ABSTRACT: We carried out density functional theory calculations to investigate the ripening of Pd clusters on CeO$_2$(111). Starting from stable Pd$_n$ clusters (n = 1−21), we compared how these clusters can grow through Ostwald ripening and coalescence. As Pd atoms have mobility higher than that of Pd$_n$ clusters on the CeO$_2$(111) surface, Ostwald ripening is predicted to be the dominant sintering mechanism. Particle coalescence is possible only for clusters with less than 5 Pd atoms. These ripening mechanisms are facilitated by adsorbed CO through lowering barriers for the cluster diffusion, detachment of a Pd atom from clusters, and transformation of initial planar clusters.

INTRODUCTION

Metal nanoparticles dispersed on high surface area oxide supports are widely applied as catalysts in diverse technology areas such as energy conversion, chemicals manufacture, and environmental protection. Considerable effort has been devoted to understanding the influence of the nanoparticle size on catalytic performance. The active phase can vary in size from isolated metal atoms or clusters of a few atoms up to nanoparticles containing thousands of atoms. A usual deactivation mechanism of supported nanoparticle catalysts is sintering, as it causes an undesired reduction in metal surface area. Sintering is usually thought to involve either particle migration (Smoluchowski ripening), in which nanoparticles diffuse over the surface and coalesce with other particles, or atomic migration, in which atoms of the nanoparticles are detached and diffuse over the support to attach to another nanoparticle. The latter mechanism is well-known as Ostwald ripening, and the main driving force is the minimization of the excess surface free energy. Based on the Gibbs–Thomson relation that describes the concentration of atomic species at support sites near a nanoparticle, various mean-field kinetic models for describing the sintering process have been considered.

Experimental data on nanoparticle sintering usually favor Ostwald ripening as the main sintering mechanism. On the other hand, Jak et al. found by scanning tunneling microscopy study that particle coalescence is the main mechanism for the sintering of very small Pd particles supported on TiO$_2$. Datye and co-workers mention that particle coalescence can be relevant at high temperature and for nanoparticles in close proximity on an oxide support. It has also been observed that common adsorbates such as CO can affect the sintering process.

Ouyang et al. showed the importance of metal–carbonyl complexes in atomic transport pathways during Ostwald ripening but also mentioned their role in the redispersion of supported metal nanoparticles.

Ceria is extensively used as a support material mainly because of its high oxygen storage capacity. The primary application of ceria-based catalysts is in automotive three-way converter technology, which is essential to the cleanup of gasoline engine exhaust gas. Pd is now frequently used as a cheaper alternative to Pt for catalyzing CO and hydrocarbon oxidation. As thermal sintering of the active phase contributes to the deactivation of these catalysts, it is important to gain a deep understanding of the sintering mechanisms of initially highly dispersed Pd/CeO$_2$ systems. Ceria as a support is also known for the unusual sinter resistance of noble metals supported on its CeO$_2$(111) surface. The agglomeration of Pd on ceria has not yet been investigated with atomic-level precision. This can among other ways be achieved by quantum-chemical calculations as, for instance, those shown for the sintering of initially highly dispersed Pt on TiO$_2$. Although isolated Pd atoms on ceria display promising low-temperature performance, sintering during occasional high-temperature operation will cause sintering and reduced catalytic performance. Accordingly, it is interesting to investigate the ripening mechanism of Pd on ceria.

In the present work, we employed density functional theory (DFT) to determine the stability and mobility of isolated Pd atoms and Pd$_n$ clusters (n = 2−21) on CeO$_2$(111), which is the most stable surface termination of ceria. On the basis of activation barriers for the migration of such adsorbed atoms and clusters, we discuss possible ripening mechanisms for Pd/
We investigated the role of CO as an adsorbate on the sintering process.

**COMPUTATIONAL DETAILS**

We carried out spin-polarized calculations within the DFT framework as implemented in the Vienna ab initio simulation package (VASP). The ion-electron interactions are represented by the projector-augmented wave (PAW) method and the electron exchange-correlation by the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional. The Kohn–Sham valence states were expanded in a plane-wave basis set with a cutoff energy of 400 eV. The Ce(5s,5p,6s,4f,5d), O(2s,2p), Pd(4d5s), and C(2s,2p) electrons were treated as valence states. The DFT+U approach was used, in which $U$ is a Hubbard-like term describing the on-site Coulombic interactions. This approach improves the description of localized states in ceria, where standard LDA and GGA functionals fail. For Ce, a value of $U = 4.5$ eV was adopted, which was calculated self-consistently by Fabris et al. using the linear response approach of Cococcioni and de Gironcoli and which is within the 3.0–4.5 eV range that results in the localization in Ce 4f orbitals of the electrons left upon oxygen removal from ceria.

