Ostwald ripening microkinetic simulation of Au clusters on MgO(001)

Samantha Francis a, Alexandre Boucher a, Glenn Jones b, Alberto Roldan a,*

a Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff, CF10 3AT, Wales, United Kingdom
b Johnson Matthey Technology Center, Blanells Ct Rd, Sunning Common, Reading RG4 9NH, United Kingdom

1. Introduction

Heterogeneous catalysts provide an alternative, more favourable, reaction pathway for many chemical industry processes such as manufacturing and energy conversion. [1] The efficacy of these catalysts is determined by their composition, size, shape and resilience of the active sites under reaction conditions. [2–6] Commonly built by late transition metal nanoparticles (NPs), the desired active phase of the catalyst is dependent on the application in question. Nevertheless, catalysts must generally possess a large area of active sites and be highly resilient towards changing conditions and the presence of pollutants. Many processes can lead to catalyst deactivation, including poisoning, phase changes and mechanical straining, in addition to sintering. [7] Poisoning occurs when species are irreversibly adsorbed onto the catalyst surface, preventing other species from adsorbing to undergo surface reactions. A step further from poisoning is a phase change, where the adsorbate is incorporated into the lattice structure. Mechanical strain can also cause changes in the active sites’ shapes and size through attrition, which can commonly occur from temperature fluctuations in the catalyst preparation and during the reaction. As mentioned, one of the most common processes that affect NP’s size and shape is sintering. This process has been shown to have a dramatic effect on catalytic activity [8] as it influences the number of active sites and their electronic structure. [9] Sintering is driven by reducing the surface-bulk ratio [10] and can be exacerbated by heat treatment during catalyst synthesis methods and reaction conditions. [11–14] Two principal mechanisms have been established to contribute to the enlargement of NPs: coalescence and Ostwald ripening. [15] During coalescence, [16] a whole cluster will migrate, collide with another particle and merge to form a single larger nanoparticle, also known as Smoluchowski ripening. During Ostwald ripening, a single atom breaks off (digests) from the less stable moiety (Ostwald digestion) and diffuses randomly across the surface until interacting with another cluster, where it is enveloped onto the new, more stable structure. [17] The sintering process is challenging to reverse, and the cost of replacing inactive catalysts can be very high not only from an engineering perspective, but also due to the cost of the expensive metals generally involved in catalysis. Through a better understanding of sintering rates and its mechanisms, deactivating processes can be minimized or possibly reversed by redispersion of the metal on the catalyst surface. [18]

Nanosize gold has been investigated for its catalytic properties since discovering the reactivity of Au NPs for reactions such as oxidation of CO at low temperatures, [19] acetylene hydrochlorination, [20] alcohol oxidation, [21] and activation of molecular oxygen. [22] These significant findings have prompted a flurry of research into understanding the activity of supported gold catalysts and the discovery of new uses.

* Corresponding author.
E-mail address: roldannmartinez@cardiff.ac.uk (A. Roldan).

https://doi.org/10.1016/j.apsusc.2021.151317
Received 7 June 2021; Received in revised form 11 August 2021; Accepted 14 September 2021
Available online 25 September 2021
0169-4332/© 2021 The Author(s). Published by Elsevier B.V. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).
Correspondingly, magnesium oxide (MgO) has been used extensively as support material for metal catalysts,[23–25] in surface science[26] and electronics.[27,28] MgO is a prototypical example of a non-reducible metal oxide support, which crystallizes in a simple rock salt structure[29,30] exposing, relatively defect-free, its most stable surface, MgO (0 0 1).[31,32] This size-dependent activity of Au/MgO(0 0 1) systems has been comprehensively discussed previously, and has been attributed to the properties that NPs exhibit,[33] i.e. a high surface-to-bulk ratio, (0 0 1).[31,32] This size-dependent activity of Au/MgO(0 0 1) systems are also influenced by the substrate-induced strain at the interface and the epitaxial stress within the cluster itself.[36] In a study measuring the magnitude of moiré fringes on a range of clusters supported on MgO, the authors found that Au clusters change morphology to become 3D clusters at Au weight loadings above 1.5 wt%.[37]

Previous microkinetic models built by Campbell et al.[12,13] rationalized Oswald’s ripening of supported Au NPs on TiO2 using a relation between the coverage of TiO2’s surface as a function of the temperature, providing the NPs’ growth speed as a function of time. Using experimental data in such model with a heating rate of 1 K s−1, they found results in a good agreement with experimental measurement of the Au covering on a TiO2 surface. This method can be seen as a ‘top-down’ approach, starting from macroscopic observations such as surface coverage and approximated particles’ mean average radius. We developed a bottom-up approach in the present work and applied it to the ripening and digestion of Au/MgO clusters (n < 10 atoms). We combined electronic structure analysis and microkinetic simulations to rationalize the cluster size distribution as a function of the temperature and Au loading.

