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January 21, 2011

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Gold Cluster Diffusion Kinetics on Stoichiometric and Reduced Surfaces of Rutile TiO$_2$ (110)

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Abstract

Gold clusters on rutile TiO_2 are known to serve as efficient industrial oxidation catalysts, although the exact nature of their catalytic activity is unknown. Detailed study of gold diffusion kinetics on the metal oxide surface is likely to be valuable in characterizing this important catalytic system. We report herein on *ab initio* simulations of the diffusion of atomic gold clusters up to the trimer on rutile TiO_2 (110) surfaces. We show that both the gold dimer and trimer can diffuse quickly on a reduced surface despite high energetic barriers to diffusion due to the large degree of vibrational entropy in their transition states. This is in contrast to previous studies based on surface adsorption energies, which show that oxygen vacancies on the reduced surface slow down cluster diffusion significantly. Our computed diffusion times provide a point of comparison for future experiments and will aid in development of models of gold cluster island sintering.

The catalytic activity of oxide-based gold clusters holds promise for use in a wide variety of industrial applications,[1] including large scale chemical synthesis and oxidation of pollutants and environmental contaminants.[2] However, the catalytic activity from these metal particles is not well understood, in part because they are highly non-uniform and their properties depend strongly on their interactions with the substrates (which are themselves highly non-uniform). Gold on the rutile $TiO_2(110)$ surface is a model example of such a system, and is a highly active catalyst for CO oxidation and selective for various partial oxidations. This system itself has potential importance for a number of industrial applications, including the removal of CO from catalytic converters for smog reduction.[3] The exact nature of the gold/oxide interaction and its function in catalytic activity is still not well known, despite many active areas of research. These include investigations of the role of TiO_2 surface defects,[4,5] the oxidation state of the gold species,[6] the degree of hydroxylation of the TiO_2 surface,[7,8] and the size of the supported gold species themselves[9,10] (see Ref.[11] for review). Site-isolated gold atomic clusters up to the pentamer have been imaged on metal oxide supports.[12,13] Complexes with as few as a single gold atom have been inferred to be catalytically active for alkene hydrogenation and CO oxidation on metal oxide[14] and zeolite supports.[6]

The nature of chemical bonding and changes in electronic structure associated with catalysis from gold clusters can be elucidated through use of quantum *ab initio* calculations, such as Density Functional Theory (DFT). DFT has been used in a number of studies to determine surface adsorption energies (vs. diffusion energetic barriers) and lowest minimum energy structures of gold atomic clusters thought to be relevant to catalysis.[4,5,15,16] However, gold on the rutile TiO_2 (110) surface is known to be highly mobile at relatively low temperatures,[17] and DFT calculations generally neglect gold particle diffusion pathways and the spatial dependence of their physical and chemical properties. Energy minimization calculations have shown that the charges on the gold clusters[15,16] and the band gap of the system[18,19] can change significantly depending on whether the gold cluster lies in a global minimum. Gold atomic clusters are computed to have significant adhesion energies on the reduced surface,[16] implying that oxygen vacancy sites on the TiO_2 surface can act as "anchoring" sites for cluster migration. Surface vacancies have been shown to act as traps for diffusing metal clusters on metal oxide systems.[20] A joint experimental and theoretical study has shown that a single oxygen vacancy site will bind up to three gold atoms on average.[4] However, previous computational mappings of the Au/TiO_2 potential energy surface have been limited to gold mononuclear species.[5,21] Thus, to date, little is known about the diffusion energetics and pathways of clusters larger than a single gold atom, and the mechanism and kinetics of gold cluster migration remains an unresolved issue.[13] Determination of diffusion rates and transition states of migrating gold atomic clusters on both stoichiometric and reduced surfaces could help answer key questions regarding the growth of larger clusters and the role of gold in the catalytic process. For example, developments in dynamic transmission microscopy experiments may permit images to be obtained with combined ∼0.1 nm spatial resolution and ∼100 ns temporal resolution,[22] providing direct experimental correlation with simulations of gold cluster diffusion. Simulations of gold cluster diffusion can help elucidate regions of interest for such experiments, and can provide estimates of particle diffusion times.

