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When Fluxionality Beats Size-Selection: Acceleration of Ostwald Ripening of Sub-Nano Clusters

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ABSTRACT

Size selection was demonstrated to suppress Ostwald ripening of supported catalytic nanoparticles. We show here that when the supported clusters are sub-nanometer in size and highly fluxional, such as Pt clusters on the rutile $\text{TiO}_2(110)$ surface, this paradigm breaks down, and the established theory of sintering needs a revision. At temperatures characteristic of catalysis (i.e. 700 K), sub-nano clusters thermally populate many low-energy metastable isomers. As these isomers all have different geometric and electronic structures, and thus, formation and dissociation energies (in lieu of surface energy), Ostwald ripening is not suppressed, despite the size-selection. However, some clusters arise as magic numbers in terms of sintering stability at the ensemble level. The acceleration of sintering by metastable species persists though weakens in polydisperse cluster systems. Lastly, we propose a competing pathways theory for sintering, which at the atomistic level, describes the found size-specific sintering behavior.

INTRODUCTION

Subnanometer metal clusters are, in general, thermodynamically less stable than larger clusters, since they have numerous low-coordination sites, large surface area to volume ratio, and fewer metal-metal bonds that can stabilize the cluster. As a result, they tend to sinter more rapidly than larger nanoparticles.^[1-4] Sintering, the process in which smaller clusters are consumed by and grow into larger clusters is driven by increasing stability of clusters as they grow, and is one of the primary deactivation pathways of nanoparticle catalysts.^[5,6] Metal nanoparticles sinter via either particle migration and coalescence, or Ostwald ripening.^[1,7,8] Weak cluster-support interaction promotes Brownian-type motion of particles on the support, favoring the particle migration and coalescence mechanism. In contrast, during Ostwald ripening, atoms detach from clusters, diffuse along the surface, and join other clusters. Since smaller clusters generally dissociate more easily, while larger clusters are better at retaining the arrived monomers, larger clusters tend to grow to the expense of the smaller ones. This mechanism is more prevalent in clusters that are bound strongly to the support and are therefore less likely to move around the surface. Sintering of supported metal catalysts has been studied extensively by several groups.^[9-13] For instance, Campbell et al. showed that accurate size dependence of particle energies (measured directly) is crucial for kinetic models and one cannot use the Gibbs-Thompson relation,^[14] which relates the chemical potential of a metal atom in a particle of radius R to the one in the bulk, to estimate the dependence of particle energy.^[11] There are many other models of Ostwald Ripening that explicitly incorporate kinetics in their derivations, many of which treat the metallic nanoparticles as spherical structures with varying degrees of wetting on the surface support, depending on surface-support interactions.^[14-16] Our approach differs from these works, as we focus on sub-nano clusters, and therefore do not consider the clusters as “wetting” the support to varying degrees, dependent on the interfacial surface energies of the cluster/air, support/air, and cluster/support. Instead, we

consider the full electronic energy of the entire Pt_n cluster, $n = 1-8$, in order to explicitly incorporate the isomeric diversity in the model. Using these electronic energies, we model the sintering process as the result of the thermodynamic driving force of the different chemical potentials of the clusters, and evaluate differences in these driving forces as a result of isomeric diversity.

Supported small clusters can be extraordinary catalysts, particularly at nano- and subnanometer sizes, which are then desirable to preserve. Also, nearly every atom in small clusters is surface-exposed and can participate in catalysis, thus reducing the amount of precious metal needed. For these reasons, there have been many efforts to prevent cluster catalyst sintering. Some of these efforts include doping or alloying with other elements to tune clusters' electronic structure,^[17-21] size selection of deposited clusters,^[22] and introduction of capping agents to metal nanoparticles.^[23] Among these approaches, size-selection has been shown to effectively suppress Ostwald ripening, because of the elimination of the main driving force for ripening: different surface energies of different cluster sizes.^[22] Specifically, this was shown for Pt_n ($n > 21$) on several different supports including Si_3N_4 and SiO_2 .^[22]

However, we showed on a number of examples that, in sub-nanometer regime, for a specific cluster size, under typical reaction conditions (e.g. temperature of ~ 700 K), several metastable cluster isomers in addition to the global minimum (GM) structure are present, interconvert, and affect all catalyst properties.^[24-27] We argue here that sintering must be impacted by this dynamic fluxionality. We show that, although size selection is an effective method to prevent sintering for large and relatively rigid clusters, smaller size-selected clusters sinter rapidly because of their access to multiple isomers, all having different surface energies, and thus preserving a driving force for sintering. Our model of Ostwald ripening of Pt clusters on the $TiO_2(110)$ surface shows

that the presence of metastable structures increases the driving force for the sintering of subnanometer Pt clusters. Additionally, the extent of the effect is in fact size-dependent.

Note that our approach will hold for all catalytic systems regardless of the complexity of the surface (with step edges, vacancies, and other defects), and it is useful when the system is prone to dynamism in reaction conditions and thus to exhibiting isomeric diversity. However, this work focuses on one surface as an example, and it is purposefully chosen to be simpler, in order to deconvolute the effect of isomeric diversity from support-induced complications, including support restructuring. On the other hand, cluster-support interaction can also affect the sintering rate of clusters. For weaker cluster-support interaction our revised theory for Ostwald ripening would still hold, but would have to be appended with particle migration and coalescence, and we hypothesize that the particle mobility would also be size- and isomer-dependent.

Finally, note that this study is largely based on thermodynamics, whereas the kinetics of all elementary steps in principle could be important for sintering. However, the main driving force of particles leaving smaller clusters and joining larger ones is a thermodynamic one, stemming from the difference between chemical potentials of clusters with different size (a ‘thermoactivated’ process).^[28] In this work, the kinetics for the monomer migration is taken into account explicitly, while the dissociation kinetics is approximated from the BEP relations, which we test and find holding true for the problem at hand.