### 2. Computational details

Supported Au clusters of up to 10 atoms in size were modelled using spin-polarized periodic plane-wave density functional theory (DFT) calculations performed within the Vienna Ab Initio Simulation Package (VASP).[38–40] The PBE density functional of Perdew, Burke, and Ernzerhoff[41] was used to calculate the exchange and correlation contributions and projector-augmented wave (PAW) pseudopotentials to describe the core electrons.[40,42] Dispersion interactions were computed using Grimme’s empirical dispersion correction DFT-D3.[43] The plane-wave kinetic cut-off was set at 450 eV, and a 3 × 3 × 1 Monkhorst-Pack k-point grid was used after benchmarking the Brillouin zone. Dipole corrections were applied perpendicular to the surfaces upon Au adsorption.

A MgO slab model of the most stable (0 0 1) surface was created from the optimized bulk structure, with lattice parameter 4.195 Å. Considering the computational time and the strength of the lateral interactions between periodically repeated Au clusters, we considered a slab with a surface area of 281.6 Å2 built with a thickness of two-layer consisting of 64 magnesium and 64 oxygen where the bottom layer was fixed. The slabs were separated by 20 Å vacuum fitted in the z-direction. This slab model’s accuracy was measured by appropriate benchmarking, see reference 44.

We calculated the adhesion energy (Eadh) using Eq. (1) to measure the interaction’s strength between the cluster and the surface. The clusters’ morphology in the gas phase (Aud) is the same as the optimized cluster on the support (Aud/Surf), and therefore, Eadh does not include any deformation energies, i.e., the adsorption energy is referred to gas-phase clusters at the same geometry as supported.

$$E_{\text{adh}} = \frac{E_{\text{Aud/Surf}} - (E_{\text{Surf}} + nE_{\text{Aud}})}{n}$$

In the Eq. (1) above, ESurf indicates the energy of a naked MgO(0 01) surface. We also calculated the binding energy per cluster atom (E_b) using Eq. (2) and an isolated single gold atom (Egd).

$$E_b = \frac{E_{\text{Aud/Surf}} - (E_{\text{Surf}} + nE_{\text{Aud}})}{n}$$

The clusters’ cohesion energy (Ecob) provides a measure of the interaction strength between atoms in the cluster and is calculated using the following Eq. (3):

$$E_{\text{cob}} = \frac{E_{\text{Aud}} - nE_{\text{Aud}}}{n} = \frac{E_b - E_{\text{adh}}}{n}$$

The energy barriers across the energy profile were determined by locating the transition states for atomic diffusion and attachment. A static path extrapolation technique was initially used to search for transition states along the reaction pathways, followed by a complete quasi-newton optimization of the identified transition state (TS). Frequency calculations were used to characterize the minima and transition states, based on the absence or presence of a single imaginary mode respectively.

#### 2.1. Au structures

We used an unbiased genetic algorithm to search low energy structures of small Au n clusters (n ≤ 5 atoms) and build larger moieties exploring an extensive range of structures.[44] Single-atom attachment and diffusion activation energies (E_a) were calculated with Eq. (4) to understand ripening processes:

$$E_a = E_{TS} - E_{ad,1}$$

Where the Ea,1 is the energy of the system with both, the Aud cluster and the single atom on the same slab before attachment, and the ETS is the energy at the transition state along the attachment reaction coordinates.

#### 2.2. Microkinetic methodology

We employed microkinetic modelling to extrapolate DFT results within a transition state theory (TST) framework, including the mean-field effect of temperature and Au coverage (0).[45] TST limitations include a disregard for short-lived intermediates and failure at high temperatures.[46] This approach has shown to be very effective to describe reaction dynamics and rates from a bottom-up perspective. The methodology here employed is detailed elsewhere.[45,47–50] Applied to Oswald coalescence processes, the elementary steps are diffusion, attachment and detachment of single atoms. The constant rate (k) of each elementary surface step is commonly computed using the following equation of Eyring, Evans and Polanyi:[51]

$$k = Ae^{-\frac{E_a}{RT}}$$

$$A = \frac{K_BTQ_{TS}}{hQ_b}$$

Where h is the Plank constant, K_B is the Boltzmann constant and T the temperature. The calculated partition function for the transition state (QTS) and the reactants (Q_b) are used to calculate the pre-exponential factor (A). The entropic and the enthalpic contribution to the Gibbs free energy equation are derived from the partition functions. The reaction activation energy (ΔG) is calculated from the Gibbs free energies of the TS and the reactants.

As part of the discussion regarding the microkinetic simulations, the metal dispersion was also calculated. In the first microkinetic experiment, we considered one atom per simulation cell leading to 3.552 × 1012 Au atoms per m2, equivalent to 1.16 × 104 g Au m−2, and a metal dispersion of 8604.44 m² gAu⁻¹.