To this end, we have computed gold atomic cluster diffusion pathways and kinetics through a combination of DFT calculations with the nudged elastic band (NEB) method.[23] We have cal-

culated the minimum energy path (MEP) and transition states for diffusion of the gold monomer, dimer, and trimer on both stoichiometric and reduced surfaces. The degree of hydroxylation and oxidation is known to effect the surface properties of oxide supports,[7,8] which is the subject of a future study. Kinetic rate constants and subsequent diffusion hopping times as a function of temperature were computed through harmonic transition state theory[20] (see Supporting Information).

The stoichiometric TiO_2 (110) surface (Figure 1) consists of two types of Ti atoms and two types of O atoms: five-fold coordinated Ti sites (Ti5c), six-fold coordinated Ti sites (Ti6c), two-fold coordinate protruding O atoms (bridging oxygen), and a three-fold coordinate in-plane O atom (basal oxygen). The reduced surface is prepared by removing one the of the bridging oxygen atoms, which results in two unpaired electrons in the system.[21] Experiments[24] and calculations[25] have shown that oxygen vacancy sites generally remain isolated and do not form larger vacancy clusters. In the discussion below, the first lowest energy minimum along a minimum energy pathway is referred to as the "first minimum", and the second lowest as the "second minimum". In this work we focus exclusively on the hopping motion out of the first minimum into the second minimum, which we call a "forward hop". For the stoichometric surface, a gold cluster in its second minimum has a 50% chance of hopping into a minimum one lattice spacing over, and a 50% chance of returning to the first minimum at its original location. The MEPs for monoatomic gold on both stoichiometric and reduced surfaces (Figure 2(a) and Figure 2(b)) compare well with previous results.[5,21] The monomer on the stoichiometric surface exhibits a low diffusion activation energy barrier of 0.1 eV, consistent with experimental observation of easy gold diffusion at low temperatures.[26] On this surface, the gold atom starts in a hollow site (H1) and diffuses over the Ti5c site into an energetically equivalent H1 site. For the reduced surface, we compute a significantly higher diffusion activation energy barrier of 0.57 eV due to the enhanced gold/TiO_2 surface interaction resulting from the oxygen vacancy.[5] Here, we compute the first minimum to have the gold atom sitting directly above the oxygen vacancy site, and the second minimum to have the gold atom directly above the closest Ti5c site.

Our computed MEP for the gold dimer on the stoichiometric surface (Figure 3(a)) exhibits an

E_A value of 0.44 eV for the forward hop. The transition state occurs with the dimer straddling a second hollow site (H2), with each gold atom between a Ti5c and a basal oxygen site. The computed MEP is relatively flat around the transition state. The Au-Au bond distance remains relatively constant (2.53 – 2.56 Å) as the dimer diffuses along this pathway. The dimer on the reduced surface (Figure 3(b)) exhibited a relatively high activation energy for the forward hop (0.57 eV). In this case, the dimer showed a significantly different diffusion mechanism where one gold atom diffuses away from the oxygen vacancy and rests itself above a Ti5c site. The second gold atom then swings over from above a basal oxygen site to directly above the oxygen vacancy site. We compute Au-Au bond distances of 2.49 Å and 2.53 Å for the first minimum and transition state, and a distance of 2.78 Å for the second minimum.

The gold trimer on the stoichiometric surface exhibited diffusion to the second minimum through a two hop process (Figure 4(a)). All structures along the diffusion pathway are triangular. The first minimum is approximately an isosceles triangle, with Au-Au bond distances on the sides of ~2.60 Å, and a bond distance of 2.86 Å at the base. The base of the triangle has each gold atom in an H1 site and the apex over a Ti5c site. For the first maximum in the MEP, the isosceles triangle structure (base = 3.01 Å) has rotated such that one gold atom remains in the same H1 site and the second has diffused one lattice spacing over into a neighboring H1 site. The intermediate structure is a triangle with a base of 2.77 Å and sides of 2.66 Å. The second maximum in the MEP is a scalene triangle in which the sides have bond distances of 2.59 and 2.67 Å and the base a bond distance of 2.77 Å. The second minimum structure is an isosceles triangle again with sides of 2.62 Å and a base of 2.73 Å. Here, the trimer has rotated and translated down the (001) surface axis from its intermediate state, and both gold atoms in base of the triangle are positioned directly above bridging oxygen sites. We compute an E_A value of 0.50 eV for the first forward hop and an E_A value of 0.49 eV for the second forward hop.

