Influence of the metal−support and metal−metal interactions on Pd nucleation and NO adsorption in a Pd$_4$/γ-Al$_2$O$_3$ (110D) model

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Abstract
The role played by the metal−support (MSI) and metal−metal (MMI) interactions on two important processes in controlling the catalyst performance — nucleation and molecular adsorption — has been investigated using density functional theory (DFT), by means of B3LYP functional, combined with localized molecular orbital energy decomposition analysis (LMOEDA), and natural bond orbital (NBO) calculations, with aid of a Pd$_4$/γ-alumina (110D) model (Pd$_4$/Al$_{13}$O$_{23}$H$_7$). Our results indicate the occurrence of an electronic metal−support interaction (EMSI) which induces a most intense charge transfer in the Pd$_4$→γ-alumina backdonation direction, most expressive in Pd→Al, promoting an electronic redistribution within the units and attenuating the MMI. Nevertheless, the MSI/MMI synergistic effect seems to favor slightly the nucleation of a fifth palladium atom, leading to a distorted square pyramidal arrangement for Pd$_5$. The LMOEDA analysis points to a mostly covalent character in the Pd−Al bonds, whereas the Pd−O bonds are mainly electrostatic in nature. The palladium atoms deposited on oxygen anions are the acid centers, where both NO molecule and an additional palladium atom anchor more strongly. In addition, the MSI/MMI effect, through the electronic and geometric contributions, drives the adsorption of the NO molecule to the mode which most favors the Pd→NO (4dz$^2$→2π*) backdonation (bridge mode).

Keywords Metal−support interaction · Metal−metal interaction · Nucleation · Adsorption · DFT · NBO

Introduction
The promotion of chemical interactions at the metal−support interface of heterogeneous catalytic systems has been subject of discussion since the 1930s [1–6]. The classical consequence of this phenomenon, coined by Tauster and coworkers in 1978 with the term strong metal−support interaction (SMSI), is the decrease or even the suppression of the chemisorption capacity of an adsorbate on the catalyst [7, 8]. Currently, however, it is well established that the metal−support interactions (MSI) come from different origins and they can also improve the stability, selectivity, and activity of the catalytic systems [9–14].

A specific type of MSI arises from the electron flux between the metal and the support, inducing redistribution of local charge in non-reducible supports and/or change in the oxidation states of the metal atoms and the ions of reducible supports [9, 10, 12, 15–22]. Such an effect was named by Campbell electronic metal−support interactions (EMSI) [23]. Some studies suggested the existence of a cyclic electron flux between the metal and the support [5, 17, 24, 25]. Electronic rearrangements within both the support and the metal moieties have been also reported [13]. The adsorption of Cu/Pd clusters on γ-Al$_2$O$_3$ (γ-alumina) is stabilized by electron transfer between the oxygen and aluminum atoms at the innermost layers of the support [26]. The adsorption of a Pt$_4$ cluster on a CeO$_2$(111) support involves charge redistribution within the metal cluster, in addition to change transfer from the metal to ceria [19]. It has been reported that even the adsorbate molecule can participate in the electron flux [24, 27–30].

The existence of competition between metal−metal interactions (MMI) and MSI has also been pointed [16, 26, 31, 32]. These processes determine not only the magnitude of charge transfer, but also the steps of growth and nucleation of the metal cluster, impacting its morphology, and,
consequently, its stability to sintering [13, 16, 31–37]. The interaction of the catalyst with the adsorbate molecule is also affected by these effects [26, 30], since supported metal particles with different shapes expose distinct faces where an adsorbate can bind with higher or lower intensity [36, 38, 39]. The mode of distribution and the coordination environment of the ions exposed to the support surface are directly related to all these processes [13, 21, 24, 27, 31, 33–35, 37, 40, 41]. For this reason, the correct description of the surface exposed to the adsorption of metal particle is, therefore, fundamental to an improved understanding of the MSI effect.