COMPUATIONAL METHODS

Global Optimization

Global optimization of Pt_n/TiO₂(110) (n = 1–8) was performed using plane wave density functional theory (PW-DFT) implemented in the Vienna Ab initio Simulation Package (VASP)^{[29–}

^{32]} and projector augmented wave (PAW) potentials^[33] and the PBE^[34] functional. The kinetic energy cutoff of 400.0 eV was chosen for the plane waves. A convergence parameter of 10^{-6} eV for the electronic relaxation was used. Geometric relaxations were performed until forces on all atoms are less than 0.01 eV/Å. Gaussian smearing with the sigma value of 0.1 eV was used. The TiO₂(110) surface was previously optimized,^[35] and modeled as a (2 × 4) unit cell with four trilayers along the z-direction. A vacuum gap of 13 Å was used to avoid interactions between repeated images. During the geometric optimization the lower half of the slab was kept fixed. Only Γ -point sampling was used to obtain the energy due to a fairly large size of the super cell. For Pt₁/TiO₂(110) PES sampling, the unit cell was divided into an 11 × 11 grid, and the relaxation was done on the z coordinate of Pt while its x and y coordinates were fixed (Figures 1a and S1).

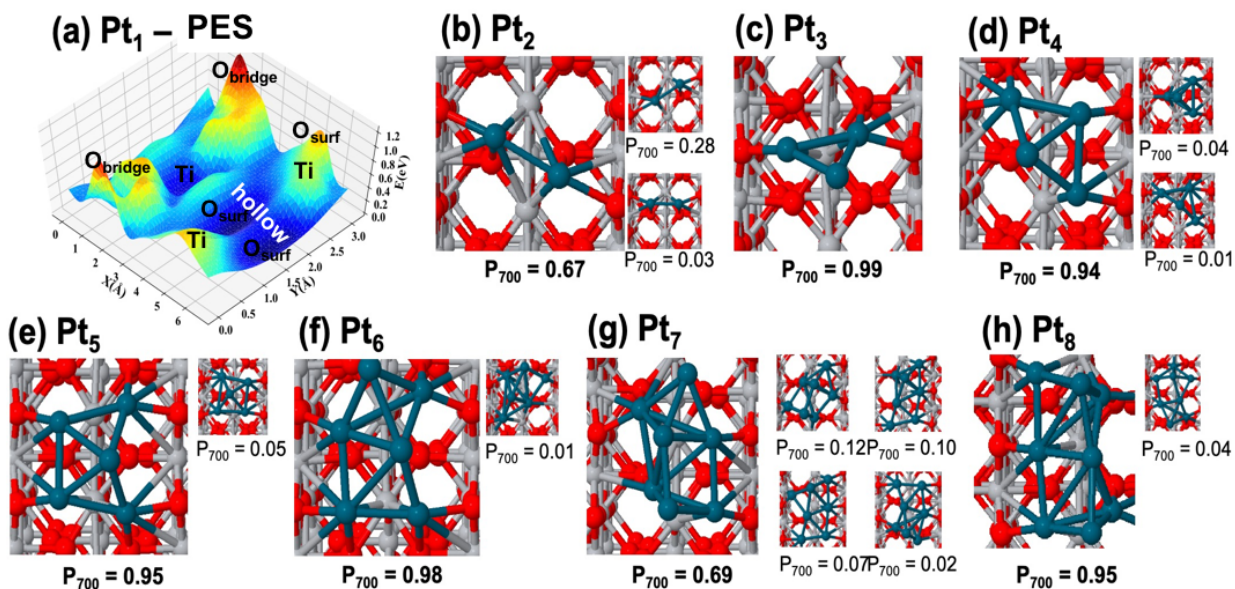


Figure 1. (a) The PES for the Pt monomer on TiO₂ (see SI Figure S1 for full PES along with the surface model). (b-h) GMs and accessible low-energy isomers of Pt_n (n = 2–8) on TiO₂(110); P_{700} signifies the Boltzmann probability of population at 700 K. Cyan – Pt, red – O, grey – Ti.

In order to produce the initial geometries for sampling of Pt_n , a parallel global optimization and pathway toolkit (PGOPT) was used.^[36] PGOPT generates structures based on the bond length distribution algorithm (BLDA), restricting the distance of each atom to its first and second nearest neighboring atoms to follow a normal distribution. This results in creating initial structures which are more chemically relevant, and thus easier to converge. We generated 25, 35, 50, 60, 80, 120, and 180 different initial structures for sampling of Pt_2/TiO_2 , Pt_3/TiO_2 , Pt_4/TiO_2 , Pt_5/TiO_2 , Pt_6/TiO_2 , Pt_7/TiO_2 , and Pt_8/TiO_2 respectively. In order to reach local minima on the PES, every structure was then fully optimized using DFT until forces on all atoms are less than $0.01 \text{ eV}/\text{\AA}$. Obtained structures were compared to each other in order to filter out the duplicates. Finally, in order to select the thermodynamically accessible isomers at relevant temperatures a cut-off energy of 0.4 eV was used. The GM structures for each sampled cluster size (Pt_2 – Pt_7) and several local minima with appreciable populations at 700K are shown in Figure 1 (b-h). Finally, the charge analysis was done using the Bader scheme.^[37–40]

Monte Carlo Simulations

The 2D Ostwald ripening model was based on precomputed cluster structures and energies. Every Pt_n/TiO_2 ($n = 1$ – 7) structure was obtained from global optimization and projected onto the 2D model of the support. Note that Pt_8 was not used as a starting size for sintering, in order to always have a possibility of the $n+1$ clusters to form with the isomeric diversity (Pt_9 and larger clusters were considered without isomeric diversity; see below). The size of the support was $\sim 158 \text{ \AA} \times \sim 72 \text{ \AA}$, or (24×24) unit cells of $\text{TiO}_2(110)$. The total number of clusters in the starting configuration was 100, for all systems. Note that most obtained local minima occupy the same hollow site on the slab. In our sintering model, we disregard the site and make all sites on the 2D

