Computational details

The aim of this work is to find the necessary condition that a gold catalyst has to fulfil to be active for hydrogen dissociation, and this implies to determine the exact nature of the sites that are able to dissociate H_2. To this end, we have chosen three different kind of models, including extended single crystal surfaces, a monoatomic row model which provides a suitable model for an extended line defect, and isolated Au_{25} particles, having gold atoms with different degree of coordinative unsaturation. Au(111) and Au(001) surfaces were modelled by periodic slabs containing four atomic layers and a vacuum region larger than 20 Å between vertical repeated slabs. Large enough — (4x4) for Au(111) and (3x3) for Au(001) — supercells were used to avoid interaction between the adsorbates. The defective gold surface was constructed from a (5x5) supercell slab model for Au(111) model with five atomic layers and removing four rows from the first layer and three rows of the second one. The resulting model is similar to the one proposed by Tielens et al.[1] and provides a monoatomic row combining low and high coordinate atoms. The energy convergence with respect to the number of layers for this monoatomic-row model was tested, and the results are summarized in Table S.1. Finally, the two different Au_{25} gold particles were situated in a 20 Å x 20 Å x 20 Å cubic box. Particle A consists of three layers of 12, 7 and 6 atoms parallel to the (111) surface. It was directly cut out from bulk gold in such a way that it contains three corner atoms on top layer of the particle, each of them directly bonded to only four other gold atoms. Particle B has a hemispherical structure and is formed by the interconnection of Au(001) (top and bottom) and Au(111) (side) faces. It contains, on top layer of the particle, four corner atoms each of them directly bonded to five other gold atoms. The geometry of the two particles was fully optimized, the final shape is reminiscent of the initial one with isomer B being 3.6 kcal mol^{-1} more stable than isomer A. The influence of the energy cutoff on the adsorption energy of H_2 on particle A has been explored in some detail; results are summarized in Table S.2.

For the Au models outlined above — periodic models or discrete particles — Density Functional (DF) calculations were carried out with exchange correlation effects being described by the Perdew-Wang (PW91)[2,3] version of

the Generalized Gradient Approximation (GGA). The density was expanded in a plane wave basis set whereas the effect of the inner cores was taken into account through the Projected Augmented Plane Wave (PAW) method of Blöchl as implemented by Kresse and Joubert,[4] which allows one to obtain converged results with a cutoff kinetic energy of 415 eV for the plane-wave basis set. The partial occupancies in each Bloch function were determined with the second-order method of Methfessel-Paxton using a k_BT = 0.2 eV smearing of the electron density in the corresponding one electron wave functions, but the total energy was extrapolated to k_BT = 0 eV upon convergence of the self-consistent field procedure. The Residual Minimization Method Direct Inversion in the Iterative Subspace (RMM-DIIS) was employed as electronic minimization algorithm. The Brillouin zone of the gold surfaces unit cells was described with a 3 x 3 x 1 *k*-points grid within the Monkhorst-Pack scheme except for the Au_{25} cluster where calculations were carried out for the the Γ k-point.

For geometry optimization, the conjugate-gradient algorithm was used to relax the atomic positions whereas transition state structure searches for H_2 dissociation were carried out by means of the climbing image Nudged-Elastic-Band (NEB).[5] When the forces on the atoms of the structure found by this algorithm were not small enough, further structure refinement was carried out using a quasi-Newton algorithm until forces in each relaxed atom were smaller than 0.01 eV/Å. The resulting structures were further characterized either as minima or as saddle points by a pertinent frequency analysis calculation. This was carried out by diagonalizing the block Hessian matrix corresponding to displacements of the coordinates of the H atoms.

All calculations were carried out using the VASP code.[6,7]

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Table S.1. Influence of the number of layers in the monoatomic row model on the calculated energies (in kcal/mol).

nº layers	Adsorption energy	Activation energy
5	-12.6	6.7
7	-9.6	6.8

Table S.2. Influence of the cut-off energy on the adsorption energy of H_2 on particle A. All values are given in eV.

Cutoff	Total energy			Adsorption energy
	H_2	particle A	adsorbed H_2	
415	-6.782764	-61.388247	-68.483432	-0.312
465	-6.789006	-61.412495	-68.515657	-0.314
515	-6.791926	-61.505848	-68.609543	-0.312

Table 2. Optimized bond lengths (Å) in the reactants (adsorbed H_2), transition states, and reaction products (dissociated H_2).

	reactants		transition state			products	
	r_{HH}	$r_{H\text{-}Au}$	r_{HH}	$r_{H\text{-}Au(low)}$	$r_{H\text{-}Au}$	r_{HH}	$r_{H\text{-}Au}$
Au(111)	0.75	3.71, 4.12				3.12	1.91-1.92
Au(001)	0.75	4.38, 4.53				3.06	1.76-1.78
monoatomic row	0.78	2.09, 2.13	1.25	1.66, 1.80	3.74, 1.92	3.01	1.78
Au_{25} (A, corner)	0.84	1.84, 1.84	2.77	1.63, 1.63	2.57, 2.72	3.46	1.74, 1.84
Au_{25} (B, top)	0.75	4.29, 4.31	1.03	1.90, 1.91	2.13, 2.14	4.21	1.78
Au_{25} (B, corner)	0.75	3.33, 3.37	2.36	1.60, 1.61	2.69, 3.00	2.96	1.78, 1.80