A special highlight is given to the catalytic efficiency of the alumina support in the γ phase, a consequence of the existence of a large quantity of defects in its crystalline structure, what confers high specific area (≈200–240 m² g⁻¹), well-defined pore size, thermal stability, and moderate acidity [33, 42–44]. The precise elucidation of the γ-alumina structure has been the subject of discussion over the years [45–48]. Such complexity exists due to its insulating character, high porosity, and low crystallinity. In addition, the choice of thermal treatment necessary for obtaining the γ phase in a high degree of purity is a complex issue, since it highly depends on the precursor species [31, 48].

The main discussions about the structure of γ-Al₂O₃ are related to the presence and position of hydroxyl groups, the crystalline lattice, and the distribution of the aluminum cations with different coordination, octahedral (Al₆), or tetrahedral (Al₄), in the bulk and on the surface [48]. Focusing on the last two points, the first model to represent the structure of γ-alumina, developed by Lippens [47], is based on a spinel-like lattice. In this model, the (110) crystallographic plane, which the literature agrees is the most exposed (70–83%) [49–51], splits into two types of layers that are intercalated: the (110C), containing both Al₆ and Al₄ cations, and (110D), exhibiting only the octahedral aluminum. Models based on spinel lattice have been adopted in several studies [40, 52–60]. With the premise that Al³⁺ cations occupying only spinel positions can be challenged [61], non-spinel models emerged, the most widespread one being that of Krokidis and coworkers [51, 62, 63]. According to Ferreira and coworkers [64], the theoretical infrared spectrum for a spinel model presents higher similarity with the experimental one [65] than the spectrum for a non-spinel model, the former being thermodynamically more stable than the latter by 4.6 kcal mol⁻¹. As for the γ-alumina surface characteristics, some works have pointed out that when the (110C) termination is exposed, it undergoes a spontaneous reconstruction process [66, 67]. Sohlberg and coworkers [68] reported the migration of the Al₄ cations to vacant octahedral interstices in the inner layer, where they become hexa-coordinate. Under conditions of partial dehydr(oxyl)ation, however, low coordinated Al³⁺ (penta- (Al₆), tetra- (Al₄), and tri- (Al₃) have been identified as surface sites with Lewis acidity [34, 69–74].

Catalysts produced by supported size-selected subnanometer metal clusters have received considerable attention, because of their unique electronic and catalytic properties, which differ from bulk metal surfaces and larger nanoparticles [5, 14, 75–78]. The use of computational tools allows an in-depth investigation, at the atomic level, of chemical and structural properties of metal particles and supports and their intercorrelation, a key information for the rational development of more efficient catalysts.

In previous works, we employed DFT plus natural bond orbital (NBO) calculations to understand the influence of MSI and MMI on the adsorption of formaldehyde [24] and nitric oxide [29, 30] molecules on Pd₄ supported by (110C) γ-Al₂O₃ surface. In this approach, we investigate the behavior of such interactions facing two processes—nucleation of one palladium atom and NO adsorption on Pd₄—however considering the participation of the (110D) surface (found as more stable than (110C) [66, 67]), using a γ-alumina model of Al₁₃O₂₃H₇ stoichiometry. In addition to DFT/NBO methodology, we performed the localized molecular orbital energy decomposition analysis (LMOEDA) to give insight into the nature of the palladium-ion bonds and electronic transfers at the metal—support interface.

Computational details

This work presents a study of the MSI and MMI effects in a Pd₄/γ-alumina aggregate, face the nucleation of a fifth palladium atom and the adsorption of a single NO molecule, by the exposition of the (110D) surface of the support. The model to represent the γ-alumina structure, Al₁₃O₂₃H₇ (Fig. 1), was constructed based on X-ray diffraction data [54, 79] (Table S1, see Supporting Information), and it follows a spinel-like lattice, pointed by Ferreira and coworkers [64] as the most thermodynamically stable arrangement and considered in several studies [40, 56–60]. The aluminum cations and oxygen anions are arranged in three layers, in the DCD sequence, to expose the (110D) face mostly (Fig. 1b). To balance the total charge and yield a neutral model, seven hydrogen atoms were added to the terminal oxygen atoms, leading to a partially hydroxylated structure. During the optimization process, only the hydrogen atoms were allowed to relax, and the C₄v symmetry was imposed.

