A density functional theory study of the dissociation of \( \text{H}_2 \) on gold clusters: Importance of fluxionality and ensemble effects

L. Barrio  
*Instituto de Catálisis y Petroleoquímica, CSIC, Marie Curie n° 2, 28049 Madrid, Spain*

P. Liu and J. A. Rodríguez\(^{(a,b)}\)  
*Chemistry Department, Brookhaven National Laboratory, Upton, New York, 11973*

J. M. Campos-Martín and J. L. G. Fierro\(^{(b,c)}\)  
*Instituto de Catálisis y Petroleoquímica, CSIC, Marie Curie n° 2, 28049 Madrid, Spain*

(Received 8 March 2006; accepted 20 September 2006; published online 27 October 2006)

Density functional theory was employed to calculate the adsorption/dissociation of \( \text{H}_2 \) on gold surfaces, \( \text{Au}(111) \) and \( \text{Au}(100) \), and on gold particles from 0.7 (\( \text{Au}_{14} \)) to 1.2 nm (\( \text{Au}_{20} \)). Flat surfaces of the bulk metal were not active towards \( \text{H}_2 \), but a different effect was observed in gold nanoparticles, where the hydrogen was adsorbed through a dissociative pathway. Several parameters such as the coordination of the Au atoms, ensemble effects and fluxionality of the particle were analyzed to explain the observed activity. The effect of the employed functional was also studied. The flexibility of the structure, i.e., its adaptability towards the adsorbate, plays a key role in the bonding and dissociation of \( \text{H}_2 \). The interaction with hydrogen leads to drastic changes in the structure of the Au nanoparticles. Furthermore, it appears that not only low coordinated Au atoms are needed because \( \text{H}_2 \) adsorption/dissociation was only observed when a cooperation between several (4) active Au atoms was allowed. © 2006 American Institute of Physics. [DOI: 10.1063/1.2363971]

**INTRODUCTION**

Whereas bulk gold is considered an inert material, gold nanoparticles exhibit a high activity in a wide variety of reactions. Depending on particle size, gold is able to catalyze different reactions. For instance, CO oxidation or hydrogennation reactions require particles below 2 nm in size, whereas propylene epoxidation takes place on bigger particles (up to 4–5 nm).\(^1\) Shape,\(^1\) size,\(^2\) and support interactions\(^3\) have been suggested as the main factors explaining the astounding properties of nanosized gold particles.

Several theoretical works have addressed the issue of the intrinsic reactivity of free Au clusters.\(^4–6\) It is very important to establish the characteristic behavior of Au nanoparticles in the presence of adsorbates. Generally small clusters, up to 55 gold atoms, have been considered for the study of the adsorption of molecules. Some key parameters taken into consideration in the literature have been the coordination number of the Au atoms (i.e., the less coordinated are the more active),\(^3,4\) fluxionality of the cluster or nanoparticle,\(^4,5\) and charge transfer effects between adsorbate and metal.\(^5\) Thus, it has been established that unsupported nanoparticles of gold can carry out the oxidation of \( \text{CO} \),\(^4\) which can be favored by the effects of metal-support interactions.\(^3,5,7\)

Most of the theoretical studies are concerned with the interaction of oxygen with gold and few deal with hydrogen.\(^8–10\) Also from an experimental point of view, much fewer data on \( \text{H}_2 \) adsorption compared to \( \text{O}_2 \) adsorption are available. Nevertheless, \( \text{H}_2 \) is a reactant or product in many reactions catalyzed by Au nanoparticles.\(^1,11,12\) The adsorption of molecular hydrogen on bulk gold does not occur,\(^13\) but chemisorption on nanoparticles has been reported, although quantitative experimental data are still lacking.\(^12\) Theoretical work on hydrogen adsorption on gold nanoparticles is limited as it deals either with small clusters (up to three gold atoms) (Ref. 8) or fixed geometry of the cluster (13 gold atoms).\(^9\) Modeling the right size and right shape of gold clusters is therefore fundamental in obtaining reasonable results. It is not clear if the ability of a gold cluster to adapt its structure (fluxionality) is a key phenomenon in the thermodynamics for the adsorption/dissociation of \( \text{H}_2 \).