In contrast, the gold trimer on the reduced surface (Figure 4(b)) exhibits an approximately linear structure throughout its computed diffusion pathway. The first minimum has Au-Au bond lengths of 2.58Å and 2.62Å, where one gold atom is positioned almost directly above the oxygen

vacancy site and the remaining two are located in H1 sites. At the transition state two gold atoms are straddling the oxygen vacancy site while the third is positioned above a Ti5c site, with gold bond distances of 2.59 Å and 2.56 Å. The second minimum occurs with the central gold atom directly above the oxygen vacancy site and the other gold atoms positioned roughly above the neighboring Ti5c sites. Here the gold bond distances are both equal to 2.64 Å. We compute an E_A value of 0.42 eV for the forward hop which is similar to the results for the stoichiometric surface.

The rate constants for diffusion hops were estimated using harmonic transition state theory (hTST):[27,28]

$$k^{hTST} = \frac{\prod_i^{3N} \nu_i^{\text{init}}}{\prod_i^{3N-1} \nu_i^{\ddagger}} e^{-(E^{\ddagger} - E^{\text{init}})/k_B T}.$$

Here, N is the number of moving atoms, $E^{\dagger}$ is the energy of the saddle point, E^{init} is the energy of the local minimum correspondoing to the initial state, and the ν_i are the real normal mode frequencies of the saddle point ($\ddagger$) and initial state (init), respectively. The vibrational prefactor corresponds to the entropy term S of the vibrational energy partition function. The hopping time for diffusion is computed as the reciprocal of the rate constant. The vibrational normal modes are determined by evaluating the Hessian matrix by finite differences, followed by evaluation of the eigenvalues and eigenmodes (see Supporting Information).

The diffusion hopping times for all systems as a function of temperature are summarized in Figure 5. On the stoichiometric surface, we compute a vibrational prefactor of 1 THz for the trimer's first transition, and a prefactor of 9 THz for the second transition. The higher degree of vibrational entropy of the second transition state is due to a low frequency hindered rotation mode. Here, the apex of the gold triangle tilts towards the TiO$_2$ (110) surface while its base remains in the plane of the surface. We compute trimer forward hop times for the first barrier that are roughly one order of magnitude slower than those for the second barrier at all temperatures (4 s vs. 0.2 s at 200 K; 10^{-7} s vs. 10^{-8} s at 500 K). Thus, the transition over the first barrier is the rate limiting step for diffusion. The gold monomer (3 THz) has the fastest computed diffusion hop time, as expected, with a value of 10^{-10} s at 200 K and a value of 10^{-11} s at 500 K. The dimer on the stoichiometric

surface (1 THz) has a hop time of 0.1 s at 200 K and one of 10^{-7} s at 500K.

The dimer on the partially reduced surface had an unexpected large vibrational prefactor of 140 THz due to the presence of two relatively low frequency modes in its transition state. The first of these resembles a hindered sliding motion, where both gold atoms move up and down the (001) axis. The second is a hindered rotation, where the gold atom closest to the Ti5c site rotates while the gold atom closest to the oxygen vacancy site largely acts as a pivot. At 200 K we observe that the effects of its high activation energy dominate, and we compute a forward diffusion hop time of approximately 100 s, which is the highest value for all systems in this study. However, as the temperature is increased to 500 K, the entropic effects of the transition are more significant and the diffusion hop time drops to 10^{-8} s. This is equivalent to the forward hop time of the dimer on the stoichiometric surface. The gold monomer had a relatively low vibrational prefactor (3 THz) and relatively high energetic barrier, which resulted in forward diffusion hop times of 100 s at 200 K and 10^{-7} s at 500 K. In contrast, the trimer has an appreciably high vibrational prefactor (9 THz) which resulted in forward diffusion hopping times of 0.01 s at 200 K and 10^{-9} s at 500 K. The lowest frequency mode of its transition state is a bending vibration where the gold atom at the end closer to the oxygen vacancy moves back and forth along the $(1\bar{1}0)$ axis while the remaining two gold atoms remain stationary. The trimer's forward diffusion hop times are approximately two orders of magnitude faster than those of the rate limiting step for the trimer on the stoichiometric surface, at all temperatures.