The interaction between a palladium cluster and the Al₁₃O₂₃H₇ model was performed depositing a Pd₄ cluster in a planar geometry (dPd-Pd = 2.751 Å) [80] with a rhombohedral arrangement (D₃h symmetry) on the center of the (110D) face (Fig. 1a). Two distinct approximation modes for the Pd₄ cluster were considered: (i) — parallel and (ii) — perpendicular to the γ-alumina surface (Fig. S1). Intending to reduce the computational cost, only the palladium atom positions were allowed to relax during the geometry.
optimization of the Pd₄/Al₁₃O₂₃H₇ complex, in Cs symmetry. In addition, the influence of the remaining palladium atoms on the interaction of a specific palladium with the γ-alumina model was evaluated with aid of single point calculations. In these calculations, three of the four palladium atoms were removed, while the remaining palladium atom was kept frozen in its original position, producing the Pd₁/Al₁₃O₂₃H₇ structures. Single point calculations were also performed for Pd₄ clusters in planar (D₂h symmetry) and tetrahedral (Td) arrangements and for the forms resulting from the optimization in the presence and in the absence of the γ-alumina support (Cs).

To obtain information about the process of growth of the Pd₄ cluster on the (110D) face of γ-alumina, a fifth palladium atom was added to the resulting Pd₄/Al₁₃O₂₃H₇ structure. In this case, all palladium coordinates were allowed to relax during the geometry optimization, while keeping the γ-alumina geometry fixed.

The effect of MSI on the adsorption catalytic step was investigated using nitric oxide (NO) as a molecular prototype. One NO molecule was deposited and optimized on the Pd₄/Al₁₃O₂₃H₇ complex and on the isolated Pd₄, in several orientations, including the on-top, bridge, hollow, di-σ, and π adsorption modes. In this step, only the NO coordinates were relaxed. Importantly, no NO adsorption mode involving alumina directly was tested.

A set of energy parameters was obtained for the optimized complexes. The strength of the interactions on the adsorption interfaces, within the proposed models, was measured by calculating the adsorption energy (E_ad, Eq. (1)). This was computed by subtracting the energy of the AB complex (NO/Pd₄, NO/Pd₄/Al₁₃O₂₃H₇ or Pd₄/Al₁₃O₂₃H₇) from the sum of the energies of the separated species (A = NO molecule or Pd₄ and B = Pd₄, Pd₄/Al₁₃O₂₃H₇ or Al₁₃O₂₃H₇).

\[
E_{ad} = E_{AB} - (E_A + E_B)
\]  

To quantify the degree of structural modification in the optimized planar Pd₄ cluster, the reorganization energy (E_reorg) was computed. This energy was obtained by subtracting the absolute energy of Pd₄ in the planar form (E_Pd₄(planar)) from the absolute energy of Pd₄ in the distorted arrangement (E_Pd₄(dist)), according to Eq. (2):

\[
E_{reorg} = E_{Pd₄(dist)} - E_{Pd₄(planar)}
\]

All the energy values were corrected for basis set superposition error (BSSE), employing the counterpoise correction method [81]. In addition, an energy decomposition analysis (EDA) of the palladium interaction on the (110D) face of the proposed γ-alumina model was performed using the LMOEDA method [82]. Due to the computational cost involved, we chose to use the Pd₄/Al₁₃O₂₃H₇ clusters in the calculations. In this approach, the interaction energy is decomposed into electrostatic, polarization, exchange, repulsion, and dispersion contributions.

A measure of the intensity of the electron transfer occurring in the metal – support and metal – molecule interfaces was obtained by the natural bond orbital (NBO) approach [83–86]. The stabilization energy for these systems, resulting from the main NBO’s interactions, was calculated according to the second-order perturbation theory.
\[ E^2 = \Delta E_{ji} = \frac{F(i,j)^2}{q_i - \epsilon_j - \epsilon_i} \quad (3) \]

In Eq. (3), the hyperconjugative interaction energy between a filled (i) and an unoccupied (j) NBO is quantified, where \( q_i \) is the occupancy of the donor orbital, \( F(i,j)^2 \) is the NBO Fock matrix between orbitals i and j and \( \epsilon_j - \epsilon_i \) is the difference between the energies of the j and i NBOs \([87, 88]\). The contribution to the stability of the \( \text{Pd}_4/\text{Al}_{13}\text{O}_{23}\text{H}_7 \) and \( \text{NO}/\text{Pd}_4/\text{Al}_{13}\text{O}_{23}\text{H}_7 \) systems of the deletion of interactions between pairs of atoms \([89, 90]\) of the metal – support and the metal – metal interface was estimated by the deletion energy. The charge densities were computed to identify the main electron flux between the interacting units, with the NBO \([85]\), Mulliken \([91]\), Hirshfeld \([92]\), and Merz–Singh–Kollman (MSK) \([93, 94]\) methods.

