Density Functional Theory Study on the Nucleation and Growth of Pt\textsubscript{n} Clusters on \textgamma-Al\textsubscript{2}O\textsubscript{3}(001) Surface

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ABSTRACT: Little is known about the detailed structural information at the interface of Pt\textsubscript{n} cluster and \textgamma-Al\textsubscript{2}O\textsubscript{3}(001) surface, which plays an important role in the dehydrogenation and cracking of hydrocarbons. Here, the nucleation and growth of Pt\textsubscript{n} (n = 1–8, 13) clusters on a \textgamma-Al\textsubscript{2}O\textsubscript{3}(001) surface have been examined using density functional theory. For the most stable configuration Pt\textsubscript{n}/\textgamma-Al\textsubscript{2}O\textsubscript{3}(001) (n = 1–8, 13), Pt\textsubscript{n} clusters bond to the \textgamma-Al\textsubscript{2}O\textsubscript{3}(001) surface through Pt–O and Pt–Al bonds at the expense of electron density of the Pt\textsubscript{n} cluster. With the increase in the Pt\textsubscript{n} cluster size, both the metal–support interaction and the nucleation energies exhibit an odd–even oscillation pattern, which are lower for an even Pt\textsubscript{n} cluster size than those for its adjacent odd ones. Both the metal–surface and metal–metal interactions are competitive, which control the nanoparticle morphology transition from twodimension (2D) to three-dimension (3D). On the \textgamma-Al\textsubscript{2}O\textsubscript{3}(001) surface, when the metal–support interaction governs, smaller clusters such as Pt\textsubscript{1}, Pt\textsubscript{2}, Pt\textsubscript{3}, and Pt\textsubscript{4} prefer a planar 2D nature. Alternatively, when the metal–metal interaction dominates, larger clusters such as Pt\textsubscript{5}, Pt\textsubscript{6}, Pt\textsubscript{7}, Pt\textsubscript{8}, and Pt\textsubscript{13} exhibit a two-layer structure with one or more Pt atoms on the top layer not interacting directly with the support. Herein, the Pt\textsubscript{3} cluster is the most stable 2D structure; Pt\textsubscript{5} and Pt\textsubscript{6} clusters are the transition from the 2D to the 3D structure; and the Pt\textsubscript{7} cluster is the smallest 3D structure.

1. INTRODUCTION

In recent years, Pt-based catalysts have attracted particular attention with respect to their catalytic performance toward the dehydrogenation and cracking of hydrocarbons, ranging from energy-efficient and environmentally friendly synthesis strategies to the replacement of petrochemical feedstocks by abundant small alkanes.\textsuperscript{1–3} In this heterogeneous catalysis, metal–support interaction is of great importance because it can influence the heterostructural properties of metallic nanoparticles (NPs), that is, the degree of dispersion, morphology, and nucleation. Therefore, a fundamental question in catalytic research is how to exploit metal–support interaction to optimize the NP morphology to achieve good catalytic activity, selectivity, and sintering suppression.

An important factor in Pt-based catalysis is the size effect of NPs. This has been nicely corroborated for the catalytic dehydrogenation of hydrocarbons by Pt\textsubscript{n}/\textgamma-Al\textsubscript{2}O\textsubscript{3} cluster. Here, we discuss several typical examples. Experimentally, it was discovered earlier that the neutral Pt\textsubscript{2} clusters (n ≤ 24) can efficiently activate CH\textsubscript{4} whereas Pt\textsubscript{2} (n = 2–5) clusters are more reactive than the mononuclear platinum atom.\textsuperscript{4} Later, theoretically, it was reported that the neutral clusters Pt\textsubscript{3}, Pt\textsubscript{4}, and Pt\textsubscript{6} can activate the first C–H bond of CH\textsubscript{4} with small barriers, accompanied by the breakage of the second C–H bond in CH\textsubscript{4} as the rate-determining step.\textsuperscript{5–7} More recently, we have studied the competitive activation mechanism of C–H and C–C bonds in C\textsubscript{2}H\textsubscript{6} and/or C\textsubscript{3}H\textsubscript{8} catalyzed by the Pt\textsubscript{n} (n = 1, 2, and 4) cluster\textsuperscript{8,12} and explained why the C–H insertion product is experimentally observed while the C–C insertion product is not formed in observable quantity\textsuperscript{8,9} and why both Pt\textsubscript{3} and Pt\textsubscript{4} clusters exhibit more promising catalytic performance toward C\textsubscript{2}H\textsubscript{6} activation compared with the Pt atom.\textsuperscript{10,12} These experimental and theoretical studies emphasize that the size of transition-metal clusters plays an important role in the catalytic reactivity.