For our computed diffusion pathways, the transition state of the dimer on the reduced surface has a degree of vibrational entropy that is approximately two orders of magnitude higher than that on the stoichiometric surface. Thus, at 500 K, we predict that the diffusion time for the forward hop will be equivalent for the dimer on both surfaces. Similarly, the transition state of the trimer on the reduced surface exhibited a vibrational entropy that was significantly larger than that of the rate limiting steps on the stoichiometric surface, resulting in computed hopping times that are two orders of magnitude faster at all temperatures studied. This is in contrast to previous works where computed adsorption energies have been used to determine that diffusion on metal oxide surfaces

with oxygen vacancy defects will be significantly slower due than on a stoichiometric surface. Thus, both the energetic barriers to diffusion and entropic effects need to be considered when constructing nucleation and growth models on TiO_2. Our simulations provide a valuable means for comparing to future experiments both through direct imaging of clusters and by providing estimates of experimental observables. Such knowledge will help to elucidate the nucleation and growth mechanisms of larger gold clusters that are likely important to its catalytic activity. This in turn can help establish simple rules for gold cluster heterogeneous catalysis, which could help with the creation of novel catalytic materials for industrial use and energy creation.

Computational Details

All calculations were performed using the VASP planewave basis set DFT code[29] in conjunction with VASP transition state tools available on the internet (http://theory.cm.utexas.edu/vtsttools/). Fractional electron occupancies were calculated using the Mermin functional[30] with the smearing set to 0.03 eV. We performed climbing image NEB calculations[23] with the wavefunction convergence criteria set to 10^{-5} eV, and the spring constant set to 0.05 eV/Å. All of our calculations were performed using spin polarization with projector-augmented wave (PAW) pseudopotentials[31,32] and the PBE Generalized Gradient Approximation (GGA) functional. Use of a hybrid exchange-correlation functionals[18] or onsite Coulomb interactions[33] is known to affect the computed electronic density of states of the system. However, our calculations were focused exclusively on the minimum energy pathways and kinetics of a migrating gold cluster. Au adsorption energies were found to be converged with a basis set cutoff of 300 eV, although we used a cutoff of 354 eV for all reported results. Similar to previous calculations,[16] the number of unpaired electrons was held fixed at a value of zero for systems with an even number of electrons and at a value of one for systems with an odd number of electrons. The surface was modeled with a four-layer slab geometry (4 O-Ti_2O_2-O units, hence 12 atomic layers) in which the two bottom layers were fixed at bulk positions, and a 12 Å vacuum region was created above the (110) surface. We used a system size

of 3 X 2 surface unit cells for all simulations (48 Ti and 96 O atoms for the stoichiometric surface). Calculation of both the stoichiometric and reduced systems with surface sizes of 3 X 3 and 4 X 2 unit cells yielded desorption energies that agreed within <0.1 eV. Sampling of the Brillouin zone was performed with a Monkhorst-Pack grid[34] of up to 2 X 4 X 4, and was found to be converged with a grid of 1 X 2 X 2. The first two lowest energy structures for each gold cluster on TiO_2 system were determined from an extensive search and were found to be identical to those from previous DFT-GGA calculations.[5,15,16]

