Experimental and DFT studies of gold nanoparticles supported on MgO(111) nano-sheets and their catalytic activity

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A wet chemical preparation of MgO with the (111) facet as the primary surface has recently been reported and with alternating layers of oxygen anions and magnesium cations, this material shows unique chemical and physical properties. The potential to utilize the MgO(111) surface for the immobilization of metal particles is intriguing because the surface itself offers a very different environment for the metal particle with an all oxygen interface, as opposed to the typical (100) facet that possesses alternating oxygen anion and magnesium cation sites on the surface. Gold nanoparticles have demonstrated a broad range of interesting catalytic properties, but are often susceptible to aggregation at high temperatures and are very sensitive to substrate effects. Here, we investigate gold-supported on MgO(111) nanosheets as a catalyst system for the aerobic oxidation of benzyl alcohol. Gold nanoparticles deposited on MgO(111) show an increased level of activity in the solvent-free benzyl alcohol aerobic oxidation as compared to gold nanoparticles deposited on a typical MgO aerogel. TEM studies reveal that the gold nanoparticles have a hemispherical shape while sitting on the main surface of MgO(111) nanosheets, with a large Au–MgO interface. Given that the gold nanoparticles deposited on the two types of MgO have similar size, and that the two types of unmodified MgO show almost the same activities in the blank reaction, we infer that the high activity of Au/MgO(111) is due to the properties of the (111) support and/or those of the gold–support interface. To understand the binding of Au on low-index MgO surfaces and the charge distribution at the surface of the support, we have performed density functional theory (DFT) calculations on all low-index MgO substrates (with and without gold), using a model Au10 cluster. Due to similar lattice constants of Au(111) and MgO(111) planes, the Au cluster retains its structural integrity and binds strongly on MgO(111) with either oxygen or magnesium termination. Furthermore, we have found that for the (001) and (110) substrates the charges of the ions in the top surface layer have similar values as in bulk MgO, but that on (111) surfaces these charges are significantly different. This difference in surface charge determines the direction of the electronic transfer upon adsorption of gold, such transfer occurring so as to restore the bulk MgO charge values. Using the results from theoretical calculations, we provide an explanation of our observations of increased catalytic activity in the case of the Au/MgO(111) system.

Introduction

Alcohol and polyol oxidations are important processes in industrial chemistry and supported gold nanoparticles have been reported to be very effective in the oxidation of alcohols, including diols in the presence of bases. Subsequent studies found that gold catalysts can also be used in the oxidation of sugars, glucose, and sorbitol. In those reactions, the choice of supporting material for gold catalysts is an interesting topic. Rossi and co-workers initially found that unsupported colloidal gold particles are as active as Au nanoparticles supported on active carbon under the same conditions in the oxidation of glucose to gluconic acid. PVP-stabilized gold nanoparticles also show good catalytic activity in the oxidation of alcohol.

Then, Corma and co-workers proposed that the support of Au/CeO2 catalysts can help stabilize a reactive peroxy intermediate from O2, and therefore can enhance the activity...
of gold catalysts in the selective oxidation of alcohols to aldehydes/ketones and in the oxidation of aldehydes to acids. Recently, the Hutchings research group found that the Au/Pt alloy supported on TiO2 was a highly active catalyst for the oxidation of benzyl alcohol, cinnamyl alcohol, and vanillyl alcohol,14 inferring that the type of support is important given the fact that TiO2 is one of the best supports of gold catalysts in the CO oxidation.

The effects of the gold catalyst support on CO oxidation are well studied. It is generally accepted that various preparation routes lead to catalysts with different activities.15–17 and that gold catalysts supported on reducible metal oxides are typically more active than those supported on non-reducible metal oxides.18–24 The activity of Au/MgO catalysts can be enhanced by increasing the number of corner and edge sites in MgO structures such as nanocubes.25 In a DFT study, Rodriguez et al.26 found that the Au–TiO2 contact can enhance the chemical activity of the gold nanoparticles by electronic transfer. Electrons from the vacancies of the support transfer to the gold nanoparticles through the contact and make them electronically rich.27 Further calculations showed that O2 adsorbs preferentially and readily dissociates at the interface.28 In the case of Au/MgO, Molina and Hammer29,30 assumed that MgO has an active role in the bonding and activation of adsorbates bound to Au and the most active site was formed at the Au–MgO interface whereby several low coordinated Au atoms along with Mg2+ cations can interact simultaneously with an adsorbate.

