Redox properties of gold-substituted zirconia surfaces

Ricardo Grau-Crespo, a,b Norge Cruz Hernández, b Javier F. Sanz c and Nora H. de Leeuw a

Received 17th July 2008, Accepted 29th October 2008
First published as an Advance Article on the web 16th December 2008
DOI: 10.1039/b812245h

We report the use of quantum mechanical calculations based on the density functional theory (DFT) to investigate the redox properties of zirconia surfaces with cationic gold centres. Two different charge compensation mechanisms for the Au/Zr substitution at the cubic zirconia (111) surface are investigated: formation of oxygen vacancies and surface protonation. Regardless of the mechanism of charge compensation, gold dopants are more likely to accumulate at the surface than to migrate to the zirconia bulk. We investigate the formation of oxygen vacancies in the pure and gold-substituted surfaces, exploring a range of vacancy configurations, and we show that the presence of gold in lattice positions at the zirconia surface induces a dramatic change in the redox properties of the surface, which becomes easily reducible thanks to Au(III) → Au(I) transitions.

I. Introduction

Recent years have seen an increasing interest in oxide-supported gold catalysts, which are used in technologically important processes such as the oxidation of carbon monoxide, the water gas shift (WGS) reaction and the hydrogenation of unsaturated compounds. While the exceptional activity and selectivity of these heterogeneous catalysts is now well established, the current understanding of the microscopic mechanisms and the nature of the active sites is far from complete. One of the most debated issues in heterogeneous gold catalysis is the role of cationic gold species in the mechanisms of these reactions. Bond and Thomson have proposed a microscopic model for gold-catalyzed CO oxidation, where the Au atoms at the interface between the Au nanoparticle and the oxide support are the active centres, and suggested that they could be cationic gold species. Spectroscopic studies by Hutchings et al. have given support to the notion that Au + species are central in the catalytic mechanism of CO oxidation with iron-supported gold catalysts, while Fu et al. have provided strong experimental evidence of the role of isolated Au + species in the gold-catalyzed WGS reaction, showing that the activity of the catalyst is retained if all the metallic gold is removed via a leaching treatment (after which only cationic species of gold are present). Au(III) has also been suggested to be the active species in hydrogenation reactions by Zhang and by Guzman and Gates, using different combinations of catalytic tests and spectroscopic techniques.

However, other authors have neglected the possible role of cationic gold in these catalytic processes. Goodman and coworkers have focused on size effects of the gold nanoparticles to explain the activity of supported gold catalysts in CO oxidation and an XAS study by Schwartz et al. has indicated that, although a fresh Au/CeO2 catalyst contains isolated gold cations, only metallic gold could be detected by XANES measurements under WGS reaction conditions. More discussion about the nature of the active sites in supported gold catalysis can be found in recent reviews by Hashmi and Hutchings and by Chen and Goodman, but this is clearly a topic that is still open to debate.

Zirconia (ZrO2) is an attractive support material, owing to its stability at high temperatures and other convenient mechanical and chemical properties. Zirconia-supported gold has been investigated as a catalyst for the low-temperature WGS reaction, for CO oxidation and for the selective hydrogenation of unsaturated compounds.

In recent years computer modelling techniques have increasingly been applied to the investigation of the geometric and electronic structure 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. We have recently investigated the adsorption of Au, Ag and Cu atoms at perfect ZrO2(111) surfaces using density functional theory (DFT) techniques, while the adsorption of small Au clusters at perfect and defective zirconia surfaces has been studied theoretically by Liu et al. More recently, the same authors have used DFT techniques to study the properties of cationic gold species at zirconia surfaces in the form of Au(OH) n monomers. To the best of our knowledge, the presence of positively charged gold species at cationic lattice positions in zirconia surfaces has not been investigated previously. A different mechanism for stabilising...
positively charged states of noble metal atoms at oxide surfaces, involving direct charge transfer from the adatom to the surface, has been suggested for Pd adsorption on ceria, but in the case of zirconia surfaces this is unlikely to happen because Zr$^{4+}$ cations are very difficult to reduce.

