On the activation of molecular hydrogen by gold: a theoretical approximation to the nature of potential active sites†

Avelino Corma,*[a] Mercedes Boronat,[a] Silvia González[b] and Francesc Illas[b]

Received (in Cambridge, UK) 4th June 2007, Accepted 9th July 2007
First published as an Advance Article on the web 19th July 2007
DOI: 10.1039/b708468d

The study of adsorption and dissociation of molecular hydrogen on single crystal Au(111) and Au(001) surfaces, monoatomic rows in an extended line defect and different Au nanoparticles by means of DF calculations allows us to firmly conclude that the necessary and sufficient condition for H_2 dissociation is the existence of low coordinated Au atoms, regardless if they are in nanoparticles or at extended line defects.

While bulk gold is chemically inert,[1] gold nanoparticles supported on inorganic oxides have attracted increased interest in the past few years as catalysts for a number of reactions, such as CO oxidation,[2] water–gas shift,[3] alcohol oxidation,[4] propylene epoxidation,[5] hydrogenations and C–C bond forming reactions.[6,7]

It is now generally accepted that the unexpected activity of supported gold catalysts is related to the size and shape of the nanoparticles, the degree of coordinative unsaturation of the gold atoms, and the interactions between gold and the oxide support. Several theoretical studies have addressed these properties, mainly in relation to the oxidation of CO.[8] However, little attention has been paid to the dissociation of molecular hydrogen by gold, despite the interesting behaviour of gold catalysts in selective hydrogenation of alkynes to alkenes,[9] α,β-unsaturated aldehydes,[10] and nitro groups in substituted nitroaromatics.[11]

Different experiments support the idea that molecular hydrogen adsorption does not occur on clean gold extended surfaces, and that hydrogen chemisorption (or dissociative hydrogen adsorption) only occurs on thin non-sintered gold films[12] or supported gold nanoparticles.[13] Therefore, it has been proposed that hydrogen reacts and dissociates on low coordinated gold atoms at the corners or edges of single crystalline gold nanoparticles.[12,13] Theoretical investigations of molecular hydrogen dissociation on small Au_3[14] or rigid Au_{13} clusters,[15] as well as on more realistic flexible Au_{14} and Au_{29} clusters, have been reported recently.[16] In this last case, the authors concluded that low coordinated Au atoms are necessary but not sufficient to dissociate H_2, and suggest that H_2 dissociation is only favoured when cooperation of four active low coordinated Au atoms is possible.

In this work, we analyze the different behaviour of Au single crystal extended surfaces, extended defects and nanoparticles towards H_2 dissociation. We will present compelling evidence that H_2 adsorbs and dissociates with small activation barriers on low coordinated Au atoms situated in corner positions of different Au_{25} nanoparticles (∼1 nm) and in edge positions of monoatomic rows existing in defective surfaces without further conditions. It will also be shown that, contrary to what has been reported,[16] there is no need for cooperation between several active Au atoms to dissociate H_2. A single low coordinated gold atom is enough to catalyze the reaction, which will indeed occur spontaneously when the coordination number of this gold atom is four.

Three different kinds of model were used, which go from extended single crystal Au(111) and Au(001) surfaces (Fig. 1), passing through a monoatomic row model (Fig. 2) to isolated Au_{25} (Fig. 3). Particle A contains three corner atoms on the top layer of the particle, each of them directly bonded to only four other gold atoms. Particle B has a hemispherical structure and the top layer of the particle contains four corner atoms, each of them directly bonded to five other gold atoms. For the Au models—periodic models or discrete particles—outlined above, density functional (DF) calculations were carried out using the VASP code.[17] Details of models and calculations are given in the ESI.†

In agreement with experiment[12,13] and previous theoretical studies,[16] our results show that H_2 interacts weakly with Au(111) and Au(001) surfaces. The calculated adsorption energies (Table 1) are less than 0.5 kcal mol^{-1}, and in the optimized complexes (Fig. 1) the hydrogen molecule is at ∼4 Å from the gold surface, with a H–H distance equal to that obtained for isolated H_2 (0.75 Å). The most stable positions for atomic H on Au(111) and