Our research group has reported the synthesis of MgO nanosheets with large surface area (~200 m2 g–1) and with the polar (111) facet as the primary surface; such nanosheets have shown high activity in the Claisen–Schmidt condensation of benzaldehyde.31 This material also offers possibilities to study support effects, particularly the interaction of a nano-scale metal particle with the polar MgO(111) surface; such a polar surface represents a different environment than the more typical MgO(100) facet that contains alternating Mg cations and O anions on the surface. Investigations of the interaction between a catalyst and the MgO(111) substrate, as a representative support with a tailored surface structure, are important for determining the potential of these interfaces for catalytic applications.

In this work, we deposited 0.63 wt% gold nanoparticles on the MgO(111) nanosheets and tested their activity in the solvent-free aerobic oxidation of benzyl alcohol. N2 adsorption experiments show that the MgO(111) nanosheets aggregated together during the deposition of gold but maintained their plate-like morphology. For comparison, 0.72 wt% gold nanoparticles deposited on commercially available MgO aerogel–MgO(NanoActive) were also prepared and used to catalyze the reaction. TEM and XRD show that the gold nanoparticles deposited on both MgO systems have similar size. These two types of MgO supports also show similar performance in the oxidation reaction in the absence of gold. However, the gold nanoparticles deposited on MgO(111) show a significantly higher activity than those deposited on MgO(NanoActive) by a factor of 4.8 at 120 °C. In order to understand the effects of the substrate, we also performed DFT structural relaxations of small Au clusters on MgO substrates with several different orientations. From the DFT calculations, we have found marked differences between the structural integrity of the cluster, binding energy, and charge transfer to/from the cluster for the (001) and (110) substrates when compared to MgO(111). We have gained insight into the structural characteristics of the cluster from comparing surface lattice constants and interatomic distances at the interface, and rationalized the charge transfer in terms of the tendency of the (111) top surface layer to achieve a charge state similar to that in bulk MgO.

Methods and procedures

Materials and instruments

MgO(NanoActive) was obtained commercially from Nano Scale, Inc. All other reagents were from Sigma-Aldrich and were used as received. Ultrapure deionized water (Continental Water Systems) was used throughout the experiments. The transmission electron microscopy (TEM) studies were performed with a FEI CM200 operated at 200 kV. The samples were prepared by spreading an ethanolic suspension on carbon coated copper grids. BET and isothermal measurements were performed on a Micromeritics ASAP 2020 surface area and porosity analyzer. X-Ray diffraction was acquired on a Siemens D 5000 diffractometer (Cu Kα, λ = 1.5406 Å). Calcination was performed in a tubular furnace with a ramping speed of 3 K per minute.

Synthesis of MgO(111) nanosheets

The MgO(111) nanosheets were prepared with a modified sol–gel method using 4-methoxy-benzyl alcohol to direct the formation of the (111) facet.31 In a typical synthesis of MgO(111) nanosheets, 1.0 g thoroughly cleaned Mg ribbon was suspended in absolute methanol overnight under the protection of an argon atmosphere to form magnesium methoxide. Then 2.27 g 4-methoxy-benzyl alcohol was added to the solution and stirring maintained for 5 hours before adding a mixture of 1.48 ml H2 O and 30 ml methanol to form the sol. After 12 hours of stirring, the sol was transferred into a Parr autoclave and supercritically dried by heating to 265 °C for 12 hours then venting. The obtained aerogel was calcined 6 hours at 500 °C to remove the OH group. The final product is an ultrafine white powder.

Preparation of Au/MgO(111) and Au/MgO(NanoActive)

To avoid the reconstruction of the MgO(111) facet, the deposition of gold was performed in absolute ethanol. Typically, 0.2 g MgO(111) nanosheets was suspended and stirred over night in 10 ml 1.25 mM HAuCl4/ethanol solution for the deposition of gold. The formed pink powder was separated by centrifuge and re-suspended in 10 ml fresh ethanol. This process was repeated 3 times to remove the unsupported gold particles in solution. Then the powder was dried at 120 °C and denoted as Au/MgO(111). For the purpose of comparison, gold was also deposited on 0.2 g calcined commercially available MgO aerogel (MgO NanoActive) with the same procedure and denoted as Au/MgO(NanoActive). During the preparation, we observed that the deposition of
gold (color change) on MgO(111) was significantly faster than the deposition on MgO(NanoActive). It was further noted that the surface area of the MgO(111) and MgO(NanoActive) decreased during the deposition of gold. For a better comparison, MgO(111) and MgO(NanoActive) used in control experiments were also treated with the same gold deposition procedure but without the HAuCl₄. They are denoted as MgO(111)* and MgO(NanoActive)* in this report.