The effect of gold and other metal dopants on the redox properties of other oxide surfaces, like TiO$_2$ (110) and CeO$_2$(111), has been discussed in recent papers by Metiu and co-workers. Not surprisingly, the substitution of the tetravalent cations at these surfaces by lower valence cations led to a dramatic decrease of the calculated formation energy of oxygen vacancies. The low values of the formation energies reported by these authors are most likely associated with the high instability of the initial structure without vacancies, where the oxygen excess leads to the oxidation of the cations beyond their favourable oxidation states.

We present a theoretical study of the redox properties of the pure and Au-substituted (111) surface of zirconia, where we discuss different charge compensation mechanisms for the heterovalent Au/Zr substitutions, including hydroxy groups and oxygen deficiency with respect to the undoped oxide. The formation of oxygen vacancies is then investigated starting from these compensated structures, which ensures that both the initial and final compositions involve chemically sensible oxidation states for all species. It will be shown that the creation of vacancies in the doped structure is still much easier than in undoped zirconia, and in fact is also lower than in other, more reducible, pure oxides.

**II. Models and computational methods**

Our surface calculations are based on the structure of cubic zirconia, which is the stable polymorph of pure ZrO$_2$ at high temperatures (above $\approx 2650$ K). However, the cubic phase can be stabilized at lower temperatures by doping with other atoms, for example Y, Ni, Cu, Mn, Fe, and this is the phase present in some catalytic applications. We consider the stabilised cubic phase in this study, but we will investigate a surface model free of dopants in order to study the interaction of gold atoms with the zirconium and oxygen atoms at the surface. Cubic zirconia adopts the fluorite structure, which has a face-centred cubic unit cell (space group $Fm\overline{3}m$). In this structure, each zirconium cation is coordinated to eight equivalent nearest-neighbour oxygen anions at the corners of a cube, while each anion is tetrahedrally coordinated to four cations. The (111) surface has been found to be the most stable termination of this structure in a number of theoretical studies, using both interatomic potentials and quantum-mechanical methods, and it has been observed in the experimental characterization of thin films of zirconia.

The cubic zirconia (111) surface is represented in our calculations by oxygen-terminated slabs, which repeat periodically in the direction perpendicular to the surface, separated by a vacuum gap of $\approx 15$ Å. Based on the results of our previous work, each slab contains nine atomic layers (three O–Zr–O tri-layers), which was shown to be sufficient to obtain convergence of the surface properties. Parallel to the surface, the supercell consists of a $2 \times 2$ array of hexagonal surface unit cells. Each unit cell contains one ZrO$_2$ unit at the surface, and therefore the three-layer simulation supercell contains 36 atoms in total, with four oxygen ions at each surface (Fig. 1). In all calculations, the positions of the four atomic layers at the bottom of the slab were kept fixed at the bulk positions, while the first five layers of the top face, which is the surface under investigation, were fully relaxed.

All calculations were carried out using the VASP code, which employs a basis set of plane waves to solve the Kohn–Sham equations of the density functional theory (DFT) in a periodic system. We have used the generalized gradient approximation (GGA), with a density functional built from the Perdew and Zunger local functional, and the gradient corrections by Perdew et al. 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 of the heavy Au atoms. The number of plane waves in VASP is controlled by a cut-off energy, which in our calculations was set to $E_{\text{cut}} = 500$ eV (i.e., 100 eV above the recommended value for the set of potentials employed). Structural optimizations were performed using a conjugate gradients technique with an iterative relaxation of the atomic positions until the forces on the atoms were all less than 0.01 eV Å$^{-1}$. For all geometry optimization calculations a $3 \times 3 \times 1$ k-point mesh was used to sample the reciprocal space, while at the final single-point runs for the calculation of the electronic density of states, a mesh of $5 \times 5 \times 1$ k-points was employed.