For Pd/CeO$_2$(111) calculations, the model was a periodic ceria slab with a (4 × 4) surface unit cell. For Brillouin zone integration, a 1 × 1 × 1 Monkhorst–Pack mesh was used. The bulk equilibrium lattice constant ($5.49$ Å) previously calculated at the PBE+U level ($U = 4.5$ eV) was used. The CeO$_2$(111) slab model is two Ce–O–Ce layers thick, and the vacuum gap was set to 15 Å. The atoms in the bottom layer were frozen to their bulk positions, and only the top Ce–O–Ce layers were relaxed. The climbing image nudged-elastic band (CI-NEB) algorithm was used to identify the transition states for the migration of Pd over the surface and CO oxidation mechanism for selected models.

For reference purposes, we examined gas-phase Pd$_n$ clusters with $n = 2$–20, 38, 55, 85, 146, and 231. Their initial structures were taken from literature and their geometry was further optimized (Figure S1). For these gas-phase Pd$_n$ clusters, the cohesive energy ($E_{coh}$) was computed via

$$E_{coh} = \frac{nE_{Pd} - E_{Pd_n}}{n}$$

\[ (1) \]

Figure S2 shows the relation between the $E_{coh}$ and the number of atoms in the cluster ($E_{coh}$ vs. $n^{-1/3}$). Extrapolation to large $n$ results in an estimate of the bulk cohesive energy at 4.27 eV, in reasonable agreement with the experimental value of 3.9 eV.

For the generation of Pd$_n$ species ($n = 1$–21) on CeO$_2$(111), we started from several stable geometries identified for supported Pd$_{n-1}$ clusters (initially starting from Pd$_1$/CeO$_2$) and explored stable geometries upon addition of the nth Pd atom. This approach has already been adopted to investigate the polymorphism of gold nanoclusters on a reduced ceria surface. The interface of the largest Pd$_{21}$ cluster with the ceria surface is small enough to be accommodated in a (4 × 4) unit cell. For a Pd$_{41}$ cluster, we considered a larger (6 × 6) supercell.

For Pd$_n$ clusters supported on the CeO$_2$(111) surface, the cohesive energy can be obtained by taking into account the adhesional energy between the Pd$_n$ cluster and the CeO$_2$(111) slab. Then, the cohesive energy per Pd atom for the supported Pd$_n$ cluster can be computed from

$$E_{coh} = \frac{nE_{Pd} + E_{ceria} - E_{Pd_n-ceria}}{n}$$

\[ (2) \]

The stability of Pd$_n$ clusters on CeO$_2$(111) was evaluated by computing the energy involved to detach one Pd atom ($E_{det}$) considering reactions of the type

$$Pd_n-ceria + ceria \rightarrow Pd_{(n-1)} + ceria + Pd - ceria$$

\[ (3) \]

resulting in

$$E_{det} = E_{Pd(n-1)-ceria} + E_{Pd-ceria} - E_{Pd_n-ceria} - E_{ceria}$$

\[ (4) \]

In these formulas, $E_{Pd}$, $E_{Pd_n}$, $E_{ceria}$, and $E_{Pd_n-ceria}$ are the electronic energies of an isolated Pd atom, the Pd$_n$ cluster, the empty stoichiometric CeO$_2$(111) surface, and the Pd$_n$/CeO$_2$(111) model, respectively.

**RESULTS AND DISCUSSION**

**Structure of Pd$_n$ Clusters on CeO$_2$(111) ($n = 1$–21, 41).** We tackled the problem of identifying stable structures by adding Pd atom by atom to stable supported Pd$_n$ clusters starting from optimized Pd$_1$/CeO$_2$(111). We determined the most stable configuration for each ceria-supported Pd$_n$ cluster from several candidates. Figure 1 shows the structures of optimized Pd$_n$ clusters on the CeO$_2$(111) surface. Other configurations and the corresponding energy differences are