Benzyl alcohol oxidation

The liquid phase oxidation of benzyl alcohol over the supported Au catalysts was carried out in a magnetically stirred 25 ml three-neck flask with oil bath heating and reflux condenser, under the following general reaction conditions: reaction mixtures = 5 ml benzyl alcohol + 5 mg Au/MgO catalysts, reaction time = 6 hours, temperature varied from 100 °C to 140 °C in different experiments, 99.9% oxygen was bubbled into the reaction mixture at the speed around 2 ml min⁻¹. The conversion and selectivity are calculated according to GC analysis.

Details of the DFT calculations

We have performed structural relaxations at the level of density functional theory (DFT) using the VASP simulation package. The calculations were done in the framework of the generalized gradient approximation (GGA), using projector-augmented wave pseudopotentials and the Perdew–Burke–Ernzerhof exchange-correlation energy. We have used MgO surface slabs with the (001), (110), and (111) orientations, with in-plane dimensions of at least 10 Å compatible with periodic boundary conditions. The thickness of the slabs in the computational supercells is 5, 7, and 7 layers for (001), (110), and (111) slabs, respectively; of these, the bottom two atomic layers were kept fixed during the structural relaxations to simulate the underlying bulk. The rather large in-plane dimensions of these slabs have been chosen in order to ensure that the interactions between the periodic images of the substrate-supported Au cluster are reasonably small. With this choice, we can only afford to treat small nanoparticles and have chosen a pyramidal Au₁₀ cluster as the model to investigate. This Au cluster has 6, 3, and 1 atoms on the bottom, middle, and top layers, respectively, with the atoms arranged according to the fcc stacking. The Au₁₀ cluster is actually larger than clusters used in some recent works, same size as in others, and is consistent with reports that pyramidal shapes are more stable on MgO surfaces than nanorod models. The MgO lattice constant in our simulations was set at the experimental value of a = 4.2 Å. In the case of (111)-oriented surfaces, we have relaxed (non-stoichiometric) slabs terminated with the same atomic species on both faces—either with O or with Mg; the use of (111) slabs with the same termination on both faces has enabled us to perform ionic relaxations without employing dipole corrections. In all calculations, the vacuum spacing was set to 15 Å, and we used a plane-wave cutoff energy of 450 eV and sampled the Brillouin zone only at the Γ point. The structural relaxations were terminated when the total energy of the slab converged to 0.001 eV, which is sufficient for comparing the structure of the cluster on the different MgO substrates and estimate the charge transfer. We have relaxed clean MgO slabs, as well as slabs with an Au₁₀ cluster on them in order to calculate the spatial variation of the electron density due to the presence of the cluster. The main goal of the simulations is to assess which of the low-index orientations of the MgO may lead to a superior catalytic activity upon adsorption of gold, and thus to provide an explanation for our experimental observations. To this end, we have also performed a Bader analysis of the charge at MgO surfaces and at the Au/MgO interfaces. Charge densities are readily output by the VASP package and have been used to calculate charge transfer densities, which were plotted using the XCrySDen visualization package.

Table 1  N₂-adsorption data and Au content of different catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>S_{BET}/m² g⁻¹</th>
<th>Au content (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO(Nanoactive)</td>
<td>230.00</td>
<td>—</td>
</tr>
<tr>
<td>MgO(111)</td>
<td>146.06</td>
<td>—</td>
</tr>
<tr>
<td>Au/MgO(NanoActive)</td>
<td>73.81</td>
<td>0.72</td>
</tr>
<tr>
<td>Au/MgO(111)</td>
<td>32.53</td>
<td>0.63</td>
</tr>
</tbody>
</table>

* The surface area S_{BET} is calculated by the BET method.  The Au content was measured by ICP.