Another key factor in the Pt-based catalysis is the metal–support interaction that plays a crucial role in the deposition of size-selected metal clusters onto a well-defined support surface. Tremendous progress has been made in this direction. Experimentally, Vajda et al. deposited size-selected Pt\textsubscript{8}–10 clusters on a porous aluminum oxide support and found that they are over 40 times more active for the oxidative dehydrogenation of propane than the conventional catalyst, while retaining the high selectivity to propylene.\textsuperscript{2} Theoretically, several studies were devoted to understanding the growth of Pt nanoclusters on supports such as \textalpha-Al\textsubscript{2}O\textsubscript{3}(0001).\textsuperscript{13}
Al₂O₃(100), γ-Al₂O₃(110), anatase TiO₂(101), rutile TiO₂(110), graphene, ceria CeO₂(111), and boron nitride (BN). The relatively large cohesive energy of Pt makes it highly probable that atomic layer deposition (ALD) will produce a dispersion of Pt NPs and formation of 3D islands rather than thin films, as was found previously on several supports. However, the smallest cluster size of NPs, above which the growth transforms from two-dimension (2D) to three-dimension (3D), is generally the result of a delicate interplay between the metal–metal and metal–substrate interactions. These experimental and theoretical studies show that the support plays a key role in the nucleation and morphology of the Pt cluster. γ-Al₂O₃ is extensively used as the support because of its acid–base properties and mechanical and thermal resistance and plays an essential role in the catalytic performance. It has been experimentally and theoretically reported that about 70% of the exposed surface of γ-alumina can be represented by a (110) termination with three-coordinated and four-coordinated Al atoms. However, this surface is generally expected to be strongly hydrated, even at high temperatures. Therefore, no low-coordinated ions of the Al₂O₃(110) framework are available for the interaction with the adsorbed transition-metal particles. The remaining 30% of the exposed surface are expected to feature mainly (111) and (001) terminations. The γ-Al₂O₃(001) surface is dominated by five-coordinated Al atoms, with some four-coordinated Al atoms, both of which are expected to be weaker Lewis acids. The γ-Al₂O₃(001) surface, as the most stable surface, is assumed to interact mostly with the supported NPs through low-coordinated anions of the support. So far, only limited study has focused on the nucleation and growth of NPs on the γ-Al₂O₃(001) surface. However, the nucleation and morphology of the Pt cluster on the γ-Al₂O₃(001) surface is still not well-understood.

In this study, we will examine the stability and nucleation of different small Ptₙ (n = 1–8) clusters on the γ-Al₂O₃(001) surface by the density functional theory (DFT) method. The goals are to find answers to the following four questions in particular: (1) Which is the preferred adsorption configuration? (2) How do the Pt clusters bond to the γ-Al₂O₃(001) surface? (3) How does the metal–support interaction depend upon size? and (4) Is there a transition from a planar to a 3D structure and where does it occur?

2. RESULTS AND DISCUSSION

2.1. Gas-Phase Ptₙ Clusters. To understand the growth behavior of Ptₙ cluster on the γ-Al₂O₃(001) surface, it is necessary to first describe the geometries and energies of gas-phase Ptₙ clusters. For the gas-phase Ptₙ clusters, 1D, 2D, and 3D structures are considered, and only the energetically preferred geometries and the binding energy (Eₐ) are depicted in Figure S1. As shown in Figure S1, the Pt–Pt distances in the clusters are shorter than that in the bulk structure (2.775 Å), which increase from 2.401 to 2.672 Å with n = 1–6, decrease from 2.672 to 2.609 Å with n = 6–7, and then increase from 2.609 to 2.621 Å with n = 7–8, far from the bulk value (2.775 Å). The calculated bond distance of the dimer is 2.401 Å, which is close to the experimental value of 2.333 Å. The degree of bond contraction relative to the bulk follows an approximate n⁻¹/₃ (n = 1–6) relationship, which has been characterized experimentally for the Pt cluster by extended X-ray absorption fine structure (EXAFS). As expected, the binding energy increases as the cluster size increases because of increased atomic coordination. The difference between the binding energy of a cluster and the bulk binding energy scales approximately as n⁻¹/₃ (n = 1–8), which is in good agreement with the reported result.

2.2. Adsorption of Ptₙ−Ptₜ Clusters—2D Growth. The side and top views of γ-Al₂O₃(001) are presented in Figure 1. As shown in Figure 1, there are two types of Al atoms: four-coordinated and five-coordinated, denoted as Al₄ and Al₅, respectively. Moreover, there are two types of O atoms: one connecting with one four-coordinated Al atom and two five-coordinated Al atoms and another interacting with three five-coordinated Al atoms, denoted as O₂ and O₃. By Hirshfeld analysis, the charges of Al₄, Al₅, O₂, and O₃ are determined to be +0.562, +0.493, −0.334, and −0.366, respectively. Taking into account the geometrical structure, Al₄ is expected to be far from the metal cluster, as it is located in the hollow site. In addition, three possible adsorption sites can be easily recognized, namely, Al₅, O₂, and O₃. Table 1 summarizes the relevant structural parameters and adsorption energies for the lowest energy configurations that are most relevant to the nucleation process.