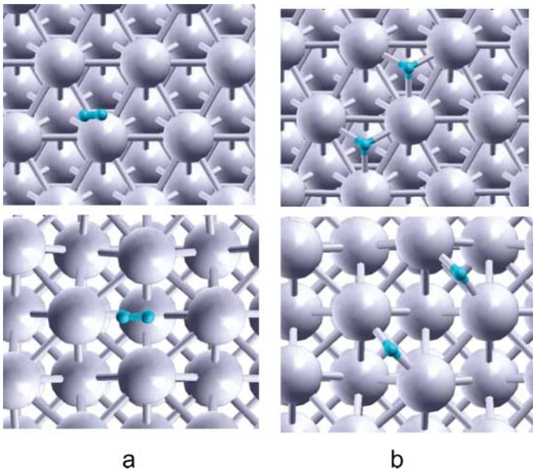

Fig. 1 Adsorption (a) and dissociation (b) of H_2 on perfect Au(111) (top) and Au(001) (bottom) surfaces.

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[a] *Instituto de Tecnología Química, UPV-CSIC, Av. los Naranjos, s/n, E-46022 Valencia, Spain. E-mail: acorma@itq.upv.es; Fax: +34 963877809; Tel: +34 963877800*
[b] *Departament de Química Física & Centre Especial de Recerca en Química Teòrica, Universitat de Barcelona & Parc Científic de Barcelona, C/Martí i Franquès 1, E-08b028 Barcelona, Spain*

† Electronic supplementary information (ESI) available: Computational details section and table with optimized geometries. See DOI: 10.1039/b708468d

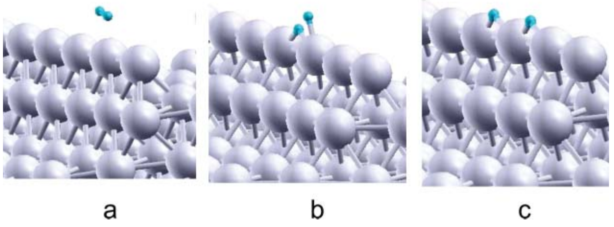

Fig. 2 Adsorbed H_2 (a), transition sate (b) and dissociated H_2 (c) on the edge of a monoatomic row on a defective Au(111) surface.

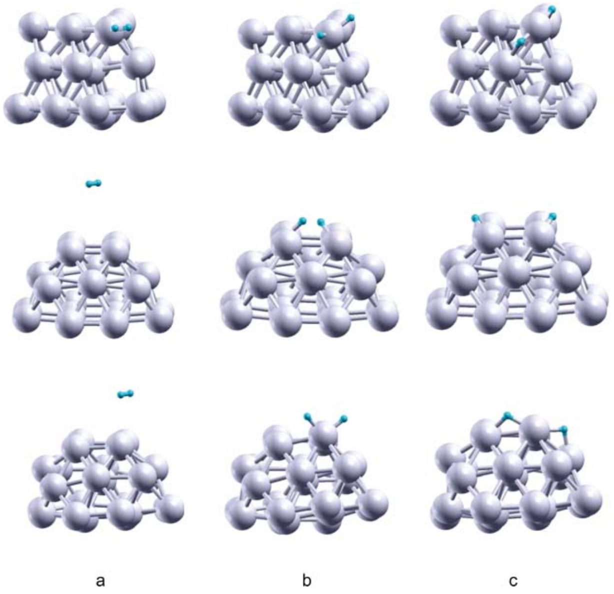

Fig. 3 Adsorbed H_2 (a), transition state (b) and dissociated H_2 (c) on the corner position of particle A (top), on top of particle B (middle) and on the corner position of particle B (bottom).