### 3. Results and discussion

The data collected in Table 1 shows that an increase in cluster size...
increases cohesion energy ($E_{coh}$) and decreases adhesion energy ($E_{adh}$) per cluster atom. Cluster structures are included in Table S1 in the supplementary Information and detailed in reference 44. The overall interaction is expressed by the binding energy ($E_b$), overall showing an increase in the Au$_8$/MgO(0 0 1) stability with increasing the clusters’ size (n). This finding is in line with the accepted idea that particle size will increase to minimize the surface-bulk ratio. [52] Along with the decrease in adsorption energy and the increase in binding energy, the Bader charge analyses show that the charge transfer from the surface to the Au atoms decreases with the cluster size, remaining close to 0.1 e per Au atom (Table 1). Such charge transfer implies that while the association between Au atoms is favoured, the interaction with the surface becomes less critical with cluster growth. The supported odd-numbered clusters of Au atoms have an unpaired electron in the 6 s orbital, the resultant magnetization of which, decreases with cluster size as the electrons are increasingly delocalized. Clusters with an even number of atoms undergo electron pairing, to reinforce their stabilization, see Table 1, which results in an overall cluster magnetization of 0 μB. Therefore, during the sintering process, one should expect a change in the catalyst’s total magnetization due to the disappearance of Au$_1$, which could be measurable, for instance, by electron spin resonance (ESR).

### 3.1. Single-atom migration mechanism

Two stable positions were found for a single Au atom on MgO(001), on top of an O atom and on top of an Mg atom. [44] Bridge sites are not stable, and upon optimization, the Au atom lay on top of an O atom. A hollow site was optimised using a conjugate gradient algorithm leading to minima in the potential energy although upon analysis of its vibrational modes, we found it to be the transition state between O-top sites with an imaginary vibrational frequency of ~32 cm$^{-1}$. The most stable of these positions, with adhesion energy of 1.37 eV is on top of an O atom, which compares to a value of 0.89 eV atop an Mg atom, in agreement with previous computational work [53] and it is also supported by experimental electron paramagnetic resonance (EPR) in combination with infrared reflection-absorption (IRA) spectroscopic data produced by Yulikov et al. [54].

We investigated two possible diffusion pathways from one O-top position to an adjacent one: i) the path in a straight line crossing the hollow site and ii) the path across the magnesium atom. The energy barrier for the process across the hollow was measured to be 0.29 eV, while the $E_b$ across the Mg is 0.22 eV higher.

The surface diffusion coefficient ($D_s$) at a temperature ($T$) of an entity performing a random walk within the validity of the transition state theory is given by the relation in Eq. (6):

$$D_s = D_{so} \exp \left( - \frac{E_s}{K_B T} \right),$$

where $D_{so}$ is a frequency factor, and $E_s$ is the activation energy controlling the diffusion pathway. For an isolated atom migrating on a surface, $D_{so}$ can be obtained from the Einstein relation of a random walk:

$$D_{so} = \frac{k_B T}{6 \pi \eta d},$$

In Eq. (7) we have neglected the entropy and the vibrational contribution to the energy, $\alpha$ is the dimensionality of the motion ($\alpha = 2$), $d$ is the jump distance, and $n$ is the number of jump directions available to the adatom on the surface of MgO(001) ($n = 4$). Using zero-point energies ($E_{ZPE}$, in Eq. (8)) to correct the energy (E) in initial and transition leading to $E_b$, the diffusion coefficient ($D_{so}$, usually in cm$^{-2}$ s$^{-1}$) becomes Eq. (9), and, at 300 K, the pre-factor ($D_{so}$) is calculated at 6.89x10$^{-5}$ cm$^2$ s$^{-1}$ and the surface diffusion ($D_s$) is 6.29x10$^{-5}$ cm$^2$ s$^{-1}$, which are comparable to those of self-diffusion atoms. [56] In Eq. (8), $c$ is the speed of light in cm$^{-1}$, in line with the vibrational frequencies ($\nu$) units (cm$^{-1}$).

$$E_{ZPE} = E + \frac{1}{2} \sum_i \hbar \nu_i,$$

$$D_s = \frac{k_B T}{h} \nu \exp \left( \frac{E_{ZPE}}{k_B T} \right),$$

#### 3.2. Ostwald ripening mechanism

We placed the migrating atom at approximately two oxygen away from the cluster, ensuring that it is on a stable position far enough to avoid any interaction with the cluster. Distances further away were investigated, which were calculated to have negligible energy differences. However, a starting distance nearer, the atomic relaxation forces the single-atom to bind the cluster. Hence, from a separated position and moving along the reaction coordinate, the coalescent atom crosses the hollow site toward the cluster and upon overcoming the $E_c$ merges with the cluster, as illustrated in Fig. 1. We have assumed that, once the Au$_1$ atom combines with the cluster Au$_{n-1}$ the atomic rearrangement to the most stable geometry of Au$_{n-1}$ has an energy barrier lower than the attachment and migration barriers. Energetic and structural information relating to each cluster size’s ripening energies can be found in Table 2.