Results

Characterization of Au/MgO(111) catalysts

The specific surface area (S_{BET}) for Au/MgO(111) is significantly smaller than that of the parent materials, as shown in Table 1. The isotherms in Fig. 1 show that the adsorption at low and medium pressure (P/P₀ = 0–0.8) was not observed after the deposition of gold; this indicates the loss of micro- and meso-pores, which is likely due to the aggregation of MgO(111) nanosheets during the drying process. However, an H₃ type hysteresis loop was found in the isothermal pattern of Au/MgO(111) as well as that of MgO(111). According to the IUPAC classification, the H₃ hysteresis loop shows that Au/MgO(111) maintained the pore shape of the parent structure.
MgO(111), slit-shaped pores, which is the non-rigid aggregation of plate-like particles.

Fig. 2 shows the wide-angle X-ray diffraction (XRD) patterns of gold catalysts supported on MgO(111) and MgO(NanoActive). The two catalysts have almost the same diffraction pattern, which indicates that they have similar gold content and gold particles size. Calculated by the Scherrer equation, the size of gold particles is around 10 nm for both Au/MgO(111) and Au/MgO(NanoActive).

The MgO(111) nanosheets were characterized by HR-TEM in our previous work. The nanosheets are typically ~50 nm in diameter, but only 3–5 nm thick. By indexing the lattice spacing of the side surface, we can conclude that the main surface of those nanosheets are (111) facets. After the deposition of gold, the MgO(111) nanosheets were found to aggregate, although they maintain a sheet-like structure in the overview TEM image (Fig. 3A). The deposited gold nanoparticles had various sizes; we observed a few large particles (of ~20 nm diameter), and many smaller ones (2–5 nm). In the HR-TEM image (Fig. 3B), the sheet-like structure is clearly shown. We study the nanosheets standing at the edge of the sample, i.e., those marked by red arrows in Fig. 3B. These nanosheets are 3–5 nm in thickness and 20–30 nm in diameter, similar to their parent MgO(111) materials. From the N2 adsorption and TEM results, we find that MgO(111) nanosheets maintained their morphology after the deposition of gold.

The ‘standing’ nanosheets make it possible to observe the interface between gold nanoparticles and MgO(111) nanosheets. However, it is difficult to find that interface considering that the gold content is low (0.63%) and that most MgO(111) nanosheets are lying flat on the grids. Two gold nanoparticles around 10 nm (labeled 1 and 2) can be found in Fig. 3B. Particle 2 is clearly situated on a ‘standing’ MgO(111) nanosheet around 5 nm thick, while particle 1 is located at the edge of the aggregation. Those two Au particles are approximately hemispherical particles and have relatively large contact areas with the MgO(111) nanosheets. Though we were unable to observe smaller gold particles (3–5 nm) on the ‘standing’ MgO(111) nanosheets by TEM, we believe they would have similar shapes as with those of the larger particles shown in Fig. 3B.

**Aerobic oxidation of benzyl alcohol**

The oxidation of benzyl alcohol, which is a model reaction for primary alcohol oxidation, was widely used to study the activity of gold catalysts. The Hutchings group has recently investigated Au/Pd alloys supported on TiO2 to achieve high conversion.14 Their study shows that the conversion of benzyl alcohol increases almost linearly with time and that the selectivity of benzaldehyde decreases with time. The key to evaluate different catalysts is to find a reaction time in which the reaction maintains an acceptable selectivity and then the conversion can be compared. When using Au/TiO2, Enache et al.14 achieved a conversion of ~10% with a selectivity of 75% for 6 hours at 100 °C. Other benzyl alcohol oxidation studies that use gold catalysts supported on TiO2,3 carbon,4 and urania41 also report a reaction time of 5–6 hours to evaluate the catalysts. In order to be able to compare our work with previous reports, we also use 6 hours as reaction time to assess the influence of the surface structure of supporting MgO on the catalytic activities in benzyl alcohol oxidation. All reactions were performed in the absence of solvent, with
6 hours reaction time. To determine the comparative performance of catalysts at different temperatures, the reactions were run at 100 °C, 120 °C and 140 °C. Results show that the catalytic oxidation of benzyl alcohol under the above conditions gives reasonable selectivity of benzaldehyde (75% to 93%), except the reaction catalyzed by Au/MgO(111) at 140 °C, which allows us to evaluate the activities of catalysts by conversion. No detectable amounts of benzene or toluene were observed in the reactions. The byproduct is mainly benzyl benzoate rather than benzoic acid indicating either the immediate esterification between benzoic acid and benzyl alcohol over the systems, or that oxidation occurs directly on the hemiacetal [PhCH(OH)OCH2Ph] formed from benzaldehyde and benzyl alcohol without forming benzoic acid. The catalysis results are shown in Table 2.