All calculations were carried out using the Gaussian 09 computational package \([95]\) with the B3LYP hybrid functional \([96–98]\). This method has been successfully employed in studies involving the interaction of adsorbate species with clusters of metal oxides and transition metals \([24, 30, 99–103]\). The palladium atoms were described with NBOs \([87, 90]\), Mulliken \([91]\), Hirshfeld \([92]\), and Merz–Singh–Kollman (MSK) \([93, 94]\) methods.

Results and discussion

**γ-alumina model: \( \text{Al}_{13}\text{O}_{23}\text{H}_7 \)**

The (110D) adsorption face contains four aluminum cations in octahedral arrangement (\( \text{Al}_c \)), which are tetra-coordinated at the surface, and six oxygen anions. These latter are present in two different coordination numbers: (i) di-coordinated (O\(_{d}\)), bonded to a tetrahedral (A\(_{t}\)), and an octahedral (A\(_{o}\)) aluminum cation, and (ii) tri-coordinated (O\(_{t}\)), bonded to three A\(_{o}\) cations (Fig. 1a', b'). The shortest ion – ion distances at the (110D) face are \( \text{Al}_{o}-\text{Al}_{o} = 5.572 \) Å, \( \text{O}_{d}-\text{O}_{d} \) and \( \text{O}_{t}-\text{O}_{t} = 2.786 \) Å, \( \text{O}_{d}-\text{O}_{o} = 3.940 \) Å, and \( \text{Al}_{o}-\text{O} = 1.970 \) Å (Fig. S2). A search for the relative stability between the different electronic spin states of the \( \text{Al}_{13}\text{O}_{23}\text{H}_7 \) model was performed. The singlet state \( (S=0) \) was found to have the lowest energy, 2.9 kcal mol\(^{-1}\) more stable than the triplet one \( (S=1) \) (Table S2). Spin contamination was not found in any of the calculated states.

The calculated total NBO charge distribution ranges from \(-1.068 \) e to \(-1.407 \) e for oxygen anions, and from \(+1.720 \) e to \(+1.994 \) e for aluminum cations. At the (110D) face, these values vary from \(-1.192 \) e to \(-1.292 \) e and \(+1.913 \) e and \(+1.950 \) e, respectively. The hydrogen atoms of the terminal hydroxyl groups assume charges between \(+0.481 \) e and \(+0.530 \) e. The complete charge distribution on γ-alumina ions obtained with NBO and other models (Hirshfeld, MSK, and Mulliken) is given in Table S3.

**\( \text{Pd}_4 \) adsorption on (110D) face of \( \text{Al}_{13}\text{O}_{23}\text{H}_7 \) model**

A cluster containing four palladium atoms (\( \text{Pd}_4 \)) with planar geometry and \( D_{2h} \) symmetry was adsorbed on the central part of the (110D) surface of \( \text{Al}_{13}\text{O}_{23}\text{H}_7 \) in two ways, parallel and perpendicular to the surface (Fig. S1). The \( \text{Pd}_4/\text{Al}_{13}\text{O}_{23}\text{H}_7 \) structure resulting from the parallel adsorption mode was chosen since it is 1.9 kcal mol\(^{-1}\) more stable than the one obtained for adsorption in the perpendicular mode. The preferential electronic spin state of \( \text{Pd}_4/\text{Al}_{13}\text{O}_{23}\text{H}_7 \) is triplet \( (S=1, \text{Table S2}) \). The adsorption energy for \( \text{Pd}_4 \) on the (110D) surface, computed according to Eq. (1), is \(-81.4 \) kcal mol\(^{-1}\) (Fig. 2a).