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*Figure 1. Stable Pd$_n$ clusters ($n = 1$–21) on the CeO$_2$(111) surface (color code: red, surface O; light yellow, Ce; coral, subsurface O; dark cyan, 1st–4th Pd; green, 5th–10th Pd; blue, 11th–20th Pd; black, 21st Pd).*
A Pd atom preferentially adsorbs close to an O-hollow site between two O anions of the CeO$_2$(111) surface (Pd1a). The adsorption energy is 2.08 eV, which is substantially lower than the cohesive energy of bulk Pd. The cohesive energy for the Pd$_4$ cluster is 2.30 eV. Two stable locations for the Pd$_4$ cluster were found. Adsorbing Pd$_4$ at the O-hollow site (Pd3a) is more stable than placing it at the Ce-hollow site (Pd3b). The three-dimensional tetrahedral Pd$_4$ cluster (Pd4a) is 0.18 eV more stable than its planar counterpart (Pd4c), which shows that Pd binds stronger to other Pd atoms than to the interface of the cluster and the ceria support.

A stable Pd$_5$ cluster is obtained by adding a Pd atom to the Pd$_4$ cluster in the Ce-hollow site of the ceria surface (Pd5a). Another nearly equally stable structure involves migration of the additional Pd atom in the top layer to a location above the Ce-hollow site (Pd5b). This migration is very easy with a barrier lower than 0.10 eV. The preferred structure of Pd$_5$ is derived from Pd$_4$ by adsorbing a Pd atom in a O-hollow site of the ceria surface (Pd6a). The cohesive energy of this cluster is 2.95 eV. The seventh Pd atom can be placed on one of the available threefold Pd sites at the interface formed by the five Pd atoms (Pd7a). Placement of the seventh Pd atom on the surface Ce-hollow site (Pd7c) is 0.39 eV less favorable. The eighth Pd atom is used to complete the filling of the three threefold sites on the Pd$_4$ layer (Pd8a) or by placing it on the ceria surface (Pd8b). These two states have almost the same energy. The ninth Pd atom completes the formation of a Pd$_4$ hexagon at the ceria surface with two Pd atoms adsorbed in the second layer (Pd9c). It should be noted that there is a slightly more stable structure (Pd9a, $\Delta E = -0.14$ eV). We show the slightly less stable structure for Pd$_9$ as the structure of the favorable Pd$_10$ cluster (Pd10b) is derived from it. Adding the tenth Pd atom to the more stable Pd$_9$ cluster results in a quite unfavorable structure (Pd10c), nearly 1 eV less stable than the most stable Pd$_10$ cluster (Pd10a). Pd10b is 0.08 eV less stable than Pd10a. The cohesive energy of the most stable Pd$_10$ cluster is 3.18 eV. The 11th Pd atom is located on a 4-fold site of the Pd$_{10}$ cluster (Pd11a), a configuration that is 0.24 eV more stable than the one obtained by adsorption adjacent to the cluster on the surface O-hollow site (Pd11c). The twelfth Pd atom is preferentially located on the ceria surface in an O-hollow site coordinating to the 11th Pd atom (Pd12a) instead of adsorbing on one of the remaining 4-fold site of the Pd$_{11}$ cluster (Pd12c). Such structures are less stable by 0.32 eV. Addition of further Pd atoms follows the same sequence until Pd$_{16}$, i.e., first, a Pd atom is added to a fourfold site followed by placement of another Pd atom on the ceria surface coordinating to this atom. This leads to formation of a symmetric Pd$_{16}$ cluster with a bilayer structure, the first layer consisting of 10 atoms, the second one of 6 atoms (Pd16a). The next three Pd atoms can be placed on threefold Pd sites, the twentieth at the resulting threefold site of the Pd$_{19}$ cluster (Pd20a). The twenty-first Pd atom is placed on a hollow site of the supported Pd$_{20}$ cluster (Pd21a), distant from the surface. We verified that placing the optimized gas-phase Pd$_{19}$ cluster on the ceria surface (Pd19b) yielded a structure that was substantially 1.77 eV less stable than the Pd$_{19}$ cluster optimized on the ceria surface. Conversely, the supported Pd$_{19}$ cluster is much less stable than the optimum gas-phase Pd$_{13}$ cluster.