In the benzyl alcohol oxidation reaction at 120 °C, treated MgO(111) and MgO(NanoActive) without gold (see the “Methods and procedures” section) exhibit very similar performances with around 2.9–3.1% conversion in 6 hours with 80% selectivity to benzaldehyde. After the deposition of gold, Au/MgO(111) gave a 14.75% conversion, nearly 5 times higher than that of MgO(111), while maintaining the same selectivity. Au/MgO(NanoActive) shows a performance similar to that of the unmodified MgO(NanoActive). The same trend was also shown in the results of reactions operated at 100 °C and 140 °C. At higher temperature, better conversion can be obtained from the Au/MgO(111) catalyst however the benzaldehyde selectivity also drops dramatically with the temperature because of the over oxidation of benzyl alcohol. To summarize, the results in Table 2 show that the Au/MgO(111) system has a significantly higher activity in the oxidation of benzyl alcohol than the Au/MgO(NanoActive) and the MgO(111) systems at our experimental conditions. We believe that the high activity of Au/MgO(111) is due to the partial removal of the hydrogen passivation from the MgO(111) support (which has significant hydroxyl coverage), as well as to the electronic transfer that occurs at the Au–MgO(111) interface (see details in “Discussion” section).

Table 2 Comparative data for solvent-free oxidation of benzyl alcohol. Results were obtained for the oxidation of benzyl alcohol after 6 hours of reaction. The oxidation was carried out by bubbling the oxygen into the reaction mixture (5 ml benzyl alcohol and 5 mg catalysts) at different temperatures.

<table>
<thead>
<tr>
<th>Temperature/°C</th>
<th>Catalysts</th>
<th>Conversion (mol%)</th>
<th>Selectivity to benzaldehyde (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>MgO(NanoActive)*</td>
<td>1.03</td>
<td>80.62</td>
</tr>
<tr>
<td></td>
<td>MgO(111)*</td>
<td>1.21</td>
<td>83.21</td>
</tr>
<tr>
<td></td>
<td>Au/MgO(NanoActive)</td>
<td>1.17</td>
<td>70.45</td>
</tr>
<tr>
<td></td>
<td>Au/MgO(111)</td>
<td>6.55</td>
<td>92.96</td>
</tr>
<tr>
<td>120</td>
<td>MgO(NanoActive)*</td>
<td>2.89</td>
<td>80.47</td>
</tr>
<tr>
<td></td>
<td>MgO(111)*</td>
<td>3.12</td>
<td>82.01</td>
</tr>
<tr>
<td></td>
<td>Au/MgO(NanoActive)</td>
<td>3.05</td>
<td>78.21</td>
</tr>
<tr>
<td></td>
<td>Au/MgO(111)</td>
<td>14.71</td>
<td>82.44</td>
</tr>
<tr>
<td>140</td>
<td>MgO(NanoActive)*</td>
<td>3.71</td>
<td>82.14</td>
</tr>
<tr>
<td></td>
<td>MgO(111)*</td>
<td>3.62</td>
<td>76.37</td>
</tr>
<tr>
<td></td>
<td>Au/MgO(NanoActive)</td>
<td>3.59</td>
<td>76.84</td>
</tr>
<tr>
<td></td>
<td>Au/MgO(111)</td>
<td>17.23</td>
<td>56.66</td>
</tr>
</tbody>
</table>

*a MgO materials were subjected to the same procedure as the Au/MgO catalysts, but without gold.

Before studying the gold cluster on the surface, it is a useful test to calculate the charge density for the substrates considered. Fig. 4 shows such charge density for the substrates that expose oxygen atoms in the top layer, i.e. (001), (110), and O-terminated (111); these results are consistent with previous DFT reports of MgO surfaces.44,45 We have also performed a Bader analysis38 of atomic charges for each of the substrates in the absence of Au. In the bulk, the O and Mg atoms have charges of 7.65 e and 0.35 e, respectively. This result is close to other reports,46,47 with the small differences attributable to our use of the experimental value of the MgO lattice constant instead of the theoretical one. On the (001) surface, interestingly, O and Mg assume the same charges as in the bulk. The situation is very similar in the case of MgO(110), in which the top layer O and Mg have charges of 7.60 e and 0.40 e, respectively. In the (111) surfaces, however, the charges at the surface are significantly different than those in the bulk indicating that these surfaces can be very reactive. In the case of the O-terminated (111) surface, the first (second) oxygen layer has 6.94 e (7.53 e) per atom, i.e., fewer electrons than in the bulk configuration. Similarly, on the Mg-terminated (111) surface, the first (second) magnesium layer has 1.0 e (0.35 e) per atom, i.e. more electrons than Mg has in bulk MgO. This suggests that during chemisorption processes on the