model equally likely for deposition. However, all the energies of the cluster isomers corresponded to their true preferred locations and were weight by the Boltzmann probabilities. Each cluster shape was approximated by the smallest circle containing all atoms in the cluster. During each step of sintering, an atom from a randomly chosen cluster (which can be a monomer) was moved using the Markov chain Metropolis Monte Carlo algorithm. The temperature of the simulation was 700 K, which corresponds to the high end of the dehydrogenation of ethylene on supported Pt clusters, measured by temperature programmed desorption (TPD).^[41,42] Every attempted cluster dissociation was associated with the precomputed thermodynamic penalty, and subjected to the Metropolis acceptance criterion. If a move brought a migrating monomer to an association with a stationary cluster, the probability of association was 100%. Atomic Pt evaporation and redeposition were ignored, as those were found to be minimal by theory and experiment.^[41,43] The sampling of the Pt_n/TiO₂ (n = 1–8) PES showed that, for every cluster size, several structural isomers should be thermally-accessible at 700 K (Figure 1). Thus, a cluster randomly selected to undergo a dissociation or association with a monomer can be any of its thermally-accessible minima, with a probability dictated by the Boltzmann populations of the given minimum. If two neighboring clusters grew enough to fuse, they were considered a single cluster, with the corresponding larger size, isomeric diversity, and energetics.

For clusters larger than Pt₈, cluster diversity was ignored in the model, and only a single structure and energy were considered. Figure S2 shows the binding energy of Pt clusters per atom as a function of the number of atoms in the cluster. This was used to estimate the energy for the larger clusters. The model for the radial growth of the larger clusters was based on Wulff constructs. First, it was determined that the Pt (100) facet of the bulk Pt was the preferred for the Pt/TiO₂(110) contact. From there, Wulff constructs based on Winterbottom constructs, therefore

taking into account the cluster/support interfacial energy, were prepared using Wulffpack^[44] (see Figure S3 for details).

The simulations were started both from the monodisperse cluster size distributions, and from the polydisperse systems with mixtures of cluster sizes (Figure 2). The monodisperse systems, thus far posited to withstand sintering better than polydisperse¹¹ systems, are the main focus of this study. Three different types of simulations were performed. In the first type, only GMs of the starting clusters were included, and in the process of sintering only GM structures of larger clusters could form. Note that the simulations starting from the monomers are specific, because the energy depends solely on the monomer location on the surface, and in this case, we do not enforce the GM-only starting configuration, to treat these systems on equal footing with others in terms of the random initial cluster placement on the support. In the second type of simulations, we start from the more realistic system characterized by temperature-dependent isomeric diversity for each cluster size, and the sintering proceeds with an access to higher-energy isomers of the forming clusters, all being based on their relative Boltzmann weights. Finally, in order to further account for the possible poorly-understood kinetic effects during cluster synthesis, we also probed the sintering of the systems that initially had fully random isomeric distributions (i.e. not obeying the Boltzmann distribution, and instead definitely exceeding the thermodynamically dictated number of higher energy isomers), but that sinter to larger clusters in accordance with the Boltzmann statistics for the forming cluster sizes. We call these three types of simulations the GM, Boltzmann, and isomer runs.

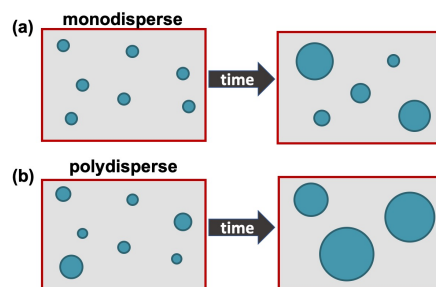


Figure 2. Schemas of the monodisperse and polydisperse setups for sintering simulations. Note that the actual unit cell and the number of deposited clusters used in the simulations are significantly larger (see text).

To ensure the rigorous averaging, for each isomer simulation, 5 different initial configurations were prepared with isomeric diversity. The coordinates and cluster sizes of each initial state with isomeric diversity were used for the Boltzmann/GM runs, simply replacing some/all of the higher-energy isomers with the GM cluster. Each of these initial states were then sintered 5 times, for 100,000 MC steps, to ensure randomization via MC. Note that the end of the simulation is somewhat arbitrary; the eventual result of sintering is rather uninteresting (one large particle), and we are interested in the sintering rate rather than the end result.

For the polydisperse systems, the procedure was identical: multiple cluster sizes were randomly placed on the surface, and the system was allowed to sinter, either accessing the isomeric diversity or not. We probed two ranges of cluster sizes at the start of sintering: $\text{Pt}_2\text{-Pt}_7$, and $\text{Pt}_1\text{-Pt}_5$, as well as three initial proportion of the monomers (10%, 25%, and 50%).

Note that, in order to obtain a more quantitative picture of sintering, the actual barriers of all involved elementary steps should be calculated,^[16] and a model such as kinetic Monte Carlo^[45-47] would have to be used. The barriers involved in the monomer migration on the surface are explicitly taken into account in our simulations, but the step of atom dissociation from a cluster is

not. Given the number of isomers and clusters sizes, as well as the choices for dissociating atoms and end products, the estimated number of pathways would be $\sim 10^3$, i.e. impracticable. However, by BEP relationships,^[48,49] barriers and energies of reaction steps should be related. In order to test the validity of the BEP relations for our fluxional clusters, we performed the explicit reaction pathway calculations for the dissociation of the GM and LM2 of supported Pt₄ (Figure S4). These clusters were chosen due to significant difference in the deposition sites and energies, and the fact that their dissociation produces different isomers of Pt₃ (and the GM of Pt₁). Despite the significantly different chemistries, and large differences in the dissociation barriers, the calculated the ratios between the dissociation barriers and the reaction energies are nearly identical for GM and LM2 (see Figure S4). While this test is by no means exhaustive, and exhaustive tests are out of reach, we infer that the established BEP relations qualitatively hold true, and the simulations produce a qualitatively reliable picture from thermodynamics alone, as indeed suggested by the Ostwald's theory.