Table 1 Calculated adsorption energies of H_2 (E_{ads}) on the different Au systems considered, and activation (E_{act}) and reaction energies (ΔE) for H_2 dissociation on the defective surface and particles. All energies are in given in kcal mol^{-1}

	E_{ads}	E_{act}	ΔE
Au(111)	−0.45	—	9.97
Au(001)	−0.36	—	4.83
Monoatomic row	−12.56	6.66	−7.47
Au_{25} (A)	−7.21	5.99	−6.19
Au_{25} (B, top)	−0.50	20.58	−2.15
Au_{25} (B, corner)	−0.86	2.14	−4.04

Au(001) surfaces, hollow and bridge positions respectively (see Fig. 1), have been considered to compute the dissociation energies ΔE given in Table 1. In both cases, molecular hydrogen dissociation is clearly endothermic, and no attempts to obtain the activation barriers for H_2 dissociation have been made. Different results are obtained for defective gold surfaces and nanoparticles. Fig. 2 and 3 show the optimized geometries of reactants (adsorbed H_2), transition states for the H_2 dissociation and products (dissociated H_2). Dissociation is found to occur on the edge of the monoatomic row model, on a corner site of particle Au_{25} (isomer A), and on two different positions (top and corner) of particle Au_{25} (isomer B).

For the monoatomic row model, it was found that molecular H_2 interacts strongly with low coordinated Au atoms situated in the monoatomic row edge, with a calculated adsorption energy of −12.6 kcal mol^{-1}. The optimized Au–H distances in the adsorption complex are ~2.1 Å, the H–H bond being 0.03 Å larger than in the isolated molecule, and the largest deformation in the gold surface is an increase of one of the Au–Au distances in the monoatomic row edge from 2.95 to 3.12 Å. In the transition state, the H–H distance increases to 1.25 Å; one of the H atoms is strongly bonded to an Au atom with a calculated Au–H distance of 1.66 Å, while the second H atom forms an almost symmetrical bridge ($r_{\mathrm{Au-H}}$ = 1.80 and 1.92 Å) between this Au atom and the next one on the monoatomic row edge. Once the dissociation process is complete, the two H atoms are located on two consecutive bridge positions on the edge of the monoatomic row. It is important to note that the Au–Au distances in the bridges (2.99 Å) are almost equivalent to the mean Au–Au distance (2.95 Å), indicating that the H_2 dissociation does not involve any significant deformation of the catalyst surface. The calculated activation energy, 6.6 kcal mol^{-1}, is smaller than the energy released by H_2 adsorption on this surface and the reaction is exothermic by 7.5 kcal mol^{-1} (Fig. 4). Even considering that the present first principle (GGA) computational method will somehow overestimate the adsorption energy of H_2 on the present surface models, one can safely predict that, for this extended line defect, the global process is energetically favourable and will occur spontaneously.

The interaction of molecular H_2 with a corner atom of particle A is also rather strong, as already seen from the calculated adsorption energy of −7.2 kcal mol^{-1}. The Au–H optimized distances are equal, 1.84 Å, and the H–H bond length increases to 0.84 Å (Fig. 3a). In the transition state, the hydrogen molecule is almost dissociated, with a calculated H–H distance of 2.80 Å, and the two H atoms are strongly bonded to the corner Au atom and oriented in opposite directions. After dissociation, the two H atoms form two nearly symmetrical Au–H–Au bridges with other Au atoms below and involving the corner Au atom. During the whole process, the shape of the Au nanoparticle remains unaltered, the largest variations in the Au–Au distances being of 0.1 Å only.

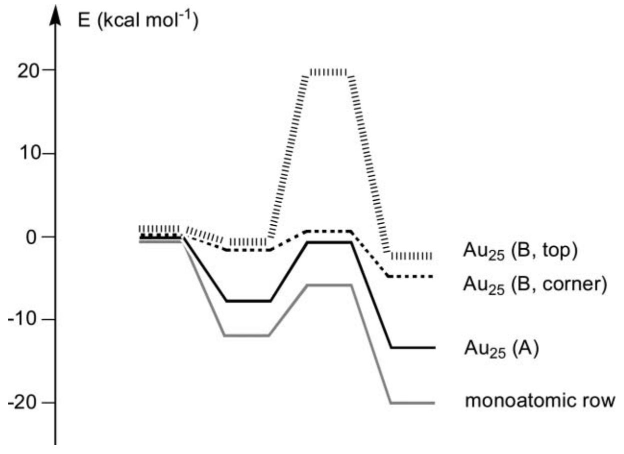

Fig. 4 Calculated energy profile for H_2 dissociation on the monoatomic row model of the defective surface and for the A and B Au_{25} nanoparticles.