The interaction with the (110D) face promotes distortion in the arrangement of the palladium atoms when compared to the starting planar form (Pd–Pd distance in bulk = 2.751 Å \([80]\), Table S4), as shown in Fig. 2c and 3a, b. A similar conformation for \( \text{Pt}_4 \) was obtained when using periodic boundary conditions DFT calculations for its adsorption on the (100) surface in a non-spinel γ-alumina model \([32]\). This distorted arrangement was called boat, the same nomenclature that will be used in this work. The analysis of the geometric parameters shows a shortening in most of the Pd–Pd distances, except for Pd(1)–(2) (2.882 Å). The largest shortening was computed for the Pd(3)–(3)† distance (from 4.765 to 4.504 Å, \( (3)\rightleftharpoons \text{Pd atom symmetric to Pd(3))} \). Additionally, small deviations were verified in the bond angles (between \(-2.3 \) and \(+4.2^\circ \)). As for the dihedral angle \( \zeta \) (Fig. 3a, b), a greater variation is verified (from 0.0 to \(+22.4^\circ \)). This result is a consequence of the shorter bond length of Pd–O in comparison with Pd–Al, leading to a significant distortion of the planar \( \text{Pd}_4 \) arrangement.

The optimization of the planar \( \text{Pd}_4 \) aggregate in the absence of the γ-alumina model (in \( C_1 \) symmetry) results in a drastic change in the geometry when compared to that observed after optimization on the surface of the support. The \( \zeta \) dihedral angle changes from 0.0 to \(-108.1^\circ \) (Fig. 3a, c), a value close to the reference \( T_d^\gamma \) symmetry (\(-109.5^\circ \), Table S4), and much larger than that observed when \( \text{Pd}_4 \) is optimized in the presence of γ-alumina. The bond angles vary in a narrower range, between \(-1.4 \) and \(+2.8^\circ \). The Pd–Pd distances suffer some shortening, assuming values between 2.605 and 2.717 Å. Several studies show that the bare metal clusters assume bond lengths shorter than the ones observed in the bulk \([31, 113, 114]\).
The structural changes and stability of the Pd$_4$ cluster were evaluated through the reorganization energy ($E_{\text{reorg}}$, Eq. (2)). The arrangement obtained on the (110D) face of the γ-alumina (boat) has stability intermediate between the planar and tetrahedral arrangements: 12.4 kcal mol$^{-1}$ more stable the former and 22.2 kcal mol$^{-1}$ less stable than the latter.

The change in the intensity of the Pd–Pd interactions (MMI) was quantified by means of the cohesion energy ($E_{\text{coh(iso)}}$, Eq. (4)). In Eq. (4), the first term corresponds to the absolute energy of the isolated Pd$_4$ cluster ($E_{\text{Pd4}}$), and the second one is the addition of the absolute energies of each palladium atom ($E_{\text{Pd1}}$). According to Fig. 4, the boat form is 12.2 kcal mol$^{-1}$ more cohesive than the planar arrangement (–80.7 kcal mol$^{-1}$ against –68.5 kcal mol$^{-1}$) and 21.7 kcal mol$^{-1}$ less cohesive than the tetrahedral geometry ($E_{\text{coh(iso)}} = –102.4$ kcal mol$^{-1}$).

$$E_{\text{coh(iso)}} = E_{\text{Pd4}} - \sum E_{\text{Pd1}}$$  \hspace{0.1cm} (4)

$$E_{\text{coh(sup)}} = E_{\text{Pd4}/\gamma-\text{alumina}} - \sum E_{\text{Pd1}/\gamma-\text{alumina}} + 3E_{\gamma-\text{alumina}}$$  \hspace{0.1cm} (5)

It is important to emphasize that this result quantifies the change in the Pd–Pd interactions promoted by MSI, but it does not include any electronic effect present in the metal – support interface (EMSI) [23]. To estimate this contribution, the cohesion energy was also calculated in the presence of the support ($E_{\text{coh(sup)}}$, Eq. (5)) [31]. Analogously, $E_{\text{Pd4/Al13O23H7}}$ is the absolute energy of the Pd$_4$/Al$_{13}$O$_{23}$H$_7$ model, which is then subtracted by the sum of the absolute energies of Pd$_4$/γ-alumina moieties ($E_{\text{Pd4/\gamma-\text{alumina}}}$) and each palladium atom at its respective anchoring site (single point calculations). The third term in Eq. (5) (3$E_{\gamma-\text{alumina}}$) represents the excess amount of γ-alumina energy to be discounted. The electronic perturbations promoted by MSI reduce the cohesion energy among the palladium atoms by 25.5 kcal mol$^{-1}$, reaching a value of –55.2 kcal mol$^{-1}$ (Fig. 4).