We should also note that there are several approaches to model sintering using kinetic Monte Carlo (kMC) or MD simulations.^[50–52] However, as already mentioned, the computational cost of kMC, with thousands of reaction pathways in our case, would be unsurmountable. On the other hand, in order to obtain a reliable result from MD simulations, a very long MD simulation is required, in order to visit enough local minima, and that is, again, computationally impractical. In addition, MD would not be able to involve more than just a few structures (usually only 2), due to the computational expense. Using accurate sampling of PES and MC simulations, we cover a huge size- and isomeric diversity, and, relying on BEP relations, cover a massive number of chemical events leading to sintering. While still containing approximations, we believe our method has a significant advantage and brings new insight.

RESULTS AND DISCUSSION

The relative sintering rates were monitored as the decay in the number of clusters with the number of MC steps, the evolution of the average and maximum cluster sizes at every stage of sintering, and the cumulative relative populations of cluster sizes.

Monodisperse systems

We find that the sintering rates of the clusters of all sizes are substantially impacted the isomeric diversity, when it is included in the simulations (Figure 3). Broadly, systems with greater isomeric diversity sinter faster than the systems represented by just the GM. Note that, while the GM-only simulations do not represent a physical reality, they serve as a contrast, and demonstration of an important phenomenon: small clusters are exempt from sintering suppression by size-selection. Interestingly, there is also a strong size-dependence to the sintering behavior. Three different categories of systems can be identified, based on the decay in the number of clusters with MC time steps, and its sensitivity to the isomeric diversity. Category 1 includes Pt₃, Pt₆, and Pt₇. These systems show the strongest difference between the sintering rates of the GM, Boltzmann, and isomer configurations (Figure 3a). Clusters of the Category 2, which includes Pt₂ and Pt₅, have intermediate differences (Figure 3b). Clusters of Category 3, Pt₁, and Pt₄, have small to negligible difference between the GM, Boltzmann, and isomer runs (Figure 3c).

The difference between the categories is further illustrated by the standard deviation over the 25 MC simulations, shown in Figure 3 (d-f) for cluster sizes representative of each category: Pt₃, Pt₂, and Pt₄. The same plots for all other sizes are given in the SI Figure S5. The total standard deviation, s , was computed by treating the standard deviation of each of the 5 different runs as

separate data sets, and combining them according to equation 1, where n_i is the number of data in set i , s_i is the standard deviation of set i , \bar{y}_i is the mean of set i , and \bar{y} is the mean of the combined sets.

$$s = \left(\sum_i^5 \frac{n_i s_i^2 + n_i (\bar{y}_i - \bar{y})^2}{n_i} \right)^{\frac{1}{2}} \quad (1)$$

There is a strong variation in the standard deviation between the simulations that start from different cluster sizes. For example, it reaches its extreme for the sintering of Pt₆ and Pt₇, regardless of the starting conditions. In contrast, for Pt₃, the standard deviation for the GM and Boltzmann simulations are significantly smaller than for the isomer simulations, suggesting that the higher-energy isomers of Pt₃, if formed, can promote sintering quite dramatically.

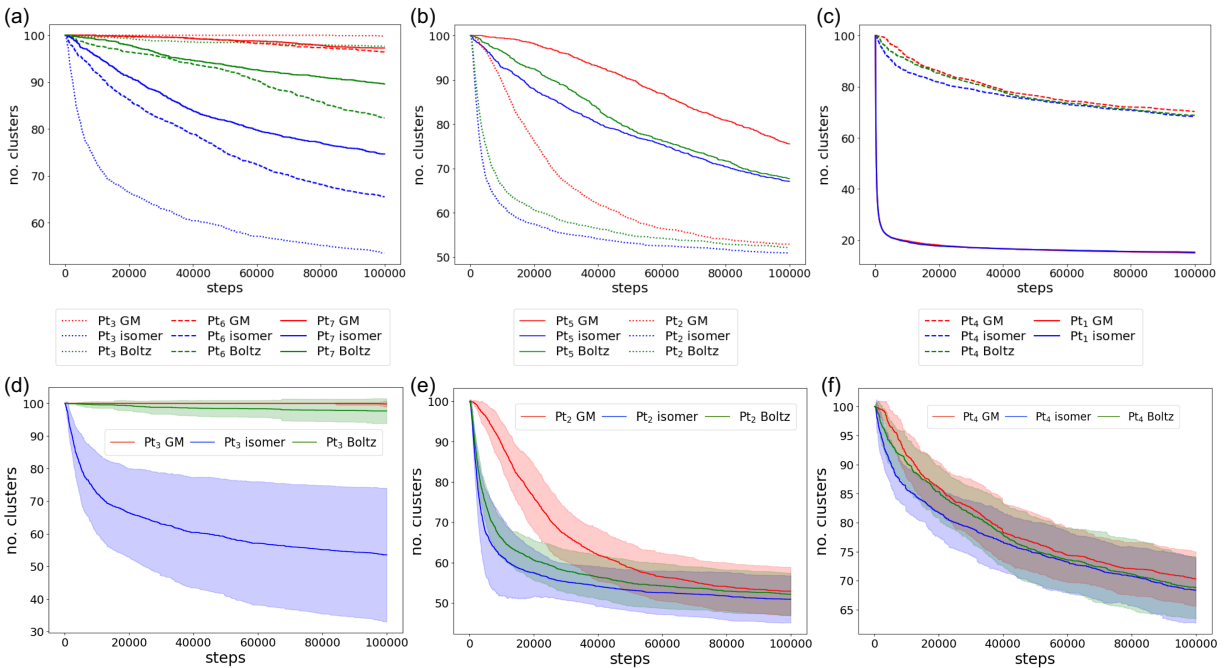


Figure 3. Sintering of monodisperse systems monitored via the total number of clusters present as a function of the MC step: Red - the GM-only sintering regime, green – sintering regime with the Boltzmann-weighted isomeric diversity, blue - sintering regime that starts from fully random isomer distributions and accesses isomeric diversity during sintering with the Boltzmann-weighted probabilities. (d), (e), and (f) show the standard deviations across the 25 MC simulations for Pt_3 , Pt_2 , and Pt_4 , respectively.