2.2.1. (Ptₜ) For the adsorption of a single Pt atom on the γ-Al₂O₃(001) surface, the obtained most stable two configurations are depicted in Figure 1.
Table 1. Relative Energies ($E_R$, eV), Binding Energies ($E_{BE}$, eV), γ-Al$_2$O$_3$(001) Deformation Energies $\Delta E_{\text{def,Al2O3}}$ (eV), Cluster Deformation Energies ($\Delta E_{\text{def,PtLE}}$ eV), Metal–Support Interaction Energies ($E_{MS}$, eV), Metal–Metal Bond Energy ($\Delta E_{\text{bond,PtLE}}$ eV), Bond Length (Å), and Electron Transfer (ET, $e$) from the Pt$_n$ Cluster to the γ-Al$_2$O$_3$(001) Surface for the Corresponding Configurations$^a$

| configuration | $E_R$ | $E_{BE}$ | $\Delta E_{\text{def,Al2O3}}$ | $\Delta E_{\text{def,PtLE}}$ | $E_{MS}$ | $\Delta E_{\text{bond,PtLE}}$ | Pt–Al $\bar{l}$ | Pt–O $\bar{l}$ | Pt–Pt $\bar{l}$ | ET |
|---------------|-------|---------|----------------|----------------|---------|----------------|----------------|----------------|----------------|-----|
| Pt1-1         | 0.00  | −1.67   | 0.49           | 0.00           | −2.16   | 0.00           | 2.608          | 1.998          | 1.084           | 0.125 |
| Pt1-2         | 0.27  | −1.40   | 0.51           | 0.00           | −1.91   | 0.00           | 2.682          | 1.993          | 1.073           | 0.107 |
| Pt2-1         | 0.00  | −2.77   | 2.22           | 0.10           | −3.50   | −1.49          | 2.604          | 2.085          | 2.521           | 0.186 |
| Pt2-2         | 1.66  | −1.94   | 1.18           | 0.19           | −1.68   | −1.44          | 2.483          | 2.476          | 0.147           |
| Pt3-1         | 0.00  | −2.97   | 1.50           | 0.10           | −2.37   | −2.10          | 2.545          | 2.159          | 0.257           |
| Pt3-2         | 0.01  | −2.97   | 1.18           | 0.00           | −2.02   | −2.13          | 2.130          | 2.550          | 0.069           |
| Pt4-1         | 0.00  | −3.23   | 2.17           | 0.06           | −3.03   | −2.37          | 2.565          | 2.297          | 0.265           |
| Pt4-2         | 0.70  | −3.05   | 1.72           | 0.11           | −2.39   | −2.39          | 2.631          | 2.163          | 0.157           |
| Pt5-1         | 0.00  | −3.31   | 1.70           | 0.23           | −2.43   | −2.57          | 2.650          | 2.073          | 0.415           |
| Pt5-2         | 0.23  | −3.26   | 2.44           | 0.52           | −3.19   | −2.51          | 2.611          | 2.241          | 0.380           |
| Pt6-1         | 0.00  | −3.40   | 1.75           | 0.67           | −2.47   | −2.68          | 2.624          | 2.081          | 2.545           |
| Pt6-2         | 0.08  | −3.39   | 1.73           | 0.46           | −2.43   | −2.73          | 2.565          | 2.107          | 2.615           |
| Pt7-1         | 0.00  | −3.42   | 1.68           | 0.22           | −2.30   | −2.81          | 2.647          | 2.090          | 0.563           |
| Pt7-2         | 0.05  | −3.42   | 2.01           | 0.38           | −2.52   | −2.91          | 2.568          | 2.174          | 0.251           |
| Pt8-1         | 0.00  | −3.53   | 2.44           | 0.96           | −3.07   | −2.90          | 2.608          | 2.105          | 2.582           |
| Pt8-2         | 0.01  | −3.51   | 2.09           | 0.56           | −2.55   | −3.06          | 2.625          | 2.348          | 0.439           |
| Pt13-1        | 0.00  | −3.76   | 2.21           | 0.80           | −2.66   | −3.31          | 2.653          | 2.164          | 0.661           |

$^a$Average bond lengths $\bar{l}$ with a threshold of 3.0 Å

Binding energies of the monomers and ordering of the different adsorption sites can be rationalized by examining the optimum structures and electronic properties. In the Pt1-1 configuration, the Pt atom binds to O3 with a bond length of 1.988 Å and binds to two Al5 atoms with the average bond length of 2.608 Å. Similarly, in the Pt1-2 configuration, the Pt atom connects to O2 with a bond length of 1.993 Å and binds to two Al5 atoms with equal bond lengths of 2.682 Å. It is apparent that there are two Pt–Al5 bonds and one Pt–O3 bond in Pt1-1, and there are two Pt–Al5 bonds and one Pt–O2 bond in Pt1-2. The shorter bond lengths of Pt–O and Pt–Al make Pt1-1 more stable than Pt1-2. This can be ascribed to the fact that O3 (−0.366) is charged more negatively than O2 (−0.334) on a pristine γ-Al$_2$O$_3$(001) surface. Charge analysis shows that there is an electron transfer of 0.125e from Pt to γ-Al$_2$O$_3$(001) in Pt1-1 and an electron transfer of 0.107e in Pt1-2. The order of ET accords stability to the two configurations. It is indicated that the atop-O3 site is more favorable than the atop-O2 one. That is to say that the Pt atom interacts more firmly with O3 than O2. This result may be ascribed to the more negative charge on O3 than that on O2.

2.2.2. (Pt)$_2$. On the basis of Pt$_1$–γ-Al$_2$O$_3$(001) configurations, the introduction of the second Pt atom may form four possible configurations. For the adsorption of a Pt$_2$ cluster on the γ-Al$_2$O$_3$(001) surface, the obtained most stable two configurations are depicted in Figure 2.