**THEORETICAL METHODS**

In the present study, density functional theory (DFT) was employed to study and compare molecular hydrogen adsorption on gold nanoparticles (sizes from 0.7 to 1.2 nm) and on periodic surfaces of bulk gold. The geometry of the clusters was fully relaxed to allow structural changes during the adsorption. All the calculations were performed with the DMOL\(^3\) program,\(^13,15\) using the generalized gradient approximation with the PW91 functional\(^16\) allowing spin polarization, as used in previous works.\(^3,17\) The most relevant results were recalculated with the BP (Becke-88 for exchange and Perdew-91 for correlation) and RPBE functionals,\(^18,19\) in order to study the influence of the functional on the mechanism of \( \text{H}_2 \) adsorption. A numerical basis set, which describes the
orbitals in the valence shell with double numerical functions and includes a polarization d function for the light atoms, was employed here. It is comparable in accuracy to a Gaussian 6-31G* basis set and it was previously very useful for examining the geometry of Au clusters and their bonding to SO$_2$.\textsuperscript{20} Gold atoms were expressed by effective core potentials to account for relativistic effects.\textsuperscript{21} A similar methodology has been widely employed to accurately describe molecular adsorption on gold clusters.\textsuperscript{3,8,22} In the calculations, we allowed the full relaxation of the gold nanoparticles and the adsorbed H$_2$. In most cases, the geometry optimization of these systems was done without symmetry constraints.

RESULTS AND DISCUSSION

First, we will start by examining the adsorption of H$_2$ on Au(111) and Au(100), the most stable surfaces of the bulk metal. In these surfaces, each Au atom has at least eight neighbors. To model the surface of gold a representative unit cell of three layers and four atoms per layer, which is shown in Fig. 1, was employed. In order to account for the rigidity of the metal structure only the first atomic layer was allowed to relax during the geometry optimization.\textsuperscript{13,17} Several adsorption sites (a-top, bridge, and hollow positions) were tested on both surfaces with H$_2$ bonded with its molecular axis parallel or perpendicular, yielding essentially the same result. The interaction between H$_2$ and bulk gold is too weak for the molecule to be chemisorbed, see Table I. In the two most stable configurations found for physisorbed H$_2$ the molecule is away from the surface with a H–H bond distance essentially equal to that seen for free H$_2$ (0.75 Å). Physisorbed states are difficult to handle with conventional DFT since there are no dispersion effects.\textsuperscript{23} The important point here is that the Au(100) surface is more open than the Au(111), but it is still not able to chemisorb or dissociate H$_2$. These results are in good agreement with experimental evidence and a previous theoretical work for H$_2$/Au(111),\textsuperscript{13} which indicates that the hydrogen molecule does not chemisorb on bulk gold, no matter the configuration of the adsorption sites.

Two options have been followed for modeling the nanosized gold clusters. First a most simple unit of 14 gold atoms in a fcc structure has been considered [see Fig. 2(a)]. This Au$_{14}$ cluster contains atoms with a high coordination number

![FIG. 1. H$_2$ on (a) Au(111) and (b) Au(100) surfaces.](image1)

![FIG. 2. Au$_{14}$ cluster (a) before and (b) after H$_2$ adsorption.](image2)

<table>
<thead>
<tr>
<th>Structure</th>
<th>H–H bond distance (Å)</th>
<th>$\Delta E_{\text{adsorption}}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au (111) surface PW91</td>
<td>0.751</td>
<td>−2.01</td>
</tr>
<tr>
<td>Au (100) surface PW91</td>
<td>0.750</td>
<td>−1.21</td>
</tr>
<tr>
<td>Au$_{14}$ PW91</td>
<td>3.532</td>
<td>−31.80</td>
</tr>
<tr>
<td>Distorted Au$_{29}$ PW91</td>
<td>3.441</td>
<td>−43.22$^a$</td>
</tr>
<tr>
<td>Fixed Au$_{29}$ PW91</td>
<td>3.245</td>
<td>25.15$^b$</td>
</tr>
<tr>
<td>Distorted Au$_{29}$ BP</td>
<td>3.645</td>
<td>−33.22$^a$</td>
</tr>
<tr>
<td>Distorted Au$_{29}$ RPBE</td>
<td>3.718</td>
<td>−19.58$^a$</td>
</tr>
</tbody>
</table>

$^a$The distorted structure of Au$_{29}$ was taken as reference for the estimation of the dissociative adsorption energies.