The practically important result is the relative sintering resistance (or the lack of) of the size-selected clusters in the presence of the isomeric diversity (green and blue curves in Figure 3). The resistance can be read from the relative steepness of the green (most realistic) and blue curves as a function of MC steps, and the number of clusters remaining on the surface at the end of the run. By this measure, Pt_3 and Pt_7 are the more stable against sintering among the considered cluster sizes, and could be called “magic number” clusters. Notice also that estimating sintering rate on the basis of just the GM can be misleading. For example, Pt_2 would be estimated to be more sinter-resistant than it really is (red versus green plots in Figure 3e). And yet, the GM-only estimation of sintering rate would not be too far off for, e.g., $Pt_{3,4}$ (Figures 3d,f). In other words, the role of isomeric diversity in sintering is cluster-size dependent and non-trivial, and the most dramatic example are clusters of Category 1, Pt_3 and Pt_7 .

The simplest, “step one” explanation for the observed size-dependence of the sintering acceleration via isomeric diversity can be derived from the first sintering step: $Pt_n + Pt_n \rightarrow Pt_{n-1} + Pt_{n+1}$ (Table 1). The energetics of the “step one” processes suggests that clusters of certain sizes need to overcome a large energy penalty before clusters of different sizes can start to populate the system and shift away from monodispersity. Once the shift occurs, the more rapid sintering is

promoted, as the energy differences between the clusters increase and progressively favor the growth of large clusters out of smaller ones.

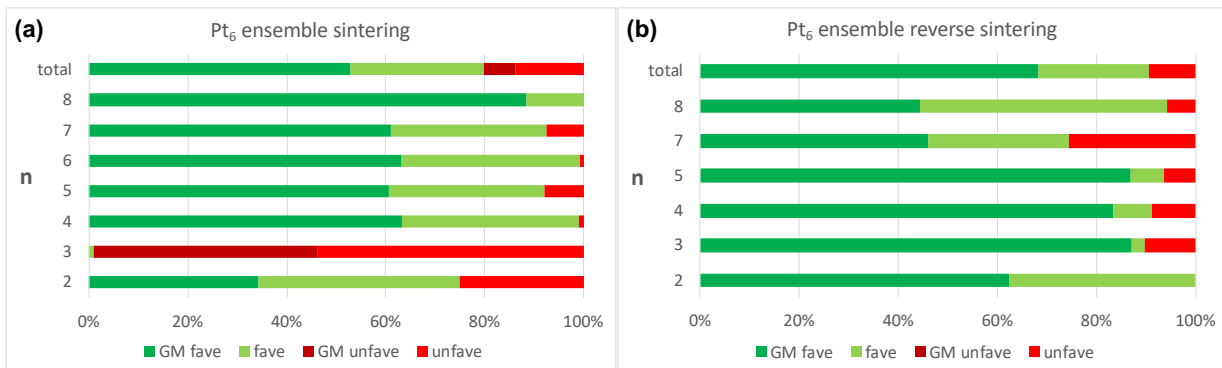
Table 1. The computed energetics of “step one” for sintering in fully monodisperse systems. Energetics derived from the GM energies of all cluster sizes.

Monodisperse Sintering Step	$\Delta E(\text{eV})$
$\text{Pt}_2 + \text{Pt}_2 \rightarrow \text{Pt}_1 + \text{Pt}_3$	-0.84
$\text{Pt}_3 + \text{Pt}_3 \rightarrow \text{Pt}_2 + \text{Pt}_4$	0.51
$\text{Pt}_4 + \text{Pt}_4 \rightarrow \text{Pt}_3 + \text{Pt}_5$	-0.05
$\text{Pt}_5 + \text{Pt}_5 \rightarrow \text{Pt}_4 + \text{Pt}_6$	0.12
$\text{Pt}_6 + \text{Pt}_6 \rightarrow \text{Pt}_5 + \text{Pt}_7$	-0.31
$\text{Pt}_7 + \text{Pt}_7 \rightarrow \text{Pt}_6 + \text{Pt}_8$	0.23

While the “step one” explanation appears to be enough to rationalize the sintering stability of Pt_3 and Pt_7 , it is insufficient for some other cluster sizes. For example, the “step one” of sintering of Pt_6 is, in fact, energetically favorable, in contrast to Pt_3 and Pt_7 , and this would suggest that Pt_6 would behave entirely differently; yet it does not (Figure 3a). Therefore, there must be additional fundamental reasons that dictate the total nature of sintering for monodisperse systems.

In order to explain the sintering behaviors across cluster sizes, we propose a “competing pathways” concept. After the “step one” of a monodisperse system sintering, other cluster sizes start to build up. Their subsequent sintering is subject to the energetics associated with the monomer exchange with clusters of other cluster sizes, the majority of which at the beginning are still of the initial size (e.g. Pt_6). The balance between favorability and unfavourability for Pt_n undergoing sintering (monomer moving from small clusters to large clusters) and reverse sintering (monomer moving from large to small clusters) with all other cluster sizes and their isomers present in the ensemble at 700 K are shown in Figure 4.

For example, Figure 4a,b shows the favorability of the forward and reverse sintering, respectively, of Pt_6 in the presence of Pt_n : $Pt_6 + Pt_n \rightarrow Pt_7 + Pt_{n-1}$, and $Pt_6 + Pt_n \rightarrow Pt_5 + Pt_{n+1}$. The magnitudes of the GM contributions to both forward and reverse processes are also highlighted (dark red and dark green portions of the plots). Hence the figure indicates whether the GM pathway is favorable or unfavorable, and the proportion relative to higher-energy pathways for the same process that contain higher energy isomers can be seen. This aids our understanding of how probable non-GM pathways are. As is clear by the proportion of green on the graphs for Pt_6 , that the forward and reverse sintering are both similarly favorable, and the GM contributes to a large fraction of the favorable pathways in both directions. However, as the forward and reverse favorabilities are fairly well-balanced, especially in the GM-only scenario, they should effectively cancel out, and hinder sintering. Once higher energy isomers can contribute, the probability of reverse sintering is lessened slightly compared to the probability of forward sintering, by the presence of higher-energy isomers of both Pt_6 and the clusters of other sizes. This isomer-induced imbalance pushes the sintering process forward, yielding the differences in sintering rates between the GM, the Boltzmann, and particularly the isomer simulations (Figure 3a).