As shown in Table 1 and Figure 2, the four stable configurations have a relative stabilization energy within 1.67 eV (see Table S1). The preferential adsorption configuration is Pt2-1 with a binding energy of −2.77 eV/atom, which is about 0.83 eV more stable than Pt2-2, Pt2-3, and Pt2-4, which have an equal binding energy of about −1.94 eV/atom. Let us inspect their optimum structure and electronic properties. As shown in Table 1 and Figure 2, in the Pt2-1 configuration, the Pt dimer is positioned nearly across the O3–O3 pair; whereas one Pt atom binds to two O3 atoms with the average bond length of 2.085 Å, another Pt atom links to two Al5 atoms with equal bond lengths of 2.604 Å. Next, in the Pt2-2 configuration, the Pt dimer is adsorbed across the O2–O2–O2 pair, whereas each Pt atom connects to two O2 atoms with the average bond length of 2.483 Å. Deformation energies mainly embody at the γ-Al$_2$O$_3$(001) surface in the range of 2.22–0.64 eV, whereas they vary little at the Pt2 cluster in the range of 0.20–0.04 eV. However, the Pt–Pt bond length is elongated by about 0.07–0.28 Å. By charge analysis, there is a charge transfer of 0.186e from Pt$_2$ to γ-Al$_2$O$_3$(001) in Pt2-1 and a charge transfer of 0.147e in Pt2-2.

2.2.3. (Pt)$_3$. In the light of Pt$_1$–γ-Al$_2$O$_3$(001) configurations, the introduction of the third Pt atom may result in six possible configurations. For the adsorption of a Pt$_3$ cluster on the γ-Al$_2$O$_3$(001) surface, the obtained most stable two configurations are depicted in Figure 3. Six stable configurations are
Figure 3. Top and side views of the trimer adsorption configurations on the γ-Al2O3(001) surface. The bond length is in Å.

As shown in Table 1 and Figure 3, the lowest energy configurations are Pt3-1 and Pt3-2 with an equal binding energy of −2.97 eV/atom. Now, it is necessary to investigate their optimum structure and electronic properties. As shown in Table 1 and Figure 3, in Pt3-1, the Pt1 triangular plane is parallel to the γ-Al2O3(001) surface; whereas one Pt atom binds to one O3 atom with the bond length of 2.159 Å, the other two Pt atoms link to two O3 atoms with equal bond lengths of 2.545 Å. Then, in Pt3-2, the Pt3 triangular plane is perpendicular to the γ-Al2O3(001) surface through the vertex of the triangle; whereas one Pt atom connects to two O3 atoms with the average bond length of 2.130 Å, the other two Pt atoms are out of the γ-Al2O3(001) substrate. Hence, there are two Pt–Al5 bonds and one Pt–O3 bond in Pt3-1, and there are two Pt–O3 bonds in Pt3-2. It is indicated that the synergism of Pt with both Al5 and O3 makes the Pt3-1 configuration more stable. Deformation energies mainly reflect at the γ-Al2O3(001) surface in the range of 1.50–0.56 eV, with hardly any at the Pt3 cluster. However, the average Pt–Pt bond length is elongated by about 0.01–0.07 Å. In the light of charge analysis, there is a charge transfer of 0.257 e from Pt3 to γ-Al2O3(001) in Pt3-1 and a charge transfer of 0.069e in Pt3-2.

2.2.4. (Pt)4. According to the Pt3/γ-Al2O3(001) configurations, the introduction of the fourth Pt atom may bring about eight possible configurations. For the adsorption of a Pt4 cluster on the γ-Al2O3(001) surface, the obtained most stable two configurations are depicted in Figure 4. Eight stable configurations are obtained with the relative stabilization energy within about 1.21 eV (see Table S1).

As shown in Table 1 and Figure 4, the most stable configuration is Pt4-1 with a binding energy of −3.23 eV/atom, followed by Pt4-2 with an almost equal binding energy of −3.04 eV/atom. Next, let us discuss their optimum structure and electronic properties. As shown in Table 1 and Figure 4, in Pt4-1, the Pt4 cluster is adsorbed as a symmetric boatlike species on the γ-Al2O3(001) surface; whereas one Pt atom links to two O3 atoms and the second Pt atom links to two O2 atoms, with the average bond length of 2.297 Å, the remaining two Pt atoms link to two Al5 atoms with equal bond lengths of 2.565 Å. Then, in Pt4-2, the Pt4 tetrahedral pyramid is deposited on the γ-Al2O3(001) surface; whereas one Pt atom connects to two O3 atoms, the second Pt atom connects to one O2 atom, the third Pt atom connects to one Al5 atom, and the fourth one is in the second layer, with average bond lengths of 2.163 Å for Pt–O and 2.631 Å for Pt–Al. Hence, there are two Pt–Al5 bonds, two Pt–O3 bonds, and two Pt–O2 bonds in Pt4-1, and there are one Pt–Al5 bond, two Pt–O3 bonds, and one Pt–O2 bond in Pt4-2. In view of the charge analysis, there is a charge transfer of 0.256e from Pt4 to γ-Al2O3(001) in Pt4-1 and a charge transfer of 0.157e in Pt4-2.

In addition, the temperature effect was taken into account on the size and shape of the typical Pt4 cluster on the γ-Al2O3(001) surface, which may be the transition of 2D to 3D. The 2D Pt4-1 configuration is more stable than the 3D Pt4-2 configuration below 75 K, whereas the 3D Pt4-2 configuration is more stable than the 2D Pt4-1 configuration above 75 K (see Figure S12).

