

Metal–Support Interaction Effect on the Nucleation of Pd_n particles (n=1-6) on (110C) γ-Al₂O₃ surface

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Introduction: It is well known that the catalytic efficiency in a heterogeneous catalyst is largely dependent on its specific area, which is related to the size and shape of metal particle.^[1] The metal–support interactions play an important role in the process of growing of metal particle, since the strength of anchorage can determine the extension of its dispersion or agglomeration over a surface.^[2,3] It is reported that the effect promoted by strong metal–support interactions (SMSI) can be provided by both morphological and electronic contributions.^[4-6] Therefore, a better comprehension of the nature of the effects promoted by the metal–support interaction and, how it influences the metal particle nucleation process, is of great importance. In this work, we performed DFT/B3LYP calculations to obtain an ensemble of structural, energetic and electronic parameters in Pd_n/Al₂₄O₄₁H₁₀ (n=1-6) agglomerates, in order to investigate the influence of metal-support interaction on the atom-to-atom growth mechanism of palladium particles on γ-Al₂O₃ support.

Key-words: nucleation, palladium particle, γ-Al₂O₃, metal-support interaction, DFT

Methodology: A model to represent the structure of γ-Al₂O₃ (Al₂₄O₄₁H₁₀) was constructed based on experimental parameters.^[7] In order to construct atom-to-atom a Pd₆ agglomerate on the (110C) γ-Al₂O₃ surface, a first palladium atom (Pd₍₁₎) was optimized in different sites on Al₂₄O₄₁H₁₀. Following, on Pd₍₁₎ placed at the most stable site, a second palladium atom was approximated. This process was successively repeated until the formation of Pd₆ agglomerate, relaxing only the nth palladium in each step (Fig. 1). The individual adsorption energy of each adsorbed palladium atom was estimated in presence (Eq. 1, $E_{ad} = E_{(Pd_n/Al_{24}O_{41}H_{10})} - [E_{(Pd)} + E_{(Pd_{n-1}/Al_{24}O_{41}H_{10})}]$) and absence (Eq. 2, $E'_{ad} = E_{(Pd/Al_{24}O_{41}H_{10})} - [E_{(Pd)} + E_{(Al_{24}O_{41}H_{10})}]$) of the other palladium atoms. The nucleation energy (E_{nuc}) for both supported and isolated (in the same geometry obtained on Al₂₄O₄₁H₁₀) Pd_n (n=2–6) was obtained (Eq. 3, $E_{nuc} = E_{ad} - E'_{ad}$). The DFT/B3LYP methodology was employed using Gaussian 03 program. The electrons of γ-Al₂O₃ and palladium clusters were described by 6-31G(d,p) and LANL2DZ, respectively. All computed energies were corrected by the basis set superposition error (BSSE), calculated by the counterpoise method. In all calculated structures, the electronic spin state of lowest energy was obtained, and spin contamination higher than 15% was not observed. Additionally, the stability of wave function was tested.

Results and discussion: For all calculated Pd_n/Al₂₄O₄₁H₁₀ structures, the electronic spin state of lowest energy is triplet, except for n = 1 (singlet). After the formation of Pd₆ agglomerate on Al₂₄O₄₁H₁₀, the Pd–Al distances assume values from 2.49 to 2.54 Å, in

good agreement with the experimental bond length (2.46 to 2.67 Å).^[8] The first palladium atom adsorbs preferentially on two octahedral aluminum cations (Al_o), with energy of $-60.4 \text{ kcal.mol}^{-1}$ (Fig. 1). The second atom ($\text{Pd}_{\text{(II)}}$) anchors on $\text{Pd}_{\text{(I)}}$ / $\text{Al}_{24}\text{O}_{41}\text{H}_{10}$ in on-top mode, involving a tetrahedral aluminum cation ($E_{\text{ad}} = -50.1 \text{ kcal.mol}^{-1}$). Removing $\text{Pd}_{\text{(I)}}$, the adsorption energy for $\text{Pd}_{\text{(II)}}$ on this aluminum (Al_t) decreases to $-24.5 \text{ kcal.mol}^{-1}$. This result points to the existence of a significant Pd–Pd interaction. However, considering an isolated Pd_2 cluster, in the same arrangement on alumina, the Pd–Pd interaction decreases to $-16.0 \text{ kcal.mol}^{-1}$. This result suggests that the palladium–alumina interaction is promoting an increase of the Pd–Pd interaction in $\text{Pd}_2/\text{Al}_{24}\text{O}_{41}\text{H}_{10}$. This fact is in accordance with the elevation in $+9.7 \text{ kcal.mol}^{-1}$ in the energy of nucleation for Pd_2 in presence of alumina, comparing with this cluster isolated (Fig. 1). However, this influence of the palladium–alumina interaction in the palladium nucleation is observed only in Pd_2 . From the third palladium atom onwards, a decrease in the Pd–Pd interaction occurs as the size of the metal agglomerate grows. It is important to note that the smallest energy of nucleation is verified when $\text{Pd}_{\text{(III)}}$ agglomerates in supported Pd_2 (Fig. 1). The $\text{Pd}_{\text{(III)}}$ atom adsorbs strongly on alumina in hollow mode, involving two Al_o and two oxygen ions. Thus, the palladium atoms that adsorb more strongly on the alumina surface ($\text{Pd}_{\text{(III)}}$ and $\text{Pd}_{\text{(V)}}$, $E_{\text{ad(Pd)}} = -51.0$ and $-26.1 \text{ kcal.mol}^{-1}$, respectively) present the smaller energies of nucleation (-2.8 and $-15.2 \text{ kcal.mol}^{-1}$, respectively).