Acknowledgement

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Figures:
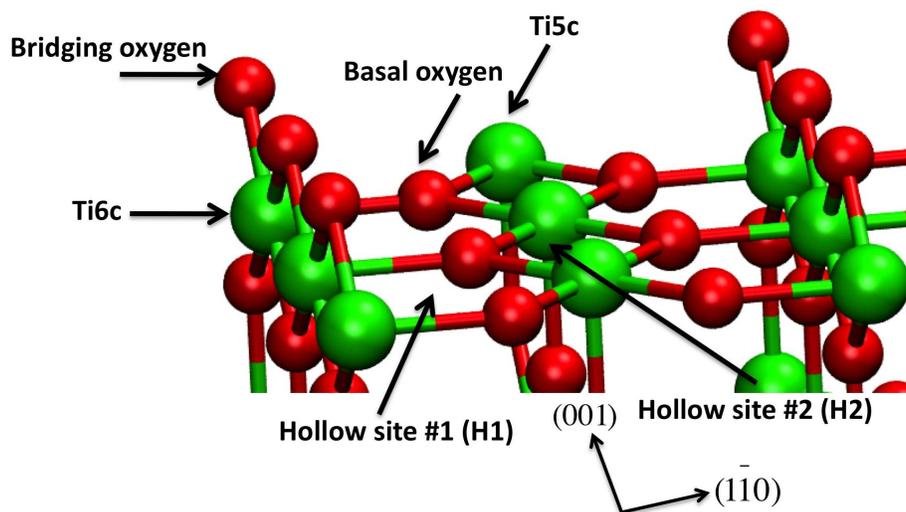
Figure 1: An extended $TiO_2(110)$ surface with possible sites for metal adsorption labeled. Oxygen atoms are colored red and titanium atoms are green. The five-coordinated titanium site is labeled Ti5c and the six-coordinated site Ti6c.
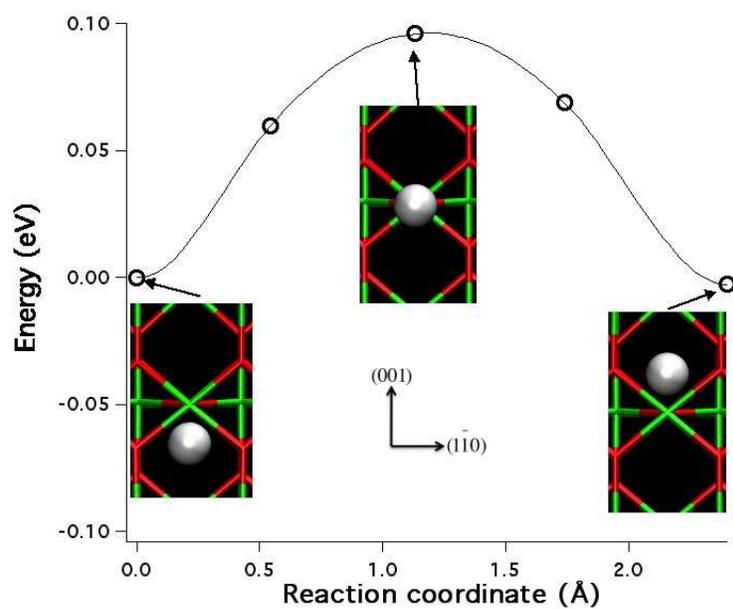
(a) Stoichiometric surface
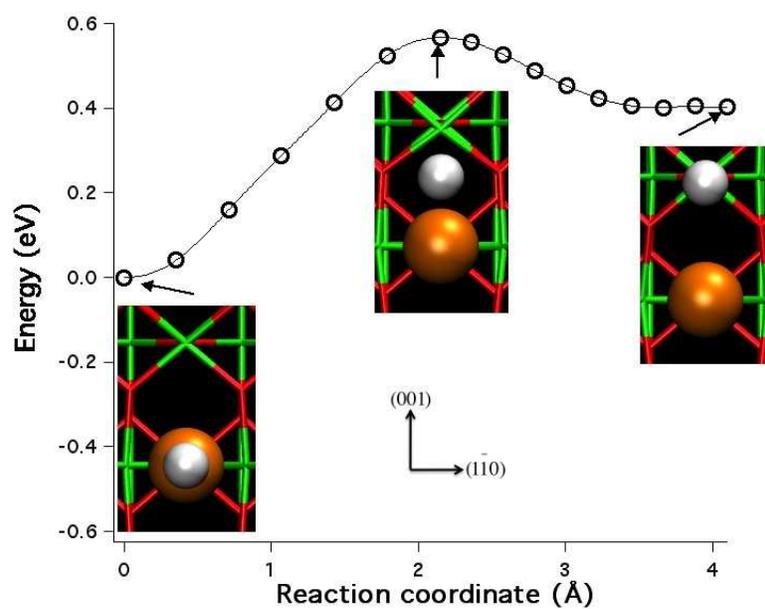
(b) Reduced surface