2.3. Adsorption of Pt5 and Pt6 Clusters—2D–3D Transition. 2.3.1. (Pt)5. In line with the Pt4/γ-Al2O3(001) configurations, the introduction of the fifth Pt atom may give eight possible configurations. For the adsorption of a Pt5 cluster on the γ-Al2O3(001) surface, the obtained most stable two configurations are depicted in Figure 5. Eight stable configurations are obtained with the relative energy within about 1.18 eV (see Table S1).

As shown in Table 1 and Figure 5, the preferable lowest energy configuration is Pt5-1 with a binding energy of −3.31 eV/atom, followed by Pt5-2 with a binding energy of −3.26 eV/atom. Now, let us examine their optimum structure and electronic properties. As shown in Table 1 and Figure 5, in Pt5-1, one Pt atom attaches to two O3 atoms, three Pt atoms attach to three Al5 atoms, and the fifth Pt atom is in the second layer, with average bond lengths of 2.073 Å for Pt–O and 2.650 Å for Pt–Al. Afterward, in Pt5-2, one Pt atom connects to two O3 atoms, one Pt atom connects to one O2 atom, three Pt atoms connect to three Al5 atoms, with average bond lengths of 2.241 Å for Pt–O and 2.611 Å for Pt–Al. Hence, there are three Pt–Al5 bonds and two Pt–O3 bonds in Pt5-1, and there are three
Pt−Al5 bonds, two Pt−O3 bonds, and two Pt−O2 bonds in Pt5-2. The reason that Pt5-2 is 0.23 eV higher in energy than Pt5-1 may be attributed to the longer bond lengths of Pt−O and Pt−Pt. In view of the charge analysis, there is a charge transfer of 0.415 e from Pt5 to γ-Al2O3(001) in Pt5-1 and a charge transfer of 0.380 e in Pt5-2.  

2.3.2. (Pt)6. On the basis of the Pt 5/γ-Al2O3(001) configurations, the introduction of the sixth Pt atom may produce six possible configurations. For the adsorption of a Pt6 cluster on the γ-Al2O3(001) surface, the obtained most stable two configurations are depicted in Figure 6. Eight stable configurations are obtained with the relative energy within about 0.67 eV (see Table S1).  

As shown in Table 1 and Figure 6, the most stable configuration is Pt6-1 with a binding energy of −3.40 eV/atom, followed by Pt6-2 with a binding energy of −3.39 eV/atom. Now, let us look into their optimum structure and electronic properties. As shown in Table 1 and Figure 6, in Pt6-1, one Pt atom binds to two O3 atoms, four Pt atoms bind to four Al5 atoms, and the sixth one is in the second layer, with average bond lengths of 2.081 Å for Pt−O and 2.624 Å for Pt−Al. In addition, in Pt6-2, one Pt atom links to two O3 atoms, two Pt atoms link to two Al5 atoms, and the other three Pt atoms are in the second layer, with average bond lengths of 2.107 Å for Pt−O and 2.566 Å for Pt−Al. It is obvious that Pt6-2 is only 0.08 eV higher in energy than Pt6-1. Such a low difference in energy makes them to coexist thermodynamically. It is indicated that the 2D–3D transition may take place in the Pt6 cluster. In a word, there are four Pt−Al5 bonds and two Pt−O3 bonds in Pt6-1, and there are two Pt−Al5 bonds and two Pt−O3 bonds in Pt6-2. Considering the charge analysis, there is a charge transfer of 0.612 e from Pt6 to γ-Al2O3(001) in Pt6-1 and a charge transfer of 0.360 e in Pt6-2.  

2.4. Adsorption of Pt7, Pt8, and Pt13 Clusters−3D Growth.  

2.4.1. (Pt)7. In the light of the Pt 6/γ-Al2O3(001) configurations, the introduction of the seventh Pt atom may produce eight possible configurations. For the adsorption of a Pt7 cluster on the γ-Al2O3(001) surface, the obtained most stable two configurations are depicted in Figure 7. Eight stable configurations are obtained with the relative stabilization energy within about 1.37 eV (see Table S1).  

As shown in Table 1 and Figure 7, the preferable stable configuration is Pt7-1 with a binding energy of −3.42 eV/atom, followed by Pt7-2 with a binding energy of −3.42 eV/atom. Now, let us inspect their optimum structure and electronic properties. As shown in Table 1 and Figure 7, in Pt7-1, one Pt atom links to two O3 atoms, four Pt atoms link to four O2 atoms, one Pt atom binds to the Al5 atom, and the other three Pt atoms are in the second layer, with average bond lengths of 2.174 Å for Pt−O and 2.568 Å for Pt−Al. Moreover, there is a close relative energy between Pt7-1 and Pt7-2, indicating that they should coexist thermodynamically. In short, there are four Pt−Al5 bonds and two Pt−O3 bonds in Pt7-1, and there are one Pt−Al5 bond, two Pt−O3 bonds, and two Pt−O2 bonds in Pt7-2.
two Pt–O2 bonds in Pt7-2. Concerning the charge analysis, there is a charge transfer of 0.621e from Pt8 to γ-Al2O3(001) in Pt7-1 and a charge transfer of 0.251e in Pt7-2.