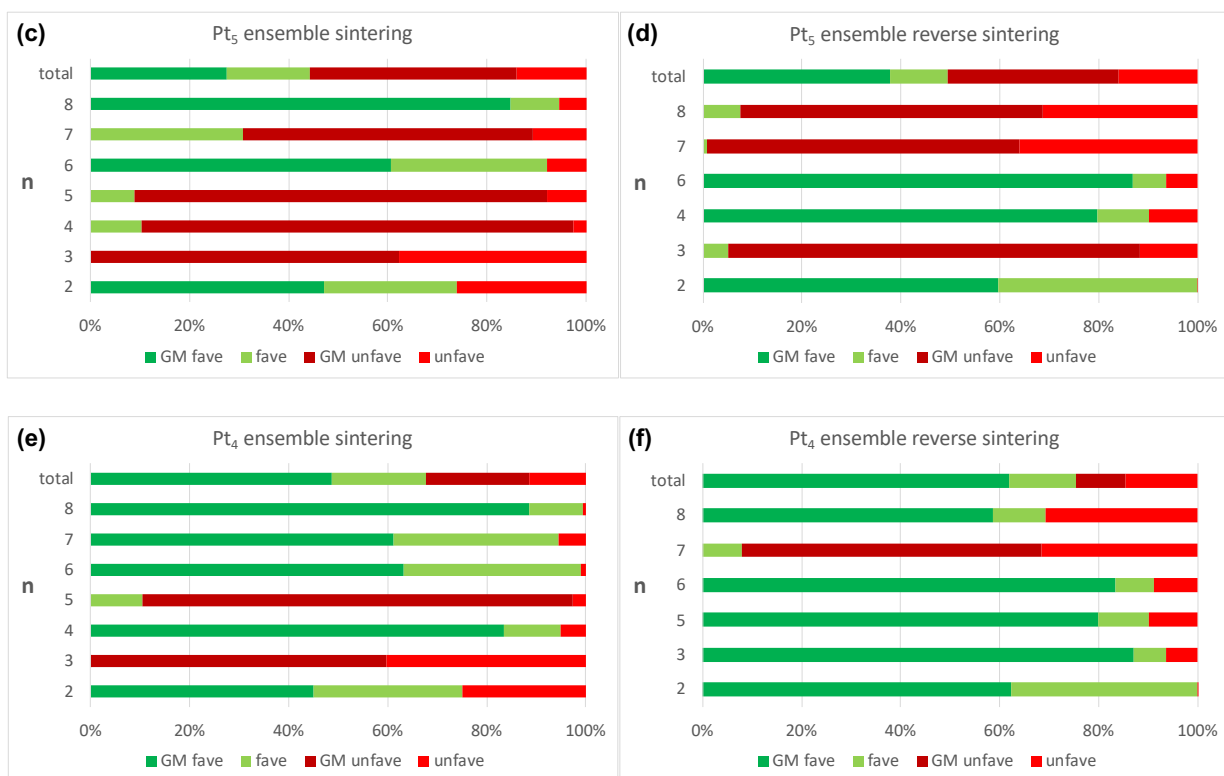


Figure 4. Favorability (in %) of (a) sintering and (b) reverse sintering of Pt₆ ((c) and (d) for Pt₅, and (e) and (f) for Pt₄) in the presence of Pt_n (n = 2–8) cluster (bottom to top row in each panel). Green and red indicate the proportion of thermodynamically favorable and unfavorable pathways respectively. The amount each possible pathway contributes to either case is scaled by the Boltzmann probability of the combination of isomers in the sintering process occurring together. The dark green or dark red indicates the GM contribution to favorable or unfavorable sintering, respectively. The data is based directly on the computed energetics of all possible sintering and reverse sintering pathways.

The sintering of Pt₅ (cluster of the Category 2) is a contrast to Pt₆. For Pt₅, the first step of sintering is energetically unfavorable. Despite this, the GM-only Pt₅ clusters sinter significantly faster than GM-only Pt₆ (Figure 3a,b), for which the first step is energetically favorable. While this appears as a paradox, it in fact emphasizes that “competing pathways” of sintering with other cluster sizes that build up in the early stages of sintering is an essential ingredient in the theory of

sintering. The competing pathways for Pt₅ (Figure 4c,d) highlight the differences in the energetic balance of the forward and reverse sintering for Pt₅, versus those for Pt₆, for example. While the energetics of Pt₅ does not favor sintering at “step one”, as soon as Pt₆ forms from Pt₅, further sintering of the system is energetically favorable. The reverse sintering of Pt₄ and Pt₆ with Pt₅ is favorable. However, cluster sizes further away from Pt₅, i.e. Pt₃, Pt₇, and Pt₈ do not tend to undergo reverse sintering with Pt₅, indicating that the overall balance is tipped in favor of sintering as a greater diversity of cluster sizes begins to build up. The inclusion of higher energy isomers, both for the initial, and all forming cluster sizes, tips the balance further in favor of sintering forward, hence why the isomer and Boltzmann sintering proceed faster than GM-only sintering, and also why the monodisperse GM-only Pt₅ may sinter faster than the equivalent of Pt₆.

Finally, Pt₄ is a representative of Category 3, and is a case where there is a small difference between the GM and isomeric runs, and the overall process of sintering proceeds with an intermediate rate. In this case, the “step one” and the “competing pathways” justifications are both necessary to rationalize the sintering behavior. The Pt₄ sintering “step one” is energetically favorable for the GMs (Table 1), which on its own would suggest facile sintering for systems both with and without isomeric diversity. However, from the competing pathways (Figure 4e,f), one can see that sintering of Pt₄ with Pt₃ and Pt₅ (which would form during “step one”) is unfavorable in the GM case. This results in a bottleneck in the sintering process; however, once either Pt₆ or Pt₂ forms in the system, Pt₄ sintering can proceed apace. When including higher energy isomers, however, this bottleneck is somewhat alleviated, as the sintering of some combinations of higher energy isomers is energetically favorable. Hence sintering with isomeric diversity proceeds at a slightly faster pace than without it, in this case (Figure 4e).