The coordinates of each palladium atom and their geometric parameters, in the optimized Pd$_4$/Al$_{13}$O$_{23}$H$_7$ cluster,
indicate that they adsorb in the ontop mode at different sites (Fig. 2b, c and 5 and Table 1). The Pd(1) atom anchors on the O₆ octahedral oxygen anion maintaining a distance of 2.046 Å, with an angle of deviation from the line normal to the surface (θ) of 21.8°. Consequently, the Pd – γ-alumina distance assumes a smaller value, 1.899 Å. This short Pd(1) – γ-alumina distance results in an approximation of the tetrahedral aluminum cation placed at the lower layer (Pd – Al₁ = 3.300 Å). The Pd(2) adsorbs on an O₆ oxygen anion with a bond distance of 2.140 Å, with θ = 8.0°. This distance is close to the Pd(2) – surface distance (2.119 Å). On the other hand, Pd(3) (and its symmetric Pd(3)*) adsorbs on Al₆ with a larger distance of 2.515 Å, with θ = 12.8°, resulting in the largest Pd – γ-alumina distance (2.452 Å). The Pd – O and Pd – Al distances are in good agreement with the experimental results found in PdO oxide (2.020 Å) and PdAl metal alloy (2.460–2.670 Å) [115–117].

To measure the intensity with which each palladium atom is bound in the Pd₄/Al₁₃O₂₃H₇ complex, the bonding energy (E_b(Pd₄/sup)) was calculated, according to Eq. (6):

$$E_b(Pd_{4/sup}) = E_{Pd_{4/Al₁₃O₂₃H₇}} - E_{Pd_{4/sup}}$$  \hspace{1cm} (6)

$$E_b(Pd_{1/sup}) = E_{Pd_{1/γ-alumina}} - E_{Pd_{1}}$$  \hspace{1cm} (7)

$$E_b(Pd_{i}) = E_{Pd_{i/γ-alumina}} - E_{Pd_{i}}$$  \hspace{1cm} (8)

The Pd(1) is the most strongly bonded atom in the Pd₄/Al₁₃O₂₃H₇ complex, with a bonding energy of −65.0 kcal mol⁻¹. Pd(2) and Pd(3) anchor both with close and much smaller bonding energies, −47.5 kcal mol⁻¹ and −48.5 kcal mol⁻¹, respectively (Fig. 5 and Table S5).

The contributions of the Pd–support (E_b(sup)) and Pd–Pd₃ (E_b(Pd₃)) interactions in the bonding energy of each palladium atom within the Pd₄/Al₁₃O₂₃H₇ complex were estimated through Eq. (7) and (8), respectively (Fig. 5 and Table S5). The palladium atom more strongly bonded to (110D) surface is deposited on a di-coordinated oxygen anion (Pd(2) – O₆), with a bonding energy of −34.1 kcal mol⁻¹. The second highest bonding energy involves Al₆, presenting a value of −24.7 kcal mol⁻¹ (Pd(3) – Al₆). The weakest bonding energy is −21.9 kcal mol⁻¹, resulted from the anchoring of Pd(2) on a tri-coordinated oxygen anion (O₆).

When the Pd–Pd₃ interaction energy is measured, it is verified Pd(1) and Pd(2) are atoms more strongly bonded within Pd₄ cluster (−54.8 kcal mol⁻¹ and −54.5 kcal mol⁻¹, respectively). For Pd(3) (and its symmetric) this energy is −33.4 kcal mol⁻¹. These energy values are consistent with the coordination number of the palladium atoms within the boat cluster, three for Pd(1) and Pd(2) and two for Pd(3).