$^b$The C$_4$ pyramidal structure of Au$_{29}$ was taken as reference for the estimation of the dissociative adsorption energy.
the molecule interacted with a limited number of Au atoms or the relaxation of the Au cluster was not allowed. The energy change for the $\text{H}_2\text{gas} \rightarrow 2\text{H}_{\text{ads}}$ reaction on Au$_{14}$ is $\sim -32$ kJ/mol (Table I). As mentioned above, it is worth noting the high distortion suffered by the cluster when adsorbing H$_2$ [Fig. 2(b)]. The high fluxionality of the small particle makes the stabilization of the dissociated hydrogen feasible. This is not possible on the Au(100) and Au(111) surfaces or on the rigid icosahedral Au$_{13}$ cluster used in Ref. 9. On the rigid Au$_{13}$ cluster there is a release of $\sim 33$ kJ/mol for the dissociation of H$_2$, but an activation barrier of 29 kJ/mol makes the dissociation of the molecule difficult. This large activation barrier is probably caused by the fact that the adsorbate only interacts with two Au atoms in a rigid particle. The calculated energy barriers for H$_2$ dissociation on a Au$_3$ cluster is at least 42 kJ/mol, depending on the functional used.8

As a second representation of a gold cluster, the reactivity of a structure of 29 gold atoms was examined. Several bonding sites have been tried for molecular hydrogen adsorption on this cluster [Fig. 3(a)]. First, the H$_2$ adsorption was tried on the bottom face, which resembles the (100) surface of gold. On the atoms of this face, no hydrogen adsorption was observed. Then, the molecule was moved to the lateral (111) face of the pyramid. Again, no significant interaction between H$_2$ and gold atoms was obtained. Edge atoms are frequently considered the most active due to their low coordination number.4,6 Thus, the next step was to study H$_2$ adsorption at the edge atoms of the Au$_{29}$ cluster. The edge and corner positions were checked but in no case was the adsorption of the hydrogen molecule seen.

Finally, the top of the cluster was tried as the site for H$_2$ approach. Only in this case, a relatively strong interaction was obtained. The direct adsorption of molecular hydrogen on the top of this cluster leads to a distorted structure of the gold aggregate and a spontaneous dissociation of H$_2$. This is an exothermic process with a stabilization energy of $\sim 43$ kJ/mol (Table I). For the H$_2$/Au$_{29}$ system, we also did calculations using the BP and RPBE functionals. The energies released by the dissociation process are listed in Table I. As expected the RPBE functional predicts a much weaker interaction than the PW91.19 Typically, adsorption energies calculated with the RPBE functional are 20–35 kJ/mol smaller than with the PW91 functional.19 Independent of the used functional (PW91, BP, or RPBE), we found no activation barrier for the dissociation of H$_2$ on the Au$_{29}$. During geometry optimization, the H–H bond broke spontaneously.

Once the H$_2$ dissociated, the gold cluster was substantially distorted [Fig. 3(b)]. The presence of hydrogen produced a rearrangement of the electron density, which led to a change in the structure of the cluster. From a $C_{4v}$ symmetric pyramid the cluster elongated to form a distorted boat-shaped structure with $C_{2v}$ symmetry. This distortion produces an arrangement of the gold atoms in the particle that gives a high number of gold atoms exposed in the (111) face. This face is the most stable surface of gold, and hence the fluxionality contributes to the cluster stabilization. As it was observed for the Au$_{14}$ cluster, the flexibility of the structure, its adaptability towards the adsorbate plays a key role in the
bonding and dissociation of H₂. This observation can explain the activity of small particles which may be due, among other reasons, to the fact that the nanosized clusters are more adaptable towards H₂ adsorption than flat (111) and (100) surfaces of bulk gold.