The cumulative size distributions in the ensembles of cluster states formed by the end of the sintering simulations are plotted in Figure 5. In general, the increase in isomeric diversity leads to the greater populations of larger, Pt_{8+} , clusters, and longer tails in the histograms toward larger nanoparticles. There is also a pronounced size-dependence. For example, for Pt_3 , the most extreme case of Category 1, the final distribution for the GM-only simulations is dominated by a single peak at Pt_3 , indicating an utter lack of sintering (red in Figure 5a). The Boltzmann-based sintering simulations, which are still overwhelmed by the GM of Pt_3 , are very similar and produce only small, though non-negligible populations of larger clusters (green in Figure 5a). The isomer runs, which were isomer-diversified on purpose at the start of the simulation, in contrast, produce much more spread-out distributions, and a significant access to larger clusters (blue in Figure 5a). While the isomeric diversity introduced at the start in the isomer runs is can be considered artificial, it suggests that kinetic effects in cluster formation may further accelerate sintering to some extent. Overall, we see further evidence that Pt_3 is a “magic number” cluster, in its stability against sintering. This can be seen also from the energetics of sintering and reverse sintering (Figure S7), and throughout Figure 4, where all the bars for sintering with Pt_3 are red. Generally, Pt_3 will not grow or be consumed, even by larger clusters.

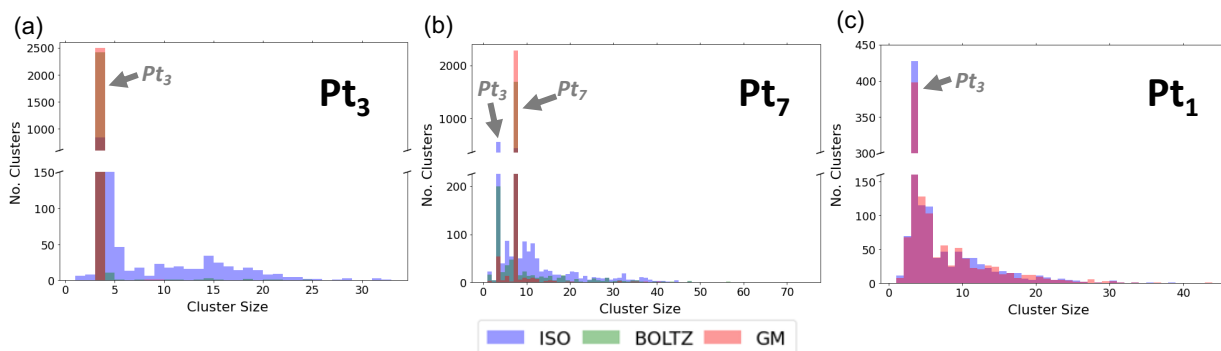


Figure 5. Cluster size distribution in the final MC step of the simulation of GM-only, Boltzmann, and isomer simulations for monodisperse $Pt_n/TiO_2(110)$ ($n = 1, 3, 7$).

Pt₇ is a more moderate case of Category 1, (Figure 5b), and interestingly, its sintering produces a double peak in the cluster size distribution, at Pt₃, and at Pt₇, as a testament to the stability of both cluster sizes. The relative heights of the peaks change with increasing isomeric diversity: while GM-only simulations result primarily in the intact Pt₇, isomeric diversity allows for the population of other cluster sizes, and in particular, produces a considerable amount of Pt₃. This is attributed to the stability of the GM of Pt₇ against sintering, and a much-reduced sintering stability of its higher-energy isomers. Notice that only 69% of the Pt₇/TiO₂ population is in the GM at 700 K (Figure 1). Some of the populated higher-energy isomers are significantly different in shape: they are quasi-single layer, i.e. flatter on the support. Notably, Pt₇ is the cluster size where all sorts of catalytic activities have been seen, from CO oxidation to ethylene dehydrogenation,^[41,53,54] the latter being attributed mainly to the flatter higher-energy isomers. Also, accessible isomeric diversity leads to the population of diverse active sites, and may indeed be the origin of catalytic activity of supported Pt₇ in a variety of reactions.

Finally, for the sintering of monodisperse Pt₁, there is virtually no impact from the inclusion of higher-energy isomers (Figure 5c). The behavior is also very similar for other clusters in Category 3: Pt₂, Pt₄, and Pt₅, (Figure S6). As another measure of sintering rates, and confirming all the conclusions already made, the maximum and average cluster sizes as sintering progresses are plotted in Figure S8.

The computed charges on all thermally accessible isomers of Pt_n (n = 1–8) clusters provide an electronic structure insight into the diverse sintering stabilities (Figure S10). First, all clusters donate electrons to the support, larger clusters generally donate more as a whole (though the trend is non-linear), but less on the per-atom basis, and local minima generally donate less than their corresponding GMs (most of the times). In other words, as temperature increases, and local minima

are introduced in the population, the ensemble-average positive cluster charge decreases. A differentiating effect is an intra-cluster charge separation, which is found only in Pt₃, Pt₇, and also in Pt₈ (Table S1). Such a separation was previously proposed to be the cause of the experimentally seen sintering resistance of Pt₄Sn₃/SiO₂,^[55] as it hindered cluster dissociation and monomer migration on the ionic support during Ostwald ripening. For Pt_n/TiO₂, a possible reason for the “magic number” stability of Pt₃ and Pt₇ can therefore be proposed: A homolytic dissociation creating a neutral Pt atom on the support requires an electronic structure reorganization within the cluster, likely associated with a concurrent shape change, and thus, being energetically costly. Dissociating a Pt atom heterolytically from a polarized cluster (though not the possibility that we explicitly consider here) would obviously create a charged Pt monomer whose migration on the ionic support would be hindered. Hence, an electronic structure argument can be made in the line with our observations (Figures 3a, 5b).