Figure 2: Diffusion MEPs for the gold monomer. The oxygen vacancy site is shown by the orange sphere.
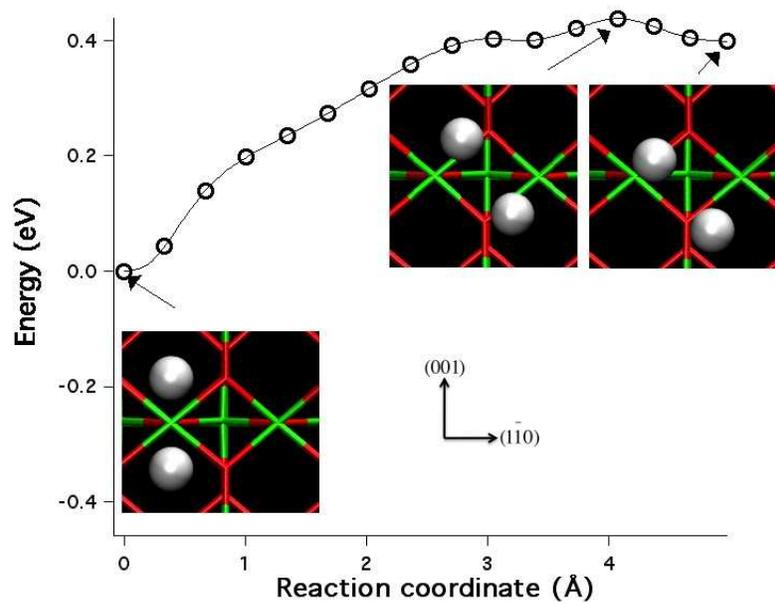
(a) Stoichiometric surface
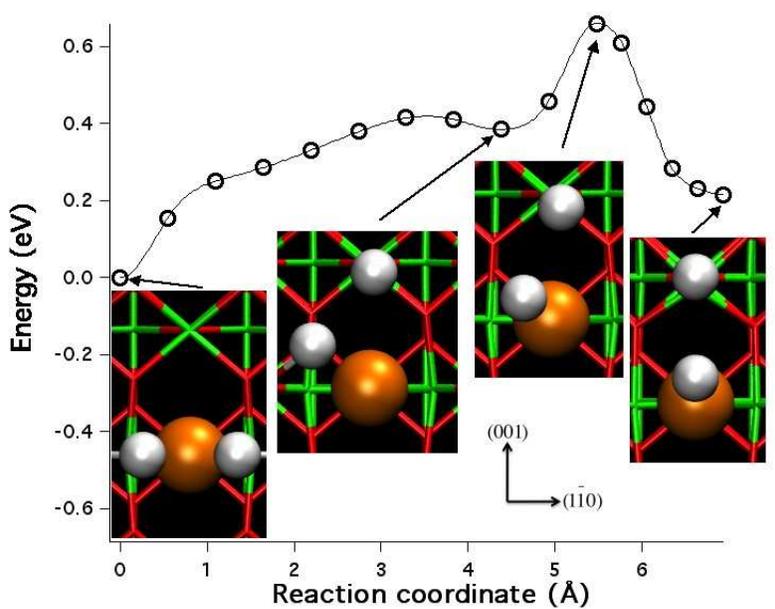
(b) Reduced surface