In general, the greater the cluster size, the greater the stability of the cluster. Additionally, the formation of an even number of atoms clusters is more favourable than odd clusters, resulting in the odd–even behaviour. The structural analysis shows that as the cluster size increases, the average surface to cluster distance ($dAu-S$) also increases due to the larger number of atoms in contact with the surface (interface atoms) although individual Au atoms’ interaction decreases. This trend is supported by the decrease in $E_{adh}$ with the cluster size. However, there is some deviation from this trend, $dAu-S$ increases from 2.2 Å to 2.7 Å between Au$_6$ and Au$_8$. This increase can be associated with the point at which the clusters lie parallel (n > 6) rather than perpendicular (n < 6) to the surface. When the clusters lie flat, parallel to the surface, the number of atoms at the interface increases suddenly and $dAu-S$ increases as the interaction of individual atoms with the surface decreases more rapidly than in perpendicular arrangements. Au$_3$ does not follow this trend due to its unique geometric feature, shown in Fig. 2, which displays the square symmetry (001)-like configuration in the centre, rather than the typical (1 1 1) arrangement seen for all other clusters at this scale. [44] The Au$_4$ configuration creates slightly shorter bonds between the Au atoms in the (001) arrangement and results in a lower $dAu-S$.

Generally, the activation barriers associated with single-atom attachment in all systems is relatively small (<1.05 eV from Table 2). This trend can be explained by the reasonably high mobility of gold atoms on the MgO support[57] and the lack of defects or adsorbed

### Table 1

Summary of the adsorption ($E_{adh}$), cohesion ($E_{coh}$), binding ($E_b$) energies, magnetization ($M_s$) and charge ($q_{Au}$) of the lowest energy configurations obtained for the Au$_n$/MgO (n ≤ 10) system. The cluster spin magnetization shows a distinct odd–even trend associated with the accommodation of the unpaired electron of Au atom.

| n  | $E_{coh}$ (eV/atom) | $E_{adh}$ (eV/atom) | $E_b$ (eV/atom) | $M_s$ (μB) | Average $q_{Au}$ |
|----|-------------------|-------------------|----------------|----------|----------------|
| 1  | 1.37              | 0.00              | 1.37           | 1.00     | 0.24           |
| 2  | 1.00              | 1.15              | 2.15           | 0.00     | 0.12           |
| 3  | 0.93              | 1.20              | 2.13           | 0.97     | 0.11           |
| 4  | 0.86              | 1.50              | 2.36           | 0.00     | 0.12           |
| 5  | 0.66              | 1.67              | 2.33           | 0.89     | 0.11           |
| 6  | 0.65              | 1.89              | 2.54           | 0.00     | 0.10           |
| 7  | 0.66              | 1.86              | 2.51           | 0.54     | 0.10           |
| 8  | 0.66              | 1.99              | 2.65           | 0.00     | 0.10           |
| 9  | 0.64              | 1.98              | 2.62           | 0.24     | 0.10           |
| 10 | 0.60              | 2.08              | 2.68           | 0.00     | 0.08           |
species stabilizing specific moieties.\textsuperscript{[58,59]} The formation of an even number cluster is associated with considerable reaction energy ($E_r$) compared to an odd-numbered cluster. Once formed, odd number clusters have an unpaired electron rendering the single atom unpaired, whereas the electrons are paired for the even-numbered clusters. This pairing interaction is evidenced by the cluster magnetization described in Table 1, Figs. 3 and 4. Fig. 4 highlights that odd-numbered clusters will react exothermically with Au\textsuperscript{+} compared to an odd-numbered cluster. Once formed, odd number cluster sizes. This pairing interaction is evidenced by the cluster magnetization described in Table 1, Figs. 3 and 4. Fig. 4 highlights that odd-numbered clusters will react exothermically with Au\textsuperscript{+} compared to an odd-numbered cluster. Once formed, odd number cluster sizes. This pairing interaction is evidenced by the cluster magnetization described in Table 1, Figs. 3 and 4. Fig. 4 highlights that odd-numbered clusters will react exothermically with Au\textsuperscript{+} compared to an odd-numbered cluster.