In order to calculate reaction energies, the energies of O$_2$ and H$_2$O molecules and of bulk ZrO$_2$ were obtained with VASP, using the same oxygen PAW potential as in the surface calculations. The O$_2$ molecule was calculated as a spin triplet, and we obtained $E[O_2] = -9.824$ eV and an equilibrium bond distance $d[O-O] = 1.235$ Å, similar to previous reports. We also obtained $E[H_2O] = -14.273$ eV ($d(O-H) = 0.976$ Å, $\angle[H-O-H] = 102^\circ$) for the water molecule and $E[ZrO_2] = -114.207$ eV for bulk cubic zirconia (equilibrium cell parameter $a = 5.130$ Å).

We have denoted the cationic gold species as Au(i) and Au(III), using Roman numerals to make clear that the specified charge state is just a formal value. Any electronic population analysis will yield significantly lower values for these charges, as will be shown below. In this study, we have performed a Bader analysis of the charges, which consists of integrating the electron density in a region defined for each atom in such a way that the density...
III. Results and discussion

Oxygen vacancies at the perfect ZrO$_2$(111) surface

We first investigated the creation of oxygen vacancies at the perfect, undoped zirconia surface. There are two types of surface oxygen positions, as shown in Fig. 1: O$_u$ (up) is the outmost oxygen, while O$_d$ (down) is the subsurface oxygen atom in the top ZrO$_2$ trilayer. The calculated vacancy formation energies, defined as the energy change in the reaction

$$\text{Zr}_{12}\text{O}_{24(\text{slab})} \rightarrow \text{Zr}_{12}\text{O}_{23(\text{slab})} + \frac{1}{2}\text{O}_2(\text{garr})$$

where $\square$ denotes an oxygen vacancy, were 5.83 eV for the O$_u$ vacancy and 5.42 eV for the O$_d$ vacancy. These energies are considerable, as is expected from the well-known low reducibility of zirconia. Although Zr$^{3+}$ cations have been detected by some authors in zirconia-related materials (e.g. ref. 61) this is not a very stable species, and upon vacancy creation the electrons prefer to remain localized at the vacancy site, forming an F centre. An illustration of this electron distribution is given in Fig. 2, where the electron localization function (ELF) is plotted in a plane that contains some oxygen anions and the vacancy site. The ELF is high in the region of the oxygen vacancy, showing that the electrons remain trapped in the defect site.

![Fig. 2 Electron localization function (ELF) plot for the unsubstituted zirconia surface with a subsurface oxygen (O$_d$) vacancy.](image)

### Au/Zr substitutions with charge compensation via hydroxy groups

First, we will consider the substitution of one of the surface zirconium ions by a gold cation. Since the oxidation state of Zr in zirconia is 4+, while the most typical oxidation states of cationic gold are 1+ and 3+ (5d$^{10}$ and 5d$^8$ electronic configurations, respectively), we should incorporate a charge compensation mechanism into our model. The simplest situation is perhaps when there is one Au/Zr substitution and one extra proton in the system forming a hydroxy group, where the substitution can result in an Au(III) species. The question now arises which position of the hydroxy group is the most stable relative to the Au(III) cation. Four different configurations can be investigated in our supercell model, depending on the position of the oxygen ion to which the proton is attached: (i) O$_u$ atom neighbouring the Au cation, (ii) O$_d$ atom neighbouring the Au cation, (iii) O$_u$ atom away from the Au cation, (iv) O$_d$ atom away from the Au cation, where ‘away’ refers to oxygen atoms which are not in the first coordination sphere around the Au/Zr substitution site. The substitution energies, relative to the most stable configuration, are given in Table 1, except for case (iv) for which no stable structure was found as the geometry optimization led to a configuration of type (i).