Figure 3: Diffusion MEPs for the gold dimer.
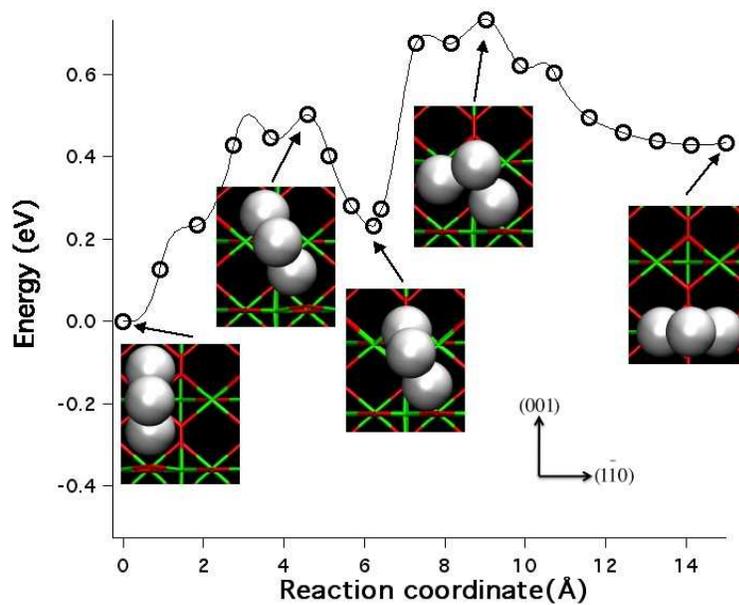
(a) Stoichiometric surface
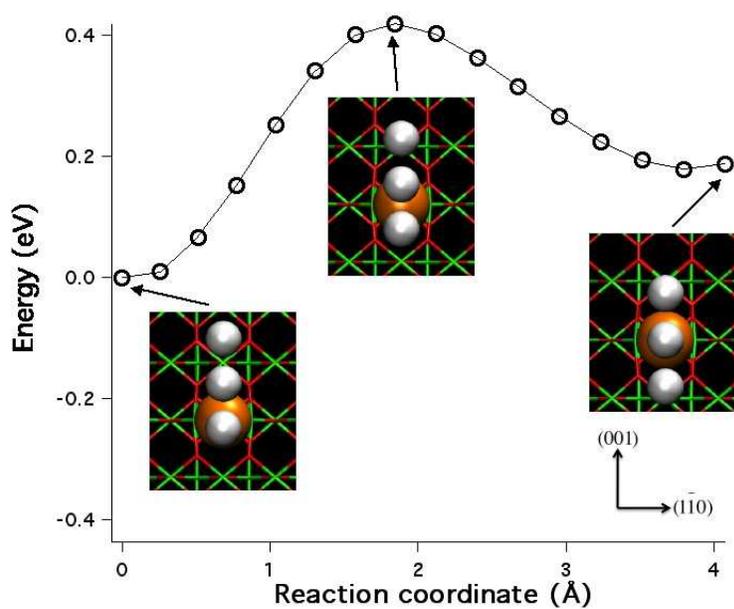
(b) Reduced surface

Figure 4: Diffusion MEPs for the gold trimer. For the stoichiometric surface, the gold atoms are enlarged in order to show the trimer's three dimensional structure.