Table 2

| $n$ | $E_r$ /eV | $E_a$ /eV | $d_{Au-S}$ (Å) | $d_{Au-Au}$ (Å) |
|-----|-----|-----|-------------|-------------|
| 1   | 2   | 0.73 | 2.198       | 2.516       |
| 2   | 3   | 0.31 | 2.292       | 2.596       |
| 3   | 4   | 0.25 | 2.207       | 2.654       |
| 4   | 5   | 1.04 | 2.239       | 2.712       |
| 5   | 6   | 0.14 | 2.705       | 2.716       |
| 6   | 7   | 0.34 | 2.695       | 2.740       |
| 7   | 8   | 0.21 | 2.676       | 2.710       |
| 8   | 9   | 0.68 | 2.710       | 2.793       |
| 9   | 10  | 0.23 | 2.731       | 2.746       |

Fig. 1. Representation of a single atom attachment path to an Au\textsubscript{4} cluster leading to Au\textsubscript{6}. Distances are represented in Angstroms between Au and the binding oxygen. The colour scheme is as follows: Orange = Mg, red = O and gold = Au.

Fig. 2. Schematic representation of the most stable geometry of Au\textsubscript{4}/MgO(001). Distances are in Angstroms between Au atoms and binding oxygen. The colour scheme is orange = Mg, red = O and gold = Au.

Fig. 3. Representation of Au\textsubscript{4} + 1 and Au\textsubscript{6} cluster systems showing (left) the magnetization located entirely on Au\textsubscript{1}, and (right) the magnetization delocalized over Au\textsubscript{6}. Distances are in Angstroms between Au atoms and binding oxygen, and isosurface level is 0.001 e/Å\textsuperscript{3}. Colour scheme is orange = Mg, red = O and gold = Au.

not only because of intaking an unpaired electron but also because it marks the transition towards moieties parallel to the surface by weakening the interphase interaction and substantially increasing its $d_{Au-S}$ from 2.239 Å in Au\textsubscript{4} to 2.705 Å in Au\textsubscript{6} (see Table 2).

Fig. 5 illustrates the trend between activation ($E_a$) and reaction ($E_r$) energies of the ripening process, which appears to follow the Brønsted-Evans-Polanyi (BEP) principle; $R^2 = 0.9$ – excluding the particular cases of Au\textsubscript{12}, Au\textsubscript{4} and Au\textsubscript{6}. These three clusters have all the electrons paired and, while the activation energy to for the process $\LambdaAu_{n+1} \rightarrow \LambdaAu_{n}$ highlights the Au\textsubscript{4} stability, the low $E_a$ on Au\textsubscript{12} and Au\textsubscript{6+1} represents the instability of Au\textsubscript{12} and Au\textsubscript{6}. Indeed, Au\textsubscript{2} sits perpendicular to the surface with a very low coordinatition, which is proportional to the surface energy. The transition state to form Au\textsubscript{13} is at 5.9 Å from Au\textsubscript{2}, which points to a dissimilar initial state compared with the other processes. Similar out-of-trend behaviour is found on $\LambdaAu_{n+1} \rightarrow \LambdaAu_{7}$ where the Au\textsubscript{6} mismatch with the support strains the Au–Au bonds, as seen on the $d_{Au-Au}$ in Table 2, promoting its growth. The BEP principle is widely used to estimate a vast number of molecular systems’ reactivity, but has not been considered in ripening mechanisms before. Further detail on such analysis would accelerate investigations on larger clusters and nanoparticles.

3.3. Ripening simulations

We have integrated the energetic information presented above into microkinetic models to simulate two processes: cluster ripening and cluster digestion. The microkinetic model’s application shows the distribution of the species in the system at a specific temperature (T) and time (t) with varying initial Au dispersions. The temperature increases to
The blue dotted line indicates a linear relationship ($R^2 = 0.9$) of the solid-black points.

510 K in 10 K steps.

Experimentally, the prepared catalysts’ metal dispersion varies depending on its composition and its preparation method. For example, a 12 wt% Ni/Al$_2$O$_3$ catalyst used for hydrogenation reactions has a metal dispersion of around 150 m$^2$g$^{-1}$,[60] a 1–20 wt% Cu in CuO/Al$_2$O$_3$–ZrO$_2$ catalysts for the synthesis of biofuel 2-methyl furan has metal dispersion ranging between 180–536 m$^2$g$^{-1}$,[61] a 1 wt% Au-SiO$_2$ catalyst has been reported with a metal dispersion of 18 m$^2$g$^{-1}$, which is increased to 101 m$^2$g$^{-1}$ when alloyed with Pd.[62] We are considering here a model with Au dispersions significantly higher than typically achieved for heterogeneous catalysts, as the implemented bottom-up approach provides control at atomic-level. We defined the initial ($t = 0$ s) coverage ($\theta$) as the occupation of cells containing Au$_X$ (X = 1 for ripening and 10 for digestion) to be 0.1, 0.5 and 0.9 monolayers (ML), giving 10% 50% and 90% of the maximum metal dispersion of 8608.44 m$^2$g$_{Au}^{-1}$. Notice that a monolayer is defined as one Au atom per slab area and, therefore, the maximum Au$_{10}$ coverage is a tenth of the initial Au$_1$ in agreement with the reaction stoichiometry. The highest initial coverage of Au$_{10}$ is 0.1 ML.