The most stable configuration corresponds to case (i), and the relaxed geometry of this configuration is shown in Fig. 3, which shows that Au adopts a distorted square planar coordination, with participation of two O$_u$ ions (at 2.07 Å) and two O$_d$ ions (at 2.16 Å). The other three O atoms that were coordinated to the surface Zr atom before Au substitution move away from the cation site to longer distances of 2.56 Å (the third O$_u$ ion previously connected to the cation site), 2.68 Å (an oxygen atom in the second O–Zr–O trilayer from the surface), and 3.00 Å (the O$_d$ forming the hydroxy group). The consecutive O–Au–O angles in the relaxed coordination square are 74.4°, 112.7°, 74.4° and 97.6°, adding up to 359.1°, which indicates a nearly perfect planar arrangement, although with individual angles deviating strongly from the 4 × 90° configuration of a regular square planar coordination. This type of coordination is typical of Au(III) species in a wide range of compounds, including gold(III) oxide Au$_2$O$_3$ and chloride Au$_2$Cl$_3$, and is due to the presence of a strong Jahn–Teller distortion.

We have also employed a bulk model with the same composition and axis orientation as the surface model (just closing the vacuum gap down to zero), to obtain the (Au,H)/Zr substitution energy for the bulk, which was 1.5–2.8 eV higher than for the surface configurations. Therefore, proton-compensated gold dopants will tend to accumulate at the zirconia surface instead of migrating to the bulk.

<table>
<thead>
<tr>
<th>Zr$_{11}$AuO$_2$OH configuration</th>
<th>$E$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) H on O$_u$ near Au</td>
<td>0</td>
</tr>
<tr>
<td>(ii) H on O$_d$ near Au</td>
<td>1.31</td>
</tr>
<tr>
<td>(iii) H on O$_u$ far from Au</td>
<td>0.57</td>
</tr>
<tr>
<td>H on O near Au, in bulk</td>
<td>2.77</td>
</tr>
</tbody>
</table>
We now wish to evaluate the change in the reducibility of the surface after gold substitution at the surface. Starting from the most stable configuration of the surface with one Au and one hydroxy group, we create an oxygen vacancy at the surface. The energy of the process

\[
Zr_{11}AuO_{23}OH^{(\text{slab})} / Zr_{11}AuO_{22},OH^{(\text{slab})} + \frac{1}{2}O_2^{(\text{gas})}
\]

depends on the relative position of the oxygen to be removed, with respect to the gold cation and the hydroxy group. We have considered five different configurations, with oxygen vacancies in the positions marked in Fig. 3: (i) Ou vacancy near Au (there are two symmetrically equivalent configurations of this type too, corresponding to the two Ou anions in the coordination square of the Au(III) cation), (ii) O_d vacancy near Au, in cis position with respect to the hydroxy group (this is the O_d that shifted away to 2.56 Å from the Au cation), (iv) Ou vacancy away from Au, and v) O_d vacancy away from Au.

The vacancy formation energies (VFE) for all configurations, calculated according to eqn (2), are given in Table 2. The values, which are all around 1 eV, are considerably smaller (~5 times) than the VFE values at the pure zirconia surface, which suggests that the reduction occurs at the gold centre, following an Au(III) → Au(I) transition. The most stable configuration for the reduced surface is depicted in Fig. 4. The positive charge of Au, calculated according to the Bader method, decreases by a factor very close to 3 (see Table 3), and the electronic density of states (DOS) in Fig. 5 shows that the empty 5d levels of Au^{3+} become populated upon the creation of the vacancy, forming a Au^{+} species with very little d contribution above the Fermi level. Furthermore, the equilibrium position of the gold cation in the reduced surface forms a nearly linear O–Au–O coordination, which is typical of Au(i) species (e.g. AuCl\textsubscript{6}^{2−} and AuBr\textsubscript{6}^{3−}). The O–Au–O angle is 162.9° and the two shortest Au–O distances are both 2.06 Å, while the next nearest oxygen ions are at 2.71 Å and 3.31 Å (two ions) from the Au ion. In order to adopt the linear coordination, the Au ion has shifted towards the position of the removed oxygen, and has also moved outwards, away from the plane of Zr cations and reaching the layer of surface Ou anions. The hydroxy group has become oriented towards the gold ion (d(Au–H) = 2.21 Å), with the OH bond almost parallel to the surface, as the repulsion of the two neighbouring Zr cations is much stronger than the repulsion by the reduced gold centre, and the resulting electrostatic field therefore points in that direction. This geometry resembles the structure of the hydrogarnet defect in silicates, where hydroxy groups surround a cation vacancy, with the protons pointing at the vacancy to compensate for the charge reduction at that site.