(a) Au_1

(b) Au_2

(c) Au_3
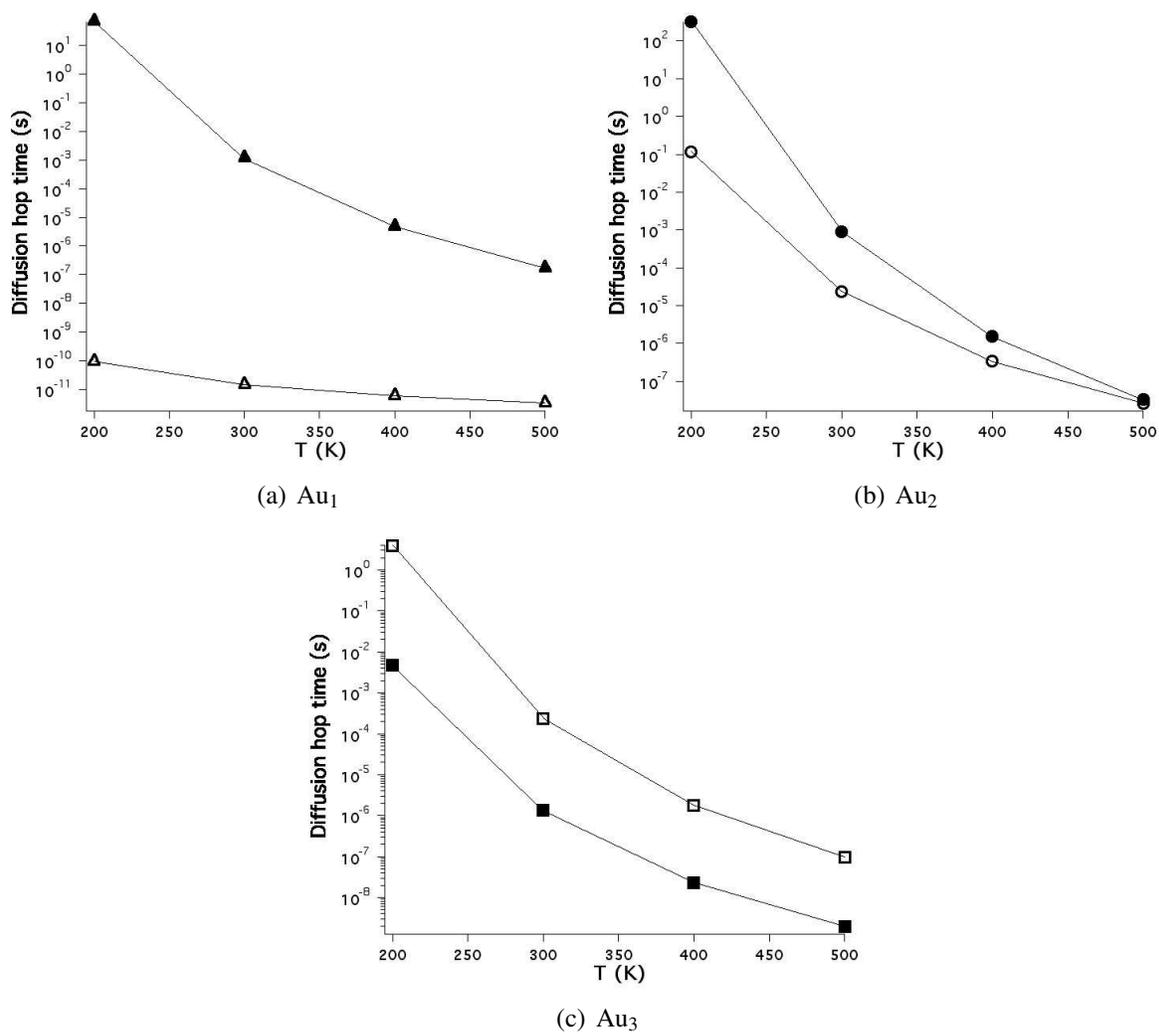
Figure 5: Diffusion hop times for forward hops for all systems. Open symbols correspond to the stoichiometric surface and closed symbols to the reduced surface. For the gold trimer on the stoichiometric surface, we display results from the rate limiting step only.

Supporting Information

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Here we present additional details of our NEB and vibrational mode calculations. The reaction coordinate for each MEP is defined as sum of the collective displacement of all atoms.[1] A cubic spline was used to interpolate between points on each MEP. For the gold dimer on the stoichiometric surface, geometry optimization of an intermediate structure (replica #11) revealed the possible presence of a shallow local minimum (0.007 eV). However, this energy difference is too small to be resolved by our GGA-DFT calculations. Similarly, geometry optimization of an intermediate structure of the dimer on the reduced surface (replica #9) revealed a possible local minimum too shallow to be resolved by our calculations (0.03 eV). For the gold trimer on the stoichiometric surface, two NEB calculations were performed: one between the first minimum and the intermediate (replica #9), and one between the intermediate and second minimum. Vibrational normal modes calculations were found to be converged with atomic displacements of 0.001 Å (same as previous results[1]). All transition states were confirmed by verifying the presence of a single imaginary frequency in the normal modes. For the second transition state of the gold trimer on the stoichiometric surface, an additional saddle point calculation with the Dimer method[2,3] was performed in order to obtain a transition state with only one imaginary vibrational frequency. A summary of our computed energetic barriers and vibrational prefactors is shown in the table below.

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Table S 1: Table of computed activation energies and vibrational prefactors for the forward diffusion pathway from the first to the second minimum (forward hop).

Cluster	Surface	E_A/eV	ν/THz
Monomer	Stoichiometric	0.10	3
Dimer		0.44	1
Trimer (1st barrier)		0.50	1
Trimer (2nd barrier)		0.49	9
Monomer	Reduced	0.57	3
Dimer		0.66	140
Trimer		0.42	9