The calculated energy profile for H_2 dissociation on a corner gold atom in Au_{25} (A) is similar to that obtained on the edge of the monoatomic row model, the only difference being the lower adsorption energy obtained for the particle. Nevertheless, the activation barrier is still smaller than the adsorption energy, and the reaction will occur spontaneously. A different situation is obtained on the more symmetric Au_{25} (B) nanoparticle, for which interaction with H_2 is almost negligible. Two different situations have been considered for H_2 adsorption: on top (second row in Fig. 3) and on a corner Au atom (third row on Fig. 3). In both cases, the H_2 molecule remains far from the metal atoms ($\sim$3.3 Å), the H–H bond length is 0.75 Å, as in the isolated molecule, and the calculated adsorption energy is less than 1 kcal mol^{-1}, indicating that molecular adsorption is unlikely to occur. Moreover, molecular hydrogen dissociation on top of particle B requires overcoming a high energy barrier. At the transition state the H–H distance has increased to 1.03 Å and the hydrogen atoms are at $\sim$2 Å from the Au atoms on top of the cluster. After dissociation, the two H atoms occupy bridge positions at opposite sides of the square formed by the four Au atoms on top of the particle. The reaction is slightly exothermic, but the activation energy involved is large (20.6 kcal mol^{-1}) and therefore it will not easily take place. These results are at variance with those reported by Barrio *et al.*,[16] who argue that direct adsorption of H_2 on top of a Au_{29} cluster leads to dissociation without activation barrier. Nevertheless it should be pointed out that Barrio *et al.* did not report the transition state structure because their geometry optimization converged to spontaneous dissociation. However, the existence of a transition state structure for H_2 dissociation on Au particles is reinforced by results obtained for the H_2 molecule adsorbing at a corner Au of the same Au_{25} (B) particle. Here, the dissociation reaction proceeds through a transition state similar to that obtained on particle A, indicating that the bulk initial geometry chosen for this particle does not bias its reactivity. In the transition state the two H atoms are far from each other and strongly bonded to one of the four low coordinated Au atoms on top of the particle. In the final state, the two H atoms are in bridge positions sharing this low coordinated Au atom, and the corresponding reaction energy is of -4.04 kcal mol^{-1}. It is interesting to note that only one of the two Au–H–Au bridges involves two Au atoms of the square on top of the cluster, the other bridge is situated on the lateral (111) facet of the particle. We have found a slightly more stable structure with the two Au–H–Au bridges on consecutive sides of the square formed by the four Au atoms on top of particle B, and have characterized it as a minimum. However, we could not find a transition state connecting this structure with adsorbed H_2, and therefore it has not been included in the discussion.

The energy profile for H_2 dissociation on a corner gold atom of particle B is also depicted in Fig. 4. The calculated activation energy is quite low, 2.14 kcal mol^{-1}, but the transition state lies at an energy that is higher than that corresponding to the separated reactants, implying that a small positive activation barrier has to be overcome in order for the reaction to occur.

To summarize, we have provided strong theoretical evidence that H_2 can be dissociated almost without additional energy by low coordinated Au atoms situated in different positions, irrespective of whether these are located at the edge of a nanoparticle or belong to an extended line defect. The most favourable situation involves Au atoms directly bonded to four other Au atoms, such as those located in the monoatomic row edge or in corner positions in particle A. The corner Au atoms in particle B are directly bonded to five other gold atoms and, although the dissociation may still occur, there is a positive energy barrier that has to be overcome. In all cases, the process implies the simultaneous interaction of one low coordinated Au atom with the two hydrogen atoms of H_2 and after dissociation the two H atoms are in bridge positions sharing the low coordinated gold atom.

SG is grateful to the Universitat de Barcelona for a pre-doctoral fellowship. Financial support has been provided by the Spanish Ministry of Education and Science (Projects MAT2006-14274-C02-01, CTQ2005-08459-CO2-01 and UNBA05-33-001) and, in part, by Generalitat de Catalunya (Projects 2005SGR-00697, 2005 PEIR 0051/69 and Distinció Gen-Cat granted to FI). The authors thankfully acknowledge the computer resources, technical expertise and assistance provided by the Barcelona Supercomputing Center-Centro Nacional de Supercomputación.

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