Polydisperse systems

To elucidate the effect of the cluster isomeric diversity on the sintering of polydisperse systems, sintering simulations were performed for sample systems with clusters, Pt₁₋₅ (Figure 6) and Pt₂₋₇ (Figure S9), and with the monomer composition of 10%, 25%, and 50%. Here again, an influence of the higher-energy isomers on the sintering rate is apparent (Figure 6), however, it is much smaller than for the monodisperse systems, and it is essentially erased at the highest monomer content of 50%. This is expected: since sintering is driven by the differences in surface energies, polydisperse systems are not immune to sintering from the start. Additionally, as the mobile Pt₁ is the natural driver of Ostwald ripening, and itself sinters rapidly (Figure 3b), its purposeful introduction produces but the expected result.

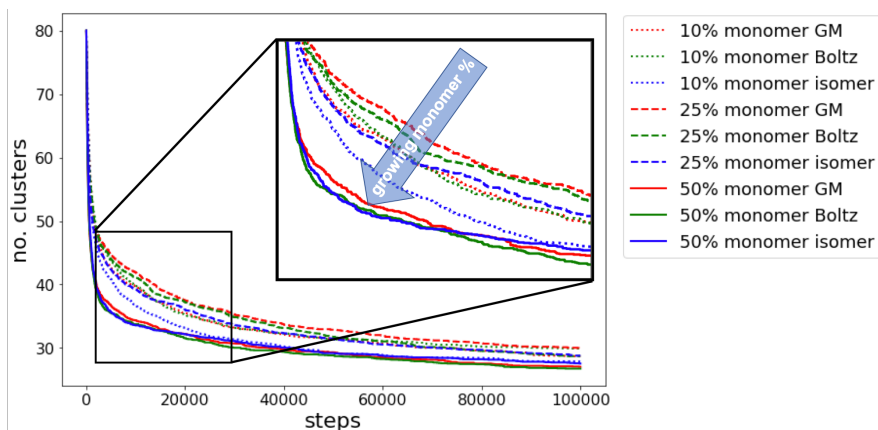


Figure 6. Sintering of polydisperse Pt_{1-5} cluster systems, with varying amounts of included monomers: 10%, 25%, and 50%. GM, Boltzmann, and isomer setups are shown in red, green and blue, respectively. The inset highlights that the increasing concentration of the monomers accelerates sintering and in fact overwhelms the effect of the isomeric diversity in the ensemble of larger clusters.

CONCLUSIONS

We showed that in the sub-nano regime, thermal Ostwald ripening of supported Pt clusters cannot be efficiently suppressed by size-selection. This is in stark contrast with larger size-selected nanoparticles. The effect is due to cluster structural fluxionality, which enables the thermal access to higher-energy cluster isomers, which have diverse surface energies. Different cluster sizes have specific isomeric distributions, with relatively more (or even significantly more) stable GMs, or instead a greater spread of the population toward the metastable minima. In addition, the GMs and metastable minima may or may not differ significantly in their stability against dissociation, in order to produce monomers for Ostwald ripening. These effects create profound differences in how the isomeric diversity impacts cluster sintering for different cluster sizes. For example, we find that Pt_3 is a “magic number” cluster, which does not sinter quickly even with the assistance of its higher-energy isomers (because those are poorly-accessible). Pt_7 is next most stable cluster,

though in this case the isomerization to metastable states is relatively easy, and to some degree facilitates the formation of Pt_3 again, and some other minority cluster sizes. $\text{Pt}_{2,4}$ sinter rapidly, etc. The sintering stabilities of specific species are linked to their electronic structure, and it appears that greater cluster-support charge transfer and intra-cluster charge separation are the stabilizing factors. The sintering acceleration role of cluster fluxionality and metastable isomers becomes less pronounced but still apparent in polydisperse systems. However, the large concentration of monomers (50% or more) can overwhelm the isomeric effect. Thus, the full thermal ensembles of metastable cluster states accessible to the system at catalytic temperatures (e.g. 700 K) has to be considered when assessing cluster sintering stability, or designing cluster catalysts that would be sintering-resistant.

The complexity of the sintering process for fluxional sub-nano clusters is encompassed in the proposed theory of “competing pathways”, which accounts for the full spectrum of forward and reverse sintering steps, starting from a given cluster size, and all the accessible isomers at the start and along the process of sintering. This statistical atomistic model of the sintering process explains the apparent disparities in the sintering behaviors and strong cluster size-sensitivities

ASSOCIATED CONTENT

Supporting Information Available:

Binding energies of $\text{Pt}_n/\text{TiO}_2(110)$ per atom as a function of number of Pt atoms in the cluster, Winterbottom constructs of Pt on a surface, Plots showing the standard deviation for the three different runs for the cluster sizes not depicted in the main text ($\text{Pt}_{5,6,7}$), Cluster size distribution in the final MC step of the simulation for monodisperse $\text{Pt}_n/\text{TiO}_2(110)$ ($n = 2, 3, 5, 6$), Favorability of sintering and reverse sintering of Pt_3 in the presence of Pt_n ($n = 2-8$) cluster, Maximum and

average cluster size for GM and isomer runs for Pt_n/TiO₂(110) (n = 2–7) at every MC step, Sintering decay for mixed system Pt₂₋₇, Bader charge analysis of Pt_n/TiO₂(110).

Sintering code along with the XYZ coordinates of the clusters used in this study can be found here: <https://github.com/bzkarimi/sintering>

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Notes

The authors declare no competing financial interest.

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Keywords: Ostwald ripening, fluxionality, isomeric diversity, metastable isomers, nanocluster catalysts

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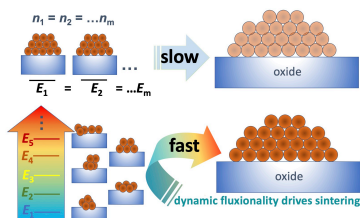
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Entry for the Table of Contents



For supported nanoclusters at typical catalytic temperatures, Ostwald ripening is strongly accelerated by structural fluxionality, even in the regime of cluster size-selection. Hence, a revision of the theory of Ostwald ripening is proposed.