As depicted in Figure 7, the growth of a Pt heptamer island differs from the previous cases. For the Pt heptamer, the preferable lowest energy configuration is 3D in nature with five Pt atoms in the lower layer and two Pt atoms in the upper layer, whereas for the previous Pt6/γ-Al2O3(001) (n < 7) heterostructures with at most one Pt atom in the second layer. For comparison, the growth of Pt8 on rutile TiO2(110) and the growth of Pt5 on Mo2S(001) showed a 3D nature with more than one atom residing in the second layer.18,44

2.4.2. (Pt)8. In view of the Pt6/γ-Al2O3(001) configurations, the introduction of the eighth Pt atom may form four possible configurations. For the adsorption of a Pt8 cluster on the γ-Al2O3(001) surface, the obtained most stable two configurations are depicted in Figure 8. Four stable configurations are obtained with the relative stabilization energy within about 2.21 eV (see Table S1).

As shown in Table 1 and Figure 8, the preferable lowest energy configuration is Pt8-1 with a binding energy of −3.76 eV/atom. In Pt8-1, one Pt atom links to two O3 atoms, two Pt atoms link to one O2 atom, four Pt atoms link to four Al5 atoms, and the other six Pt atoms are in the second layer, with average bond lengths of 2.164 Å for Pt–O and 2.653 Å for Pt–Al. Alternatively, in view of the charge analysis, there is a charge transfer of 0.661e from Pt8 to γ-Al2O3(001).

2.4.3. (Pt)13. Because the Pt13 cluster exhibits the highest stability among small clusters because of its “magic number” on various substrates, such as defective BN nanosheet25 or defective graphene,45–47 it is very necessary to examine the adsorption of the Pt13 cluster on the γ-Al2O3(001) surface. On the basis of the growth trend of Pt8 (n = 1–8) on the γ-Al2O3(001) surface, the most stable 3D configuration of Pt13/γ-Al2O3(001) was designed. For the adsorption of a Pt13 cluster on the γ-Al2O3(001) surface, the obtained stable configuration is depicted in Figure 9.

As shown in Table 1 and Figure 9, the preferable lowest energy configuration is Pt13-1 with a binding energy of −4.17 eV/atom. In Pt13-1, one Pt atom links to two O3 atoms, two Pt atoms link to one O2 atom, four Pt atoms link to four Al5 atoms, and the other six Pt atoms are in the second layer, with average bond lengths of 2.105 Å for Pt–O2 and 2.625 Å for Pt–Al. Alternatively, in view of the charge analysis, there is a charge transfer of 0.691e from Pt13 to γ-Al2O3(001).

2.5. Nucleation of the Pt n Cluster on γ-Al2O3(001). As shown in Table 1, the deformation energy exists mainly on the γ-Al2O3(001) surface other than the Pt5 moiety. The trends of energy for the most stable configuration Pt8/γ-Al2O3(001) (n = 1–8) are drawn in Figure 10.

As shown in Figure 10, with the increase in the Pt n cluster size on the γ-Al2O3(001) surface, both the binding energy (E BE) and the cohesive energy (E CE) decrease and the difference between E CE and E BE gradually lessens. Furthermore, the...
binding energies are smaller than cohesive energies. It is indicated that these clusters could cause diffusion. For the Pt1 cluster on the γ-Al2O3(001) surface, the diffusion barrier is calculated to be 0.16 eV (see Figure S10).

Alternatively, both the γ-Al2O3(001) deformation (ΔE_{def,Al2O3}) and the metal–support interaction (E_{MS}) energies display an odd–even oscillation pattern. That is, the γ-Al2O3(001) deformation energy (ΔE_{def,Al2O3}) increases with the increase in the Pt_n cluster size for both odd and even sizes, whereas it is higher for an even Pt_n cluster size than for its adjacent odd ones. Thereupon, the metal–support interaction (E_{MS}) energy decreases with the increase in the Pt_n cluster size for both odd and even sizes, whereas it is lower for an even size than for its adjacent odd sizes. That is to say, the odd–even oscillation pattern for ΔE_{def,Al2O3} has an effect on the change in the metal–support interaction energy. Moreover, the nucleation energy (E_{nuc}) also shows an odd–even oscillation pattern, in which the nucleation energy of the even Pt_n cluster size is lower than that of its adjacent odd ones.

Furthermore, taking into account both the metal–support interaction (E_{MS}) and the metal–metal interaction (ΔE_{bond,Pt_n}) energies, one can see that the E_{MS} is lower than ΔE_{bond,Pt_n} for n = 1–4 and higher for n = 5–8. Both the metal–surface and metal–metal interactions are competitive, which control the nanoparticle morphology transition from 2D to 3D. It is indicated that the cluster adopts a 2D nature for a small number of metal particles (n < 5) when the metal–support interaction governs, and the cluster gradually approaches a 3D morphology characteristic for a large number of metal particles (n > 5) when the metal–metal interaction dominates. These results can be echoed by the obtained stable geometric structures, as mentioned earlier. Combining with the results of geometric structures, one can conclude that Pt4-1 is the most stable 2D structure, Pt5-1 and Pt6-1 are the transition from 2D to 3D, and Pt7-1 is the smallest 3D structure with two Pt atoms in the second layer. Then, we will discuss the electronic properties for Pt4-1 and Pt7-1 configurations infra.