**Au/Zr substitutions with charge compensation via oxygen vacancies**

In principle, the presence of hydrogen is not necessary to stabilize cationic gold species at the zirconia surface. The lower oxidation states of gold cations with respect to Zr\textsuperscript{4+} can also be stabilized directly by oxygen vacancies. We have therefore considered a situation where two surface Zr sites (50% of the surface cationic Au(III) cation), (ii) O_d vacancy near Au, in cis position with respect to the hydroxy group (there are two symmetrically equivalent configurations of this type too, corresponding to the two O_d anions in the coordination square of the Au(III) cation), (iii) O_d vacancy near Au, in trans position with respect to the hydroxy group (this is the O_d that shifted away to 2.56 Å from the Au cation), (iv) Ou vacancy away from Au, and v) O_d vacancy away from Au.

The vacancy formation energies (VFE) for all configurations, calculated according to eqn (2), are given in Table 2. The values, which are all around 1 eV, are considerably smaller (~5 times) than the VFE values at the pure zirconia surface, which suggests that the reduction occurs at the gold centre, following an Au(III) → Au(I) transition. The most stable configuration for the reduced surface is depicted in Fig. 4. The positive charge of Au, calculated according to the Bader method, decreases by a factor very close to 3 (see Table 3), and the electronic density of states (DOS) in Fig. 5 shows that the empty 5d levels of Au\textsuperscript{3+} become populated upon the creation of the vacancy, forming a Au\textsuperscript{+} species with very little d contribution above the Fermi level. Furthermore, the equilibrium position of the gold cation in the reduced surface forms a nearly linear O–Au–O coordination, which is typical of Au\textsuperscript{i} species (e.g. AuCl\textsubscript{6}^{2−} and AuBr\textsubscript{6}^{3−}). The O–Au–O angle is 162.9° and the two shortest Au–O distances are both 2.06 Å, while the next nearest oxygen ions are at 2.71 Å and 3.31 Å (two ions) from the Au ion. In order to adopt the linear coordination, the Au ion has shifted towards the position of the removed oxygen, and has also moved outwards, away from the plane of Zr cations and reaching the layer of surface Ou anions. The hydroxy group has become oriented towards the gold ion (d(Au–H) = 2.21 Å), with the OH bond almost parallel to the surface, as the repulsion of the two neighbouring Zr cations is much stronger than the repulsion by the reduced gold centre, and the resulting electrostatic field therefore points in that direction. This geometry resembles the structure of the hydrogarnet defect in silicates, where hydroxy groups surround a cation vacancy, with the protons pointing at the vacancy to compensate for the charge reduction at that site.

**Au/Zr substitutions with charge compensation via oxygen vacancies**

In principle, the presence of hydrogen is not necessary to stabilize cationic gold species at the zirconia surface. The lower oxidation states of gold cations with respect to Zr\textsuperscript{4+} can also be stabilized directly by oxygen vacancies. We have therefore considered a situation where two surface Zr sites (50% of the surface cationic