![Fig. 4 Cross-sections through the electron density at various clean MgO surfaces: (a) (001), (b) (110), and (c) O-terminated (111). The planes of the cross-sections were selected so as to show, in each case, the largest spread of the electron distributions around the surface oxygens. The range of electron density values for the isocontours is the same in all figures, 0.1–1.0 Å².](View Online)
(111)-O surface, the oxygen atoms may acquire electrons from the adsorbates in order to approach or attain the bulk charge value; for the same reason, the Mg atoms on the (111)-Mg surface should tend to donate electrons to the adsorbates. Such a trend has been previously reported for Pd on MgO(111). As we shall see towards the end of this section, this trend is confirmed by our Bader analysis of the Au_{10} cluster on MgO(111).

We have first relaxed the binding and stability of the model gold clusters on each of the surfaces considered. These relaxations lead to various structural deformations for the Au clusters and for the MgO support. Such deformations occur mainly because of the strain mismatch between the cluster and the substrate. Specifically, the cluster relaxed in the absence of any substrate has an average Au–Au bond length of 2.74 Å, while MgO(001) has atomic spacings of 2.1 Å (in both directions in the plane of the surface), MgO(110) has spacings of 2.1 Å and 2.97 Å, and for MgO(111) the atomic spacings at the surface are 2.97 Å for the two in-plane directions. This means that an Au(111)-facetted cluster supported on MgO(001) or on MgO(110) deforms significantly. Indeed, we have found that Au_{10} clusters on Mg(001) and on MgO(110) relaxed starting from different initial configurations experience large deformations and tend to decouple from the surface, at least partially. In the case of (111), however, the atomic spacings at the surface favor much smaller deformations of the cluster both in the case of Mg- and O-terminated slabs, and the cluster remains on the substrate. We have tabulated the nearest-neighbor distances between the interfacial Au atoms and their nearest neighbors. In the case of (001) and (110) surfaces, the cluster breaks away from the substrate, at least partially, and consequently there is a very small number of Au–Mg and Au–O distances that contribute to the averages in Table 3. The results in Table 3 are consistent with strong binding of the cluster on (111) surfaces, because on these particular surfaces the Au–O and Au–Mg average distances (2.05 and 2.60 Å, respectively) are the smallest that are obtained from an averaging over a large number of cluster–substrate bonds. Our calculations of the binding energies of Au_{10} to MgO surfaces yield the values of 3.190, 5.795, 17.887, 14.740 eV for the binding of the cluster to (001), (110), (111)-O, and (111)-Mg, respectively. The significantly binding energies on (111) surfaces are consistent with the direct observations of the structures shown in Fig. 5 (and the data in Table 3), which clearly show epitaxy on the substrate and integrity of the cluster for the Au/MgO(111) systems, and partial debonding accompanied by strong deformations of the clusters on (001) and (110).

In order to bring direct simulation evidence of electronic transfer between gold and the MgO support, we analyze the variation of charge density caused by the Au cluster. This change in the electron density at any point \(r\), \(\Delta n(r)\), has been calculated via

\[
\Delta n(r) = n_{\text{surf+cluster}}(r) - n_{\text{surf}}(r) - n_{\text{cluster}}(r),
\]