As shown in Figure 10, the ET from the Pt_n cluster to γ-Al2O3(001) increases with the increase in the Pt_n cluster size number (n = 1–6) and varies little for n = 6–8. The DOS and the corresponding contour plots of the differential charge density for γ-Al2O3(001), Pt1-1, Pt4-1, Pt7-1, and Pt13-1 are depicted in Figure 11.

As shown in Figure 11, for γ-Al2O3(001), the DOS is characterized with a sharp peak from the O 2p orbital in the vicinity of the Fermi level (E_F) and two sharp peaks from the Al 3p orbital in the range of 4.0–6.0 eV. For Pt1-1, Pt4-1, Pt7-1, and Pt13-1, it is apparent that there is a sharp peak from the Pt 5d orbital near E_F, indicating strong hybridization between the Pt 5d orbital and the O 2p orbital. Furthermore, for Pt1-1 and Pt4-1, the O 2p orbital peaks around the E_F of the substrate are all shifted to low energy levels, whereas they hardly vary for Pt7-1 and Pt13-1. This phenomenon strengthens that there is a stronger metal–support interaction in Pt1-1 and Pt4-1 than that in Pt7-1 and Pt13-1. In addition, the Al 3p sharp peaks gradually decrease from γ-Al2O3(001), Pt1-1, and Pt4-1 to Pt7-1 and disappear at Pt13-1. It is indicated that the Pt–Al interaction enhances by degrees with the increase in the Pt_n cluster size after the Pt_n cluster adsorption on γ-Al2O3(001).

This result is in good agreement with the geometric features as before. The above interactions of Pt–O and Pt–Al can be explained by the fact that there is a clear ET from the O^{2-} 2p occupied orbital to the Pt 5d* empty orbital and electron back donation from the Pt 5d occupied orbital to the Al^{3+} 3p* empty orbital in the deposited Pt_n cluster on the γ-Al2O3(001) surface, as depicted in Figure 10. The net result of the ET makes the Pt_n
moiety positively charged and the $\gamma$-Al$_2$O$_3$(001) moiety negatively charged. As shown in Figure 10, the electron density difference map reveals that some Pt orbitals are depleted upon adsorption on the surface. This depletion is balanced by an increase in the electron density of the Pt–O and/or Pt–Al bonds on the interfacial $\gamma$-Al$_2$O$_3$(001).

3. CONCLUSIONS

The stability and nucleation of different small Pt$_n$ ($n = 1$–8, 13) clusters on the $\gamma$-Al$_2$O$_3$(001) surface have been examined using DFT. The following conclusions can be drawn from the present study.

There are 47 stable configurations Pt$_n$/γ-Al$_2$O$_3$(001) ($n = 1$–8) obtained, in which the preferable adsorption configuration is ascertained for each size of the Pt$_n$ cluster on the γ-Al$_2$O$_3$(001) surface. For the most stable configuration Pt$_n$/γ-Al$_2$O$_3$(001) ($n = 1$–8, 13), Pt$_n$ clusters bond to the γ-Al$_2$O$_3$(001) surface through Pt–O and Pt–Al bonds at the expense of the electron density of the Pt$_n$ cluster.

On the γ-Al$_2$O$_3$(001) surface, with the increase in the Pt$_n$ cluster size, all γ-Al$_2$O$_3$(001) deformations, metal–support interactions, and the nucleation energies exhibit an odd–even oscillation pattern. The metal–support interaction and the nucleation energies of an even Pt$_n$ cluster size are lower than those of its adjacent odd ones, whereas the γ-Al$_2$O$_3$(001) deformation energy of an even Pt$_n$ cluster size is higher than that of its adjacent odd ones.

Both the metal–surface and metal–metal interactions are competitive, which control the nanoparticle morphology transition from 2D to 3D. On the γ-Al$_2$O$_3$(001) surface, when the metal–support interaction predominates, smaller clusters such as Pt$_5$, Pt$_6$, Pt$_7$, and Pt$_8$ exhibit a planar 2D nature. On the other hand, when the metal–metal interaction governs, larger clusters such as Pt$_{11}$, Pt$_{12}$, Pt$_{13}$, and Pt$_{15}$ prefer a two-layer structure with one or more Pt atoms on the top layer not interacting with the support directly. Herein, the Pt$_4$ cluster is the most stable 2D structure, Pt$_5$ and Pt$_6$ clusters are the transition from 2D to 3D, and the Pt$_7$ cluster is the smallest 3D structure.

4. COMPUTATIONAL DETAILS

All calculations were performed by using Materials Studio 7.0 package.$^{33}$ The generalized gradient approximation (GGA) with the PW91 functional$^{34}$ is chosen together with the doubled numerical basis set and polarization basis set (DNP),$^{35}$ using the DMol$^3$ program.$^{36}$ For the 5d transition-metal atom Pt, the scalar relativistic effects (density functional semicore pseudopotentials, DSSP) were considered for its core electrons.$^{37}$ The DNP basis sets have been successfully employed in the deposition of Pt clusters on the defective hexagonal BN (h-BN) sheets.$^{38}$ For the geometrical optimization, the forces imposed on each atom were converged to be less than 0.002 hartree/Å, the total energy was converged to be less than $1.0 \times 10^{-6}$ hartree, and the displacement convergence was less than $5 \times 10^{-3}$ Å. The k-point sampling scheme is the Monkhorst–Pack grid of $2 \times 2 \times 1$. A Fermi smearing of 0.005 hartree for orbital occupancy was used to improve the computational performance.