---

**Table 2** Vacancy formation energies (VFE) at the pure and the Au-substituted (111) surface of cubic zirconia

<table>
<thead>
<tr>
<th>Reduction process</th>
<th>Description of resulting surface</th>
<th>VFE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Zr_{11}AuO_{23}OH^{(\text{slab})} \rightarrow Zr_{11}AuO_{22}\square OH^{(\text{slab})} + \frac{1}{2}O_2^{(\text{gas})})</td>
<td>Ou vacancy</td>
<td>5.83</td>
</tr>
<tr>
<td>(Zr_{11}AuO_{23}OH^{(\text{slab})} \rightarrow Zr_{11}AuO_{22}\square OH^{(\text{slab})} + \frac{1}{2}O_2^{(\text{gas})})</td>
<td>O_d vacancy</td>
<td>5.42</td>
</tr>
<tr>
<td>(Zr_{11}AuO_{23}OH^{(\text{slab})} \rightarrow Zr_{11}AuO_{22}\square OH^{(\text{slab})} + \frac{1}{2}O_2^{(\text{gas})})</td>
<td>O_d vacancy near Au</td>
<td>1.24</td>
</tr>
<tr>
<td>(Zr_{11}AuO_{23}OH^{(\text{slab})} \rightarrow Zr_{11}AuO_{22}\square OH^{(\text{slab})} + \frac{1}{2}O_2^{(\text{gas})})</td>
<td>Ou vacancy near Au, cis respect to OH</td>
<td>1.31</td>
</tr>
<tr>
<td>(Zr_{11}AuO_{23}OH^{(\text{slab})} \rightarrow Zr_{11}AuO_{22}\square OH^{(\text{slab})} + \frac{1}{2}O_2^{(\text{gas})})</td>
<td>Ou vacancy near Au, trans respect to OH</td>
<td>0.97</td>
</tr>
<tr>
<td>(Zr_{11}AuO_{23}OH^{(\text{slab})} \rightarrow Zr_{11}AuO_{22}\square OH^{(\text{slab})} + \frac{1}{2}O_2^{(\text{gas})})</td>
<td>O_d vacancy far from Au</td>
<td>1.19</td>
</tr>
<tr>
<td>(Zr_{11}AuO_{23}OH^{(\text{slab})} \rightarrow Zr_{11}AuO_{22}\square OH^{(\text{slab})} + \frac{1}{2}O_2^{(\text{gas})})</td>
<td>O_d vacancy far from Au</td>
<td>1.04</td>
</tr>
<tr>
<td>(Zr_{11}AuO_{23}OH^{(\text{slab})} \rightarrow Zr_{11}AuO_{22}\square OH^{(\text{slab})} + \frac{1}{2}O_2^{(\text{gas})})</td>
<td>2 O_d vacancies as in Fig. 7</td>
<td>0.58</td>
</tr>
</tbody>
</table>

---

This journal is © The Royal Society of Chemistry 2009

*J. Mater. Chem., 2009, 19, 710–717 | 713*
sites) are substituted by two Au centres, with the simultaneous creation of an oxygen vacancy, where the expected oxidation state of both gold ions is thus Au(III).

We have compared the stabilities of several configurations with different positions of the vacancy with respect to the two gold ions (in our model cell all the distributions of the two Au atoms at the cationic sites of the surface are symmetrically equivalent): (i) O_v between the two Au sites, (ii) O_v coordinated to only one Au, (iii) O_d between the two Au sites, and (iv) O_d coordinated to only one Au. The relative energies of the fully relaxed structures are given in Table 4.

The oxygen vacancy produces a distortion of the surface that is energetically expensive. The rearrangement of the surface after the substitution can be observed in Fig. 6, where the most stable configuration (iii) for the composition Zr10Au2O23 is shown. Both Au centres tend to adopt a square planar coordination, as expected for Au(III) species, with O–Au–O angles of 74.1°, 94.4°, 87.4° and 103.6° at one centre and 78.7°, 99.3°, 80.0° and 102.1° at the other. The two Au, 3.68 Å apart from each other, are linked by one O_v, but not one O_d. According to the Bader analysis, they have charges of +1.19 e and +1.15 e, very close to the value found for the gold ion in the system with composition Zr11AuO23OH.

As in the case of the proton-compensated substitution, the doping of the (111) surface of cubic zirconia with gold compensated by oxygen vacancies is energetically much more favourable than the same process in the bulk. A calculation of a bulk supercell with identical composition Zr10Au2O23, cell orientation and defect configuration as the surface, yielded an increase in energy of ~2.7 eV compared to the surface configurations.