Figure 2 shows that the cohesive energy increases strongly with increasing Pd cluster size up to a 10 Pd atoms. The cohesive energy for clusters between 11 and 20 atoms is nearly constant. The reason is that the number of Pd atoms forming Pd–O bonds with the ceria support is seven for all of these clusters. Although with growing cluster size there are more Pd atoms in the bottom layer, the Pd–O bond distances are much longer (∼2.20 Å) as compared to the other Pd–O distances (∼2.07 Å). We also constructed a Pd$_{41}$ cluster according to the same approach outlined above (see Figure S3a). After placing this cluster on a slightly larger ceria surface unit cell to reduce lateral interactions between the periodic images of these large particles, we found that it also forms seven strong Pd–O bonds. Its cohesive energy is 0.13 eV higher than that of the Pd$_{21}$ cluster, showing that the cohesive energy only slowly approaches the cohesive energy of bulk Pd.

We also examined the cohesive energy of the optimized clusters on the ceria support after removing the ceria support shown in Figure 2. The resulting values are substantially lower than the cohesive energies for the corresponding clusters supported on ceria. The difference, which includes the influence of the adhesion of the Pd cluster on ceria, becomes smaller for larger clusters. Figure 2 also shows the cohesive energies of optimized gas-phase clusters. These are slightly higher than those of the free Pd clusters taken from the ceria support, indicating that the supported cluster adopts a slightly less favorable structure under the influence of the support.

**Sintering.** We first computed the activation barrier for the migration of a single Pd atom on the CeO$_2$(111) surface from its most stable site to an adjacent site. The low computed barrier of 0.14 eV implies that the diffusion of atomic Pd in the Ostwald ripening mechanism is very facile. This result is similar to the low barrier reported for the diffusion of a Pd atom on Al$_2$O$_3$ surface by Sautet and co-workers. It is interesting to mention that the oxidation of a single Pd atom can stabilize the Pd atom at the ceria surface. We found that the barrier for diffusion of a PdO$_2$ cluster adsorbed on CeO$_2$(111) is 0.91 eV, substantially higher than the barrier for diffusion of a Pd atom. Relevant to Ostwald ripening is the energy needed to detach a Pd atom from a cluster and place it on the ceria support.

Figure 3 shows the energy cost to detach a Pd atom from Pd$_n$ clusters adsorbed on the CeO$_2$(111) surface and place it on the CeO$_2$(111) surface at infinite distance of the remaining cluster.
The lowest detachment energy is for the Pd$_2$ cluster (~0.4 eV), while clusters containing 11, 17, and 20 atoms also have detachment energies below 1 eV. The highest detachment energies (~1.7 eV) are for Pd$_{10}$, Pd$_{14}$, and Pd$_{19}$ clusters. These data show that some clusters are more stable than others. Adsorption of CO on the supported clusters can facilitate this process. CO adsorption lowers the detachment energy for clusters with more than 4 Pd atoms. For this, we assumed that CO remains adsorbed on the detached Pd atom. The reason for the lower detachment energy in the presence of CO is the stronger binding of CO to a single Pd atom ($E_{\text{ads}} = -2.40$ eV) in comparison to Pd clusters with more than 4 Pd atoms, which have a CO adsorption energy between ~2.00 and ~2.40 eV. Recently, Li et al. used molecular dynamics simulations to show that CO can promote single gold atom detachment from Au$_n$ clusters supported on a ceria surface.\(^{52}\) Accordingly, we expect that such process can also occur, resulting in formation of isolated Pd-CO species on ceria.

We also considered the migration of whole clusters, which is relevant for particle coalescence. Figure 4 shows two different pathways for the diffusion of the most stable tetrahedral Pd$_4$ cluster on the CeO$_2$(111) surface. The diffusion barrier, involving a translational migration of the cluster to a similar adjacent site at the surface is 1.83 eV. We also explored an alternative mechanism in which the cluster rotates in two steps over the surface, as shown in Figure 4a. This migration proceeds with an appreciably lower overall barrier of 1.35 eV compared to that of translation migration. For the rotational mechanism, we also explored how CO adsorption to the Pd$_4$ cluster influences the migration process. In the presence of one coadsorbed CO on a hollow site of the supported Pd$_4$ cluster, the barrier decreased to 1.03 eV (Figure S5). We expect that adsorption of more CO molecules will further facilitate this migration process.