In addition, the properties of the isolated Pt$_n$ clusters were calculated using a 15 $\times$ 15 $\times$ 15 Å cubic unit cell. In the present study, bulk parameters of the γ-Al$_2$O$_3$(001) surface model were first optimized according to the values of the Inorganic Crystal Structure Database (ICSD).$^{38}$ The supercell was obtained by a lattice constant of $a = 7.887$ Å, and a periodically reproduced slab supercell was then applied to simulate the γ-Al$_2$O$_3$(001) surfaces. The stoichiometry of the slab is restricted to Al$_2$O$_3$, with 32 aluminum and 48 oxygen atoms. The simulation cell dimensions were fixed to $a = b = 11.15$ Å, $c = 24.02$ Å, and $\alpha = \beta = \gamma = 90^\circ$, including three Al–O layers and two tetrahedral Al layers. The top two floors up and down are symmetrical. The vacuum region was set to 20 Å to separate the slabs in the direction perpendicular to the surface. For the optimization of the adsorption site, both the adsorbed Pt$_n$ cluster and all atoms of the uppermost layer of the γ-Al$_2$O$_3$ support were relaxed, whereas the remaining atoms of the support were fixed. The charge transfer was calculated using the Hirshfeld method.$^{39}$ The electron density difference was computed using the CASTEP program available in Materials Studio 7.0 package.$^{40}$ To gain insight into the metal–metal stabilizing interactions of Pt$_n$ on the γ-Al$_2$O$_3$(001) substrate, the binding energy ($E_{BE}$) per Pt is defined by using eq i

$$E_{BE} = \frac{1}{n}(E_{Pt/Al_2O_3} - E_{Al_2O_3} - nE_{Pt})$$

where $E_{Pt/Al_2O_3}$ is the energy of the Pt$_n$/Al$_2$O$_3$ heterostructure in the optimum geometry, $E_{Al_2O_3}$ is the energy of the pristine γ-Al$_2$O$_3$(001), and $E_{Pt}$ is the energy of an isolated Pt atom in the ground triplet state. In this expression of the binding energy, the negative values of $E_{BE}$ indicate stable adsorption configurations.

The energy ($E_{MS}$) of the metal-slab stabilizing interactions is computed by using eq ii

$$E_{MS} = E_{BE} - \Delta E_{def,Al_2O_3} - \Delta E_{bond,Pt_n}$$

where the second term $\Delta E_{def,Al_2O_3}$ (positive) measures the γ-Al$_2$O$_3$(001) deformation energy, defined as the energy penalty to deform γ-Al$_2$O$_3$(001) into the structure adopted in the bonding configuration, by using eq iii

$$\Delta E_{def,Al_2O_3} = E_{def,Al_2O_3} - E_{Al_2O_3}$$

and the third term $\Delta E_{bond,Pt_n}$ (negative) is defined as the energy gain owing to the metal–metal bonds by using eq iv

$$\Delta E_{bond,Pt_n} = \frac{1}{n}(E_{Pt_n} - nE_{Pt})$$

where $E_{Pt_n}$ is the lowest Pt$_n$ cluster energy on the surface.

The average cohesive energy, $E_{CE}$, for the Pt$_n$ cluster in the gas phase is estimated by using eq v

$$E_{CE} = \frac{1}{n}E_{Pt_n} - E_{Pt}$$

where $E_{Pt_n}$ is the total energy of the Pt$_n$ cluster in the gas phase and $E_{Pt}$ is the total energy of a single Pt atom.

In addition, the Pt$_n$ cluster deformation energy ($\Delta E_{def,Pt_n}$), which is associated with the deformation in the structure of the Pt$_n$ cluster between the gas phase and the adsorbed state, is characterized by using eq vi

$$\Delta E_{def,Pt_n} = E_{Pt_n} - E_{Pt_n}$$

Furthermore, to better understand the nucleation or growth of Pt$_n$ clusters on the γ-Al$_2$O$_3$(001) substrate, the nucleation energy ($E_{nuc}$), which is the energy gained (or lost) in
combining an adsorbed monomer with a Pt\textsubscript{n−1} cluster to form a Pt\textsubscript{n} cluster, is defined as follows

\[ E_{\text{vac}} = E_{\text{Pt}_n/\gamma-\text{Al}_2\text{O}_3} + E_{\gamma-\text{Al}_2\text{O}_3} - E_{\text{Pt}_{n-1}/\gamma-\text{Al}_2\text{O}_3} - E_{\text{Pt}_n/\gamma-\text{Al}_2\text{O}_3} \]  

(vii)

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00342.

Total energies, stable configurations, DOS, and the corresponding contour plots of the differential charge density for Pt\textsubscript{n}/\gamma-\text{Al}_2\text{O}_3 (001) (PDF)

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**Author Contributions**

The manuscript was written through contributions of all authors. Y.W. was responsible for main computation, B.X. was responsible for part of the computation, H.-Q.Y. was responsible for design, analysis, and writing, and C.-W.H. was responsible for design and revision. All authors have given approval to the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.

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