The relative stability of the vacancy-compensated structure with respect to the proton-compensated structure clearly depends on the presence of water or/and other proton sources. Water molecules, for example, can dissociate at the oxygen vacancy and form two hydroxy groups, one of them involving an oxygen ion already present in the surface:

![Fig. 4](image_url) The most stable configuration of the (Au,H)/Zr substituted zirconia (111) surface, with one oxygen vacancy (Zr11AuO22OH). (a) Plan view, (b) side view.

![Fig. 5](image_url) Projection of the electronic density of states (DOS) on the Au 5d orbitals before (top) and after (bottom) the formation of an oxygen vacancy at the gold-doped zirconia surface.

---

Table 3 | Formal oxidation states and Bader charges of Au species and shortest Au–O distances in the most stable Au-substituted zirconia surface for each composition studied in this work. Au–O distances not reported here are all longer than 2.5 Å

<table>
<thead>
<tr>
<th>Slab composition</th>
<th>Formal state</th>
<th>q_B[Au] (e)</th>
<th>d[Au–O] (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr11AuO23OH</td>
<td>Au(m)</td>
<td>+1.11</td>
<td>2.07, 2.07, 2.16, 2.16</td>
</tr>
<tr>
<td>Zr11AuO22□OH</td>
<td>Au(i)</td>
<td>+0.46</td>
<td>2.06, 2.06</td>
</tr>
<tr>
<td>Zr10Au2O23□</td>
<td>Au(m)</td>
<td>+1.19</td>
<td>1.99, 2.05, 2.06, 2.17</td>
</tr>
<tr>
<td></td>
<td>Au(m)</td>
<td>+1.15</td>
<td>1.98, 2.06, 2.09, 2.12</td>
</tr>
<tr>
<td>Zr10Au2O22□2</td>
<td>Au(m)</td>
<td>+1.27</td>
<td>2.00, 2.0, 2.13, 2.13</td>
</tr>
<tr>
<td></td>
<td>Au(i)</td>
<td>+0.44</td>
<td>2.11, 2.11</td>
</tr>
</tbody>
</table>

---

Table 4 | Relative energies of different configurations of two gold cations and one oxygen vacancy at the (111) surface and the bulk of cubic zirconia

<table>
<thead>
<tr>
<th>Zr10Au2O23□ configuration</th>
<th>E (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) O_v vacancy coordinated to 2 Au</td>
<td>0.27</td>
</tr>
<tr>
<td>(ii) O_v vacancy coordinated to 1 Au</td>
<td>0.26</td>
</tr>
<tr>
<td>(iii) O_d vacancy coordinated to 2 Au</td>
<td>0</td>
</tr>
<tr>
<td>(iv) O_d vacancy coordinated to 1 Au</td>
<td>0.16</td>
</tr>
<tr>
<td>O_v vacancy coordinated to 2 Au, in bulk</td>
<td>2.69</td>
</tr>
</tbody>
</table>

---

This journal is © The Royal Society of Chemistry 2009
We can estimate the energy balance for this reaction from our previous calculations:

$$\Delta E = 2E[Zr_{10}Au_{2}O_{23}(OH)] - (E[Zr_{10}Au_{2}O_{22}OH_{2}^{\text{slab}}] + E[Zr_{11}O_{23}] + E[H_{2}O])$$

which results in a negative value ($-0.88$ eV). Although in this approximation we have neglected the interaction between the two (Au,OH) pairs, this is only likely to increase even further the exothermic character of this reaction due to the formation of inter-hydroxy hydrogen-bonding. Since the chemical potential of water increases with its partial pressure in the gas phase, at each temperature there is an $H_{2}O$ partial pressure limit above which the free energy change of this reaction will also be negative, and the hydroxylation of the Au-doped surface will be thermodynamically more stable than the Au-doped surface with uncovered oxygen vacancies.