Fig. 6 illustrates the $\theta_{Au1}$ decrease as a function of increasing temperature due to its sintering, which initiates slightly above 100 K. After one minute at 150 K, Au$_1$ coalescence reached 0.26%, 2.26% and 12.18% of its respective initial coverage, i.e. 0.1, 0.5 and 0.9 ML. The steep slope observed between 180 and 240 K indicates that this process is happening very fast, especially at large coverages. At 370 K, the concentration of Au$_1$ is below 10$^{-6}$ ML for any simulation. Fig. 7 illustrates further details on $\theta_{Au1}$ with respect to the temperature and time (t < 0.01 s), where it is clear the accelerating effect of high temperatures, i.e. the descending slope, which perfectly fits with experimental observations on the increases of the atoms’ mobility and the diffusion rates across the surface, see 3.1 single-atom migration mechanism.[63] At lower coverages, the sintering process is slower by the fact that individual atoms have less chance of meeting another atom.

The end-results of Au$_1$ coalescence is the formation of Au$_{10}$ as can be observed in Figs. 8 and 9. In fact, most of Au$_1$ converts into Au$_{10}$ after 1 s at 290 K. The remaining 4%, 0.9% and 0.5% of the initial Au atoms are in a different clusters’ size than Au$_{10}$, respectively for the initial 0.1, 0.5 and 0.9 ML. Au$_{10}$ coverage keeps increasing with time until reaching a plateau at a tenth of the initial Au$_1$ coverage, i.e. 0.01, 0.05 and 0.09. It is worth mentioning that, among the structures remaining, Au$_{10}$ is the most prominent, see Fig. 9, in agreement with its stability and activation energy to growth, see Table 2. Au$_4$ coverage grows very quickly, acting as Au sink, before leading to larger species. Notice that Au$_{10}$ could increase further upon including the process in the simulation scheme, which implies the computationally demanding exploration of supported Au$_{10}$ (m$^2$g$^{-1}$) structures and transition states for a single atom coalescence.

### 3.4. Cluster digestion

To simulate the digestion process, i.e. forming smaller moieties from large clusters, the microkinetic experiment starts with Au$_{10}$ on the same MgO surface with a 0.1 ML coverage. The presence of Au$_{10}$ remains consistently high during the 60 s simulated, in agreement with the energy profiles, although the system’s dynamic behaviour can be seen in Fig. 10. Au$_{10}$ temporally decreases at ~ 160 K leading to Au$_9$ and Au$_8$ as well as Au$_1$ and products of its coalescence. Fig. 11 shows the species with the most significant coverages derived from Au$_{10}$ at 160 K and 1 s of the reaction time. The increase in the Au$_{10}$ occupation at higher temperature is explained by the rise in energy allowing further movement to the atoms which remain for longer in the most stable conformation, i.e. Au$_{10}$.

The observed digestion of Au$_{10}$ has significant implications in the design of supported Au nanostructures. Although they can be synthesized with minimal size dispersion, they present a dynamic size according to the conditions to which they are exposed, e.g. initial Au$_{10}$ digests to Au$_9$ and Au$_{11}$.[64]
4. Conclusion

We have combined DFT and microkinetics methods to unravel the Ostwald ripening and digestion of Au$_n$ nanoparticles ($n \leq 10$ atoms) supported on MgO(001). From the calculated adsorption, binding and cohesion energies and charge transfer analyses, we found that Au clusters’ growth leads to the increasing importance of inter-metallic interactions compared to interactions between the metal cluster and the surface. Furthermore, although significant stability was found in the largest cluster, the energies present an odd–even trend caused by the spin magnetization of odd-numbered clusters and single atoms, and the activation barriers for an Au atom to coalesce are not larger than 1.05 eV. Beyond the odd–even effect of reaction energies, it appears to be a linear correlation between reaction and activation energies in the same fashion that there is for chemical reactions, i.e. Bronsted-Evans-Polanyi, which may have important implications in predicting ripening mechanisms.