We also determined activation barriers for these two mechanisms for supported Pd$_2$, Pd$_3$, Pd$_7$, and Pd$_{10}$ clusters (see Figures S6–S9 in the Supporting Information). Figure 5 shows the strong correlation between the barrier and the number of Pd atoms in the cluster. We also added the Pd atom to the correlation for the two-step mechanism because its diffusion also involves two steps with barriers of 0.06 and 0.14 eV. The latter value is the overall barrier reported in Figure 5. These correlations indicate that the two-step mechanism is preferred over the direct one. Overall, the presented data show that Ostwald ripening will be the more likely sintering mechanism for Pd clusters dispersed on ceria. This agrees well with experimental findings and results of mean-field kinetic modeling describing nanoparticle sintering on oxide supports.\(^{5,15}\) For the smallest Pd clusters with 2 and 3 atoms, the migration barriers (0.37 and 0.71 eV, respectively) are lower than the detachment energies of these clusters (0.44 and 1.06 eV, respectively). The detachment energy for the Pd$_4$ cluster is lower than the barrier for migration over the ceria surface. On the other hand, CO can

Figure 3. Detachment energies of a Pd atom from ceria-supported Pd$_n$ clusters ($n = 2–20$) in the absence and presence of CO.

Figure 4. (a) Migration mechanism of a Pd$_4$ cluster via a direct translation mechanism and a two-step mechanism involving rotational migration. (b) Potential energy diagrams for the migration of a stable tetrahedral Pd$_4$ cluster on the CeO$_2$(111) surface via direct translational migration (black), two-step migration (red), and CO-assisted two-step migration (blue).

Figure 5. Migration barrier for Pd$_4$ cluster migration via the direct mechanism (red) and the two-step mechanism involving cluster rotation (black) against the number of Pd atoms in the clusters.
facilitate the detachment of Pd, implying that both mechanisms play a role in the sintering of Pd clusters. According to Figure 5, the barrier for Pd3 migration is 1.57 eV, which is much higher than the detachment energy of a Pd atom (1.23 eV). These results demonstrate that clusters with more than 4 Pd atoms will display only limited mobility on the CeO2(111) surface. Frenken and co-workers showed that coalescence is preferred for very small Pd clusters on TiO2.15 We also showed the importance of adsorbate-induced migration. Adsorption of CO reduces these migration barriers. In addition to CO, Pd can also be covered by O atoms during CO oxidation. On the other hand, as discussed above, oxidation of Pd causes a much lower mobility of isolated Pd atoms.28

It is important to point out that Ostwald ripening will initially lead to planar clusters. Planar Pd2 and Pd3 clusters are the most stable ones. Adding a fourth Pd atom results in a planar structure, whereas the tetrahedral Pd4 cluster is more stable. Figure S10 shows the reaction energy diagram for the migration of one of the four Pd atoms in a planar Pd4 cluster to form a tetrahedral Pd4 cluster. The activation energy barriers for this transformation in the absence and presence of CO are 0.89 and 0.72 eV, respectively. These values are lower than typical detachment energies for most clusters and, accordingly, we do not expect that such transformation will be the limiting factor in the sintering of highly isolated Pd into three-dimensional nanoparticles.

The current insights about Pd migration and sintering pertain to the most stable surface termination of CeO2. We speculate that ceria surface defects such as vacancies and steps may stabilize Pd. For instance, Petersen et al. showed that heating Pd supported on La-stabilized alumina results in redispersion of PdO, most likely due to trapping of Pd atoms in surface vacancies.58 On the other hand, it is predicted that detachment of Pd species from PdO faces high barriers.54 In this respect, it is worthwhile to emphasize that dispersion of the supported Pdag clusters in our work to form PdO2ag, an intermediate identified in catalytic CO oxidation,28 is exergonic (Figure S11). We surmise that high temperature oxidation can overcome high activation barriers for the detachment of Pd atoms from large Pd or Pd-oxide clusters. Finally, Datye and co-workers elegantly showed that Pt-oxide can disperse atomically to bind to ceria defects. Moreover, when a Pdag cluster is adsorbed along this step, it spontaneously dissociates into two isolated Pd atoms along the ceria edge (Figure S12).

**CONCLUSIONS**

In summary, density functional theory was used to clarify the structure and formation through Ostwald ripening and particle coalescence of Pdag clusters on the most stable (111) termination of ceria. Ostwald ripening is predicted to be the preferred mechanism for growth of the clusters. Small clusters of a few Pd atoms can also migrate and contribute to sintering through particle coalescence. The migration of Pdag clusters on CeO2 strongly depends on the number of Pd atoms in clusters. Adsorbed CO facilitates these sintering processes through lowering barriers for the cluster diffusion, detachment of a Pd atom from clusters, and transformation of initial planar clusters. The present work shows how Pd atoms or clusters on CeO2 are prone to thermal sintering into larger clusters via Ostwald ripening and coalescence involving small clusters.

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