We will now continue the discussion of the non-hydroxylated doped surface and consider the formation of another oxygen vacancy at the $Zr_{10}Au_{2}O_{23}^{\square}$ surface, following the reaction:

$$Zr_{10}Au_{2}O_{23}^{\square}_{\text{slab}} + H_{2}O_{(\text{gas})} \rightarrow Zr_{10}Au_{2}O_{22}OH_{2}^{\square}_{\text{slab}}$$

In order to find the optimum geometry for the $Zr_{10}Au_{2}O_{22}^{\square}$ composition, we performed energy minimization calculations starting from all the different configurations of a pair of O vacancies with respect to the two Au atoms. Each of the 4 configurations with one vacancy considered above can generate 7 configurations of two vacancies by removing an oxygen atom from each of the remaining O and O$_{2}$ surface sites, i.e. a total of 28 initial configurations. After relaxation of all of them, the most stable configuration is the one shown in Fig. 7. If we consider the most stable configurations for both reactants and products in eqn (5), the vacancy formation energy at this surface is only $0.58$ eV, which again shows that Au(III) centres at the zirconia surface are highly reducible. This vacancy formation energy is actually lower than that calculated for the proton-compensated doped surface. However, we should stress that this low energy has not been obtained assuming the pre-existence of a non-hydroxylated doped surface, which, as discussed above, might not be the most thermodynamically favourable situation in the presence of water.

The configuration shown in Fig. 7 contains one Au(III) and one Au(I) centre, clearly distinguishable from each other by the coordination: square planar for Au(III) and nearly linear for Au(I), and the analysis of the electronic DOS confirms these assignments. Also the Bader analysis (Table 3) allows a clear distinction between the two states, with the first Au ion having nearly three times the positive charge of the second. The distinction between different oxidation states of the same species in one system is usually a significant challenge for first-principle calculations, so it is reassuring that our calculations are able to properly describe the mixed valence situation.

IV. Conclusions

We have presented a density functional theory investigation of the redox properties of the gold-substituted zirconia (111)
surface. Our results show that, regardless of the mechanism of charge compensation, gold dopants are more likely to accumulate at the surface than migrate into the bulk. The incorporation of gold as Au(III) species in the cationic positions of the oxide surface can be stabilised by the formation of hydroxy groups located around the substituted site, or by an oxygen vacancy which is preferentially located between two neighbouring gold atoms. The second situation can revert to the former one in the presence of water, and this hydroxylation reaction is an exothermic process.

Our study also shows that, while un-doped zirconia surfaces are difficult to reduce and therefore do not participate in the mechanism of oxidation reactions, Au-doped ZrO$_2$ surfaces can be reduced easily due to the occurrence of Au(III) → Au(I) transitions. The energy of vacancy formation at a zirconia surface with Au(III) cations is very low (~1 eV), which allows the involvement of surface oxygen species in catalytic reaction mechanisms.

The vacancy formation energies associated with Au(III) → Au(I) transitions are also considerably lower than those associated with cation reduction in other, more reducible oxides. For example, the cost of vacancy formation at the CeO$_2$(111) surface, accompanied by two Ce$^{4+}$ → Ce$^{3+}$ transitions, has been estimated at ~3 eV from DFT calculations by Yang et al.~\cite{Yang2006}, while other authors have calculated even higher values. Similar vacancies can be the predominant mechanism in the formation of oxygen vacancies, while the reducibility of the oxide support will be less important. Recent experimental observations seem to support these conclusions: Rossignon et al.~\cite{Rossignon2006} have found similar activities of Au/ZrO$_2$, Au/Al$_2$O$_3$ and Au/TiO$_2$ catalysts in the low-temperature preferential CO oxidation in the presence of hydrogen, while Comotti et al.~\cite{Comotti2005} have indicated that, although the choice of support does affect the activity of gold catalysts in low-temperature CO oxidation, the activities do not correlate with the reducibilities of the oxides employed as catalyst supports.

Acknowledgements

Financial support from EPSRC grant EP/C51744X, the Spanish MICINN, grant MAT2008-04918, and the Ramón y Cajal program (awarded to N.C.H.) is acknowledged. Computer resources on HPCx were provided via our membership of the Materials Chemistry HPC Consortium and funded by EPSRC (portfolio grant EP/D504872/1).

References