Cu, Ag, and Au adsorbed on the ZrO2(111) surface. Dark and light gray represent density-difference isosurfaces corresponding to 0.4 electrons × cell volume/Å³ (electron-density gain with respect to the separated systems) and −0.4 electrons × cell volume/Å³ (electron-density loss with respect to the separated systems), respectively.
orbitals, as a percentage of the s contribution, is around 86% for Cu, 44% for Au, and only 14% for Ag, as measured by the area below the peaks. This trend reflects the different abilities of the metal atoms to produce s–d hybridization, which correlate with the d^{10}s^{1}–d^{9}s^{2} experimental excitation energies: very large for Ag (3.97 eV) compared to Cu (1.49 eV) and Au (1.74 eV). From our results, we also estimated that the joint contribution from the metal s and d orbitals is around 65–70% in all cases, which shows that most of the charge of the unpaired electron remains at the metal atom, although there are still significant contributions from the orbitals of the oxygen and zirconium atoms in the bridge. This delocalization of the unpaired electron can be interpreted as the result of partial charge transfer from the adatom to the surface. However, this effect could also be exaggerated by our calculations because of the well-known trend of density functional theory to produce solutions with excessive electron delocalization, as a result of the presence of electron self-interaction errors. Considering that most of the charge of the electron is still on the metal atom, we prefer to interpret these results in terms of a mixing of the s–d orbital of the adatoms and the orbitals of the surface atoms.

In the DOS plots in Figure 5, one can also observe the overlap of the metal orbitals of mainly d character with oxygen p levels in the same range of energies around 2 eV below the Fermi level. The DOS analysis therefore suggests that there could well be a chemical contribution to the interaction of the metal adatoms with the surface, which is also consistent with the observation of the strong relaxation of the oxygen atom in the bridge and with the significant strength of the metal–surface interaction.

Our results agree with those reported previously by Yudanov et al. and Neyman et al. for the adsorption of the same metals on the MgO(001) surface. These authors suggested that the weaker adsorption energies of Ag compared to Cu and Au might be related to the smaller propensity of silver for s–d hybridization and for mixing with the oxygen levels. A comparison of our results with those found for the adsorption of the same metal atoms on the rutile TiO_{2}(110) surface is also relevant. In that work, it was found that, when Cu or Ag atoms are adsorbed on...
the bridging oxygen site, the outer s electron of the metal is fully transferred to the surface Ti 3d states, which contrasts with the behavior described here for the ZrO2(111) surface. The difference in behavior between the two substrates is most likely the result of their different electronic properties: Whereas TiO2 is a well-known wide-band-gap semiconductor in which the Ti 4d−5s ions can be reduced easily to Ti3+, zirconia is an insulating oxide in which the cations are much more difficult to reduce.

The trend in the distances from the metal atoms to the zirconia surface ions is in agreement with the strengths of the metal−surface interactions, as shown in Table 3. In all cases, the surface ion nearest to the metal atom is O2−, followed by Zr, but the distances increase when going from Cu to Ag and then decrease again when going down the group from Ag to Au. The variation of these trends down this group in the periodic table is caused by the strong relativistic effects present in the gold atom. The scalar relativistic effects, included in our calculations through the PAW potentials, produce a contraction in the orbitals of the gold atoms, which results in shorter metal−surface distances for gold than for silver. In fact, in the past decade, a number of experimental and theoretical (relativistic) studies have convincingly argued that the data on the atomic radii of the coinage metals in many handbooks and textbooks should be revised, as it has been shown that gold is clearly smaller than silver.60−62 The same trend for the adsorption distances was observed in theoretical studies of the interaction of Cu, Ag, and Au atoms with other surfaces, e.g., NaCl(100) and MgO(001).56,63

IV. Conclusions

In this work, we have investigated the interaction of isolated Cu, Ag, and Au atoms with the nonpolar ZrO2(111) surface. The most stable geometric configurations of adsorption of the three metals are similar, with the metal atom in a bridge position between the outermost oxygen atom and the surface zirconium cation, but the metal−surface distances are shorter for Cu and Au than for Ag.

The absolute values of the adsorption energies were found to vary in the order Cu > Au > Ag, which is in agreement with previous theoretical studies of the adsorption of these metals on other supports. Analysis of the electronic structure suggests that no full charge transfer occurs between the metals and the support. The origin of the interaction is the polarization of the electronic densities of the interacting atoms, which is strong enough to include a significant chemical contribution mainly arising from the mixing of the orbitals of the metal atoms and the surface oxygen, involving a hybridization of the s and d orbitals of the metal.

From a methodological point of view, we have illustrated the importance of an exhaustive exploration of the adsorption energy landscape at the surface, as geometry optimizations starting from the high-symmetry adsorption sites do not necessarily lead to the most stable configuration, where it is equally important to switch off any symmetry constraints during the optimization. Future work will include investigating the interaction of clusters of these metals with the zirconia surface, as well as the effect of surface defects on this interaction.

Acknowledgment. We thank the EPSRC for financial support under Grant EP/CS1744X and the EPRSC-funded Materials Chemistry Consortium for access to the U.K.’s national high-performance computer resource HPCx. Financial support from the Spanish Ministerio de Educación y Ciencia, Grant MAT2005-01872, and the Ramón y Cajal program (awarded to N.C.H.) is also acknowledged.

References and Notes