where \(n_{\text{surf+cluster}}(r)\) is the electronic density of the relaxed surface and cluster system, \(n_{\text{surf}}(r)\) is associated with the substrate kept at the relaxed positions of the Au/MgO system but in the absence of the cluster, and the last term is the electron density associated with the deformed cluster alone (i.e. without substrate). The results of this analysis are shown in Fig. 5 in the form of isosurfaces of \(\Delta n(r)\) drawn at values of \(\pm 0.1\) electrons Å\(^{-3}\). As shown in Fig. 5b and c by white arrows, in the case of (001) and (110) surfaces, the transferred electron density is small and localized at a couple of surface atoms. In contrast, Fig. 5d and e clearly show large charge density variations at the gold–substrate interface. We have also determined the overall charge transfer between the cluster and the substrate via a Bader charge analysis. Using such analysis, we have found that the Au cluster gains a total of 0.68 e on Mg(001), and 1.08 e on Mg(110). These values are small because of the non-planar interface between Au and substrate and of the large deformations of the cluster. However, on the (111)-O surface, the Au cluster loses 3.95 e to the substrate, while on (111)-Mg the cluster gains 7.15 e from the substrate; this substantial electronic transfer is localized mostly in the six Au atoms at the interface. Therefore, the calculated overall charge transfer on the (111) surfaces indicates that the oxygen atoms tend to attain their bulk charge value of 7.65 e by taking electrons from the Au cluster. Similarly, the top layer Mg atoms on (111)-Mg, which were determined to have excess electrons in the absence of gold, donate most of these electrons to the Au cluster and

### Table 3

Analysis of the interatomic distances at the Au–MgO interfaces shown in Fig. 5. The average, minimum, and maximum distances are measured from any of the six atoms that make up the base of the Au_{10} model cluster to its nearest Au, Mg, or O neighbors.

<table>
<thead>
<tr>
<th>MgO support</th>
<th>Interatomic distance</th>
<th>Average nearest-neighbor distance/Å</th>
<th>Minimum and maximum values (Å/Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(001)</td>
<td>Au–Au 2.70</td>
<td>2.64/2.93</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Au–O 3.06</td>
<td>2.23/3.73</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Au–Mg 3.35</td>
<td>3.04/3.65</td>
<td></td>
</tr>
<tr>
<td>(110)</td>
<td>Au–Au 2.70</td>
<td>2.77/4.14</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Au–O 2.70</td>
<td>2.06/3.15</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Au–Mg 2.74</td>
<td>2.67/2.83</td>
<td></td>
</tr>
<tr>
<td>(111)-O</td>
<td>Au–Au 3.06</td>
<td>3.03/3.08</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Au–O 2.05</td>
<td>2.03/2.07</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Au–Mg 3.10</td>
<td>3.05/3.30</td>
<td></td>
</tr>
<tr>
<td>(111)-Mg</td>
<td>Au–Au 2.60</td>
<td>2.58/2.63</td>
<td></td>
</tr>
</tbody>
</table>
remain with final charges close to the ones in bulk. Based on the charge analysis of the (111) substrates with and without the gold cluster, we can therefore predict the overall electron exchange at the Au–MgO(111) interface from the trend of the substrate atoms to reach their bulk charge state.

Discussion

Our catalysis results, as summarized in Table 2, indicate the importance of the crystal facet of the MgO support for the gold nanoparticles. Since the XRD and TEM show a similar gold particle size exists on both MgO systems and both pure MgO systems have similar performance in the blank reactions, the difference observed in catalytic activity may be attributed to the presence of Au nanoparticles and to the surface orientation of the supporting surface, as it has been suggested previously.20,49 The conversion is seen to increase significantly to the presence of Au nanoparticles and to the surface charge analysis of the (111) substrates with and without the Au cluster, we can therefore predict the overall electron transfer on these two substrates as illustrated in our binding energy calculations, in the relaxed structures plotted in Fig. 5, and in the interatomic distance analysis shown in Table 3. To summarize, the important conclusions drawn from the DFT results are (i) the Au cluster retains its structural integrity and binds strongly to both (111)-O and (111)-Mg surfaces, but not to (001) and (110), and (b) there is significant charge transfer for Au on (111) substrates but weak transfer on (001) and (110). These DFT results are consistent with our experimental comparisons between the MgO(NanoActive)* and Au/MgO(111) systems. Based on Bader charge analysis of the surfaces with and without the Au cluster, we have rationalized the direction of the electron transfer at the (111) interfaces by the tendency of the (111) Mg and (111) O layers to recover the charge state that they have in bulk MgO. If the oxidation of benzyl alcohol proceeds primarily on the substrate and not directly on the gold nanoparticle (which is likely because of the very small areal coverage), then the presence of hydroxyl on the surface and our DFT results suggest an O-termination for the (111) substrates in our experiments which has been suggested in prior studies.31,50

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