The microkinetic simulations provided a bottom-up approach giving comparable results to macroscopic studies of nanoparticles coalescence. From the observations here reported, one can conclude that: (i) at low

![Fig. 7. Illustration of the Au$_1$ concentration as a function of the time and temperature at initial coverages (top) $\theta_{\text{Au}_1}^0 = 0.1\text{ML}$, (middle) $\theta_{\text{Au}_1}^0 = 0.5\text{ML}$, and (bottom) $\theta_{\text{Au}_1}^0 = 0.9\text{ML}$.](image1)

![Fig. 8. Increasing Au$_{10}$ coverage as a function of time for different initial Au$_1$ coverages at a temperature of 290 K.](image2)

![Fig. 9. Coverage of Au$_i$ ($1 < i < 10$) clusters as a function of time at an initial $\theta_{\text{Au}1} = 0.5$ ML and a temperature of 290 K.](image3)

![Fig. 10. Decrease in the Au$_{10}$ occupation as a function of the reaction time and temperature for an initial Au$_{10}$ coverage of 0.1 ML.](image4)
Au coverages, the smaller clusters will remain for longer on the surface than at high coverages as they are less likely to aggregate, (ii) at temperatures higher than 160 K, there is enough energy in the system for the atom to overcome the ripening barrier and diffuse across the pristine surface to interact with other species on the surface, (iii) large moieties, such as \( \text{Au}_{110} \), also have a dynamic behaviour, easier to observe at relatively low temperatures, leading to size dispersion such as \( \text{Au}_{8} \) and \( \text{Au}_{9} \), but also to larger clusters (not included in this report). Overall, we presented an innovative ‘bottom-up’ approach providing new insights on the behaviour of single atoms, clusters and nanoparticles and the diffusion and coalescence pathways with the rational of electronic structure calculations.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

We thank the EPSRC for the support through the EP/P005845/1 grant. Via our membership of the UK’s HEC Materials Chemistry Consortium, which is funded by EPSRC (EP/L000202), this work used the UK Materials and Molecular Modelling Hub for computational resources, MMM Hub, which is partially funded by EPSRC (EP/P020194). We also acknowledge computing time on the facilities of Supercomputing Wales and the Advanced Research Computing @ Cardiff (ARCCA) at Cardiff University. All data created during this research are openly available from the University of Cardiff Research Portal orca website: http://doi.org/10.170355.2021.0137591611.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apsusc.2021.151317.