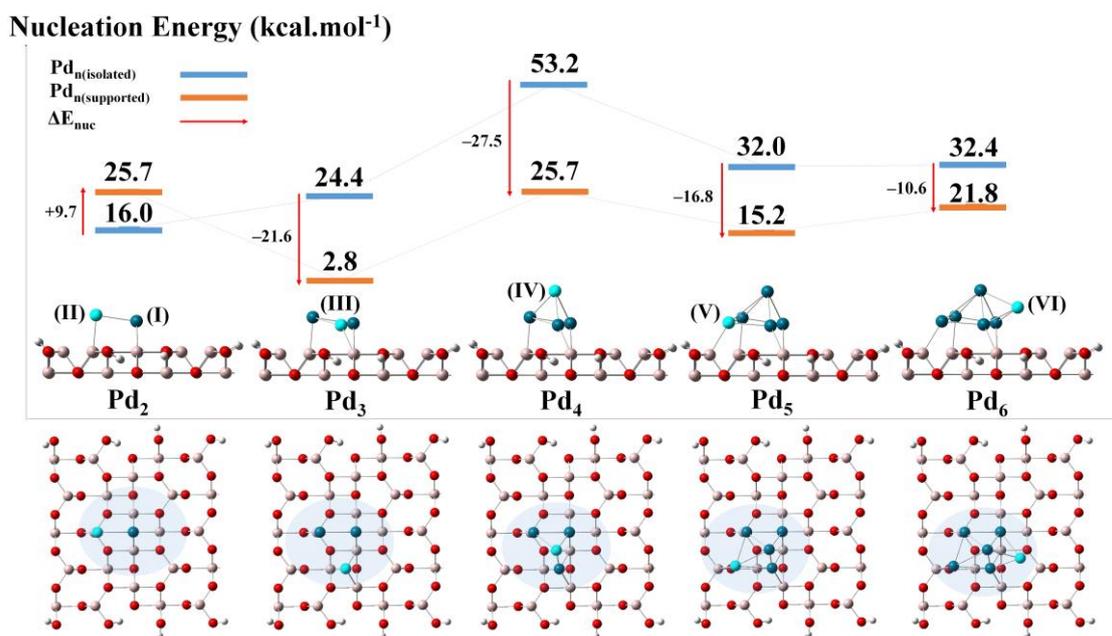


Figure 1. Nucleation energy of isolated and supported Pd_n ($n=2-6$) and superior and lateral views of $\text{Pd}_n/\text{Al}_{24}\text{O}_{41}\text{H}_{10}$.

Conclusion: Our results suggest that, in general, the effect promoted by the Pd–alumina interaction leads to a weakening of the Pd–Pd nucleation energy. The Pd–Pd interaction is weaker when it involves strongly adsorbed Pd atoms in alumina.

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References:

- [1] C. Zhou et al., *J. Phys. Chem. C*, 111, 13786 (2007).
- [2] S.-T. Zhang et al., *J. Phys. Chem. C*, 116, 3514 (2014).
- [3] M. C. Valero, P. Raybaud, P. Sautet, *Phys. Rev. B*, 75, 045427 (2007).
- [4] W. E. Kaden et al., *Surf. Sci.*, 621, 40 (2014).
- [5] C. T. Campbell, *Nat. Chem.*, 4, 597 (2012).
- [6] L. M. Prates et al., *J. Phys. Chem. C*, 121, 14147 (2017).
- [7] O. J. Maresca et al., *Theochem.*, 58, 620 (2003).
- [8] M. Eitenberg, K. L. Komarek, E. Miller, *Metall. Trans. B*, 2, 1173 (1971).