The properties of the distorted cluster are shown on Table II. As can be observed the stabilization of the structure after the distortion is as high as 97 kJ/mol. Also, the bond distances of gold atoms in every position are affected by the distortion, leading to maximum differences of 0.1 Å between both structures. The distorted structure was used as the reference to calculate the bonding energies in Table I.

In order to evaluate the influence of the fluxionality of the cluster during the chemisorption process we performed a new calculation in which the structure of the gold atoms was constrained. The top layer of four atoms was able to move freely, while the two other layers were fixed. Only the top position was tried as the approach site because it was proved above to be the active one. This restriction keeps the system under a C₄ᵥ symmetry point group during the geometry optimization, although the relaxed cluster yielded to a C₄ symmetry. Two individual H atoms were bonded to the cluster as shown in Fig. 4. The partial relaxation of the geometry affects the thermodynamics and the H₂→2H° reaction has an endothermicity of 25 kJ/mol (see Table I). When the geometry was fully relaxed the dissociation released 43 kJ/mol of heat. It is worth noting the difference in energy of 68 kJ/mol between the fixed and relaxed pathways. Hence, the electronic properties of the gold atoms in the nanoparticle help the dissociation of H₂, but it is the fluxionality of the cluster which makes the process energetically favorable.

However, there is still a question to be answered, why is the top of the cluster the preferential bonding site? The fact that there is only one active place for the adsorbate to encounter the cluster needs a careful lookup. It seems that not only low coordinated Au atoms are needed. Neither the inherent strain of the nanoparticle is enough to make the gold atoms active. The adsorption/dissociation of H₂ is only obtained when cooperation between several active Au atoms is allowed. The main difference of the corner and a-top bonding positions is that on the former only two or three atoms of gold are close enough to meet the hydrogen molecule. On the top of the cluster, four active gold atoms contribute to the dissociation of hydrogen. It is an ensemble effect of the first layer of atoms and also of the whole cluster, adapting its shape to hold the hydrogen. This cooperative effect has been observed in previous theoretical studies for the adsorption of other molecules (CO and O₂).

The reaction mechanism seen in the theoretical calculations opens the possibility of finding dissociated H atoms on gold nanoparticles when these are under moderate or high pressures of H₂. The small values of the ΔE for the dissociation of H₂ (−32 to −43 kJ/mol, PW91) make the reverse reaction easy at elevated temperatures. The lack of a strong Au–H bond facilitates the formation of H₂ during the watergas shift reaction on Au/CeO₂ catalysts. Moreover, this property could help the epoxidation of alkenes, because the easy dissociation of H₂ on the surface of gold can also favor the formation of peroxy species when oxygen is present. This peroxy moity is very active in the epoxidation of propylene as in many other oxidation reactions.

### CONCLUSIONS

In summary, H₂ adsorption/dissociation was studied for bulk surfaces of gold and for nanoclusters from 14 to 29 gold atoms by DFT calculations. On bulk Au (111) and (100) surfaces no adsorption of molecular H₂ was observed. However, the results obtained for the nanoparticles predict a spontaneous dissociation of H₂ with stabilization energies of 30–40 kJ/mol. Different functionals were tried to model the chemisorption of molecular hydrogen on a Au₂₉ cluster. Although the stabilization energies varied with the employed functional, all the results show the same mechanism of spontaneous dissociation of H₂.

It seems that several factors determine the ability of the particle to interact with hydrogen: low coordinated Au atoms, fluxionality, and ensemble effects. The flexibility of the structure, its adaptability towards the adsorbate plays a key role in the bonding and dissociation of H₂. And it appears that not only low coordinated Au atoms are needed because H₂ adsorption/dissociation is only seen when cooperation between several (4) active Au atoms is allowed.

### ACKNOWLEDGMENTS

CICYT (Spain) is acknowledged for the financial support in the project ENE2004-07345-C03-01/ALT. CTI of CSIC is also acknowledged for CPU facilities. The research carried out at Brookhaven National Laboratory was supported by the US Department of Energy, Division of Chemical Sciences (Contract No. DE-AC02-98CH10886).

---

1. M. Haruta, Cattech 6, 102 (2002).
Dissociation of H₂ on Au clusters

25 K. Nakamura (private communication).