References

[1] Tao, F. (Feng), Schneider, W. F. & Kamat, P. V. Heterogeneous Catalysis at Nanoscale for Energy Applications. (Wiley, 2015).
[2] S. Mostafa, et al., Shape-Dependent Catalytic Properties of Pt Nanoparticles, J. Am. Chem. Soc. 132 (2010) 15714–15719.
[3] Yulan Wang, Zhichao Tao, Baoshan Wu, Huimin Chen, Jian Xu, Yong Yang, Yongwang Li, Shape-controlled synthesis of Pt particles and their catalytic performances in the n-hexadecane hydroconversion, Catal. Today 259 (2016) 331–335.
[4] R. van den Berg, et al., Structure sensitivity of Cu and CuZn catalysts relevant to industrial methanol synthesis, Nat. Commun. 7 (2016) 20457–20465.
[5] Mostakke Haruna, Size-and-support-dependency in the catalysis of gold, Catal. Today 36 (1) (1997) 153–166.
[6] Q. Fu, A. Weber, M. Flynazni-Stephanopoulou, Nanostructured Au–Co2 catalysts for low-temperature water–gas shift, Catal. Letters 77 (2001).
[7] C. Mebrahtu, F. Krebs, S. Abate, G. Centi, R. Palkovits, G02 Methanation: Principles and Challenges, Stud. Surf. Sci. Catal. 178 (2019) 85–103.
[8] Calvin H Bartholomew, Mechanisms of catalyst deactivation, Appl. Catal. A Gen. 212 (1-2) (2001) 17–60.
[9] R. Ouyang, J.-X. Liu, W.-K. Li, Atomic Theory of Ostwald Ripening and Disintegration of Supported Metal Particles under Reaction Conditions, J. Am. Chem. Soc. 135 (2013) 1760–1771.
[10] L. Banke, P.W. Voorhees, Growth and Coarsening : Ostwald Ripening in Material Processing, Springer, Berlin Heidelberg, 2002.
[11] P. Wymblart, N.A. Gostein, Particle growth in model supported metal catalysts—I, Theory, Acta Metall. 24 (1976) 1165–1174.
[12] A. Baldan, Review Progress in Ostwald ripening theories and their applications to nickel-base superalloys Part I: Ostwald ripening theories, J. Mater. Sci. 37 (2002) 2171–2202.
[13] C.T. Campbell, et al., The Effect of Size-Dependent Nanoparticle Energetics on Catalyst Sintering, Science (80-.) 298 (2002) 811–814.
[14] Charles T. Campbell, The Energetics of Supported Metal Nanoparticles: Relationships to Sintering Rates and Catalytic Activity, Acc. Chem. Res. 46 (8) (2013) 1712–1719.
[15] T.W. Hansen, A.T. DeLaRiva, S.R. Challi, A.K. Dute, Sintering of Catalytic Nanoparticles: Particle Migration or Ostwald Ripening? Acc. Chem. Res. 46 (2013) 1720–1730.
[16] V. Elofsson, Nanoscale structure forming processes, (Linköping University Electronic Press, 2016).
[17] Ostwald ripening. in IUPAC Compendium of Chemical Terminology (IUPAC, 2008), doi:10.1551/goldbook.c04348.
[18] Bartholomew, C. H., Fuentes, G. A. (Gustavo A..; & International Symposium on Catalyst Deactivation 7th : 1997: Cancún, M. Catalyst deactivation 1997 : proceedings of the international symposium, Cancun, Mexico, October 5-8, 1997. (Elsevier, 1997).
[19] Mostakke Haruna, Gold as a novel catalyst in the 21st century: Preparation, working mechanism and applications, Gold Bull. 37 (1-2) (2004) 27–36.
[20] G HUTCHINGS, Vapor phase hydrochlorination of acetylene: Correlation of catalytic activity of supported metal chlorides catalyst, J. Catal. 96 (1) (1985) 292–295.
[21] Z. Wang, C. Xu, H. Wang, A Facile Preparation of Highly Active Au/MgO Catalysts for Aerobic Oxidation of Benzyl Alcohol, Catal. Letters 144 (2014) 1919–1929.
[22] M.D. Hughes, et al., Tunable gold catalysts for selective hydrocarbon oxidation under mild conditions. 407 (2005) 112–133, 135.
[23] N.M. Jullakpi, S. Bagheri, Magnesium oxide as a heterogeneous catalyst support, Rev. Inorg. Chem. 36 (2016) 1–41.
[24] Ivona Tomška-Forašeková, Michal Zielinski, Mariusz Pietrowski, Wiesław Przytajko, Maria Wojciechowska, Iridium supported on MgF2–MgO as catalyst for CO oxidation, Catal. Today 176 (1) (2011) 263–266.
[25] Mingzhou Wu, Yu Fu, Wangcheng Zhan, Yanglong Guo, Yun Guo, Yunsong Wang, Guanzhong Lu, Catalytic Performance of MgO-Supported Co Catalyst for the Liquid Phase Oxidation of Cyclohexane with Molecular Oxygen, Catalysts 7 (5) (2017) 155, https://doi.org/10.3390/catal7050155.
[26] Bajtich, M., Norskov, J. K. & Jøvovic, A., Surface Energetics of Alkaline-Earth Metal Oxides: Trends in Stability and Adsorption of Small Molecules. (2015).
[27] Y. Zhu, et al., First-principles study on secondary electron emission of MgO surface, J. Appl. Phys. 101 (2007) 083710.
[28] P. Wu, G. Cao, F. Tang, M. Huang, Electronic and magnetic properties of transition metal doped MgO sheet: A density-functional study, Comput. Mater. Sci. 86 (2014) 180–185.
[29] K.J. Chang, M.L. Cohen, High-pressure behavior of MgO: Structural and electronic properties, Phys. Rev. B 30 (1984) 4774–4781.
[30] Zhao Jian-Zhou, Lu. Lai-Yu, Y.-L. Xiang-Rong Chen, First-principles calculations for elastic properties of the rocksalt structure MgO, Phys. B Condens. Matter 387 (2005) 249–254.
[31] G.W. Watson, E.T. Kelsey, N.H. de Leeuw, D.J. Harris, S.C. Parker, Atomic simulation of dislocations, surfaces and interfaces in MgO, J. Chem. Soc. Faraday Trans. 92 (1996) 435.
[32] Claude R. Henry, Surface studies of supported model catalysts, Surf. Sci. Rep. 31 (7-8) (1998) 231–325.
[33] J.K. Norskov, T. Bilgarc, J. Rossmeisl, C.H. Christensen, Towards the computational design of solid catalysts, Nature chemistry 1 (1) (2009) 37–46.
[34] N. Lopez, et al., On the origin of the catalytic activity of gold nanoparticles for low-temperature CO oxidation. 223 (2004) 232–235.
[35] M. Cargnello, et al., Control of Metal Nanocrystal Size Reveals Metal-Support Interface Role for Ceria Catalysts, Science (80-.) 341 (2013) 771–773.
[36] M.J. Walsh, et al., On the Structural Origin of the Catalytic Properties of Inherently Strained Ultrasmall Decahedral Gold Nanoparticles, Nano Lett. 12 (2012) 2027–2031.
[37] K. Blick, et al., Methane oxidation using Au/MgO catalysts, Catal. Letters 50 (1998) 211–218.
[38] G. Kresse, J. Hafner, Ab initio molecular dynamics for liquid metals, Phys. Rev. B 47 (1) (1993) 558–561.
S. Francis et al.