The results above suggest that MMI has a higher contribution than MSI to the interaction of each palladium atom within the Pd₄/Al₁₃O₂₃H₇ complex, since E_b(Pd₄/sup) is higher than E_b(sup), regardless the involved alumina site. When the sum of both E_b(sup) and E_b(Pd₄) components is considered, it is possible to verify the obtained values are greater than the bonding energy of a single palladium atom within the complex (E_b(Pd₄/sup)). Such observation is revealing that the MSI/MMI synergistic effect acts weakening the palladium bonding energy within the Pd₄/Al₁₃O₂₃H₇ complex. This attenuation is more significant where oxygen anions are involved (ΔE = −28.9 kcal mol⁻¹ (Pd(2) – O₆) and −23.8 kcal mol⁻¹ (Pd(1) – O₆)) than Al₆ cation (ΔE = −9.7 kcal mol⁻¹).

By allowing the relaxation of the coordinates of each palladium atom individually (removing the other Pd atoms), it

![Fig. 5 Bonding energy (in kcal mol⁻¹) of each palladium atom in: Pd₄/Al₁₃O₂₃H₇ complex (E_b(Pd₄/sup)) black column) and boat Pd₄ (E_b(Pd₄/boat) blue column) and γ-alumina (E_b(sup) red column) moieties.](image-url)

![Table 1 Geometric parameters (bond distance (d) and θ bond angle) and charge on palladium atom in Pd₄/Al₁₃O₂₃H₇ and Pd₄ cluster/ Al₁₃O₂₃H₇ complexes](table-url)

| Parameter | Structure | Pd(1) | Pd(2) | Pd(3) |
|-----------|-----------|-------|-------|-------|
| dPd–Al⁺ (Å) | sp | 3.575⁰(o) | 3.108⁰(o) | 2.515⁰(o) |
| | opt | 3.258⁰(o) | 2.439⁰(o) | 1.899⁰(o) |
| dPd–O⁻(Å) | sp | 2.046⁰(o) | 2.140⁰(o) | 3.776⁰(o) |
| | opt | 2.223⁰(o) | 2.147⁰(o) | 3.328⁰(o) |
| θ (°) | sp | +21.82 | −8.00 | +12.83 |
| | opt | +17.10 | +17.63 | Pd(1)⁶ |
| dPd–face (Å) | sp | 1.899 | 2.119 | 2.452 |
| | opt | 1.683 | 2.044 | Pd(1)⁶ |
| qPd | sp | +0.194 | +0.192 | +0.190 |
| | opt | +0.282 | +0.255 | Pd(1)⁶ |

1. Aluminum cation (⁰=Al) or oxygen anion (⁰=O) and charge on palladium atom in: Pd₄/Al₁₃O₂₃H₇ and Pd₄ cluster/Al₁₃O₂₃H₇ complexes.

2. The palladium atom migrates to the same position of Pd(1)
was possible to infer the stability of each Pd—support bonding produced at (110D) surface. The structural modifications after relaxation in Pd₁/Al₁₃O₂₃H₇ are shown in Fig. 6 and Table 1. The Pd(1) atom moves to the nearest hollow site (threefold), on two O₁₀ and one Al₁₀, with distances of 2.222 Å, 2.269 Å, and 2.528 Å, respectively. This migration approximates Pd(1) to the (110D) surface (from 1.899 to 1.683 Å). The relative energy between the single point and the optimized Pd₁/Al₁₃O₂₃H₇ arrangements is 11.5 kcal mol⁻¹. The Pd(3) atom migrates to the same site, however, involving a higher relative energy of 22.8 kcal mol⁻¹. Lastly, Pd(2) slightly moves toward the neighbor Al₁₀, converging to bridge mode (O₉—Pd(2)—Al₁₀), with distances of 2.439 Å (Al₁₀) and 2.147 Å (O₉). This change of position also shortens the Pd(2)—γ-alumina distance (from 2.119 to 2.044 Å), involving a lowering in energy of 15.0 kcal mol⁻¹. Therefore, two distinct anchoring modes for a single palladium atom relaxed on (110D) surface are produced. The calculated absolute energies show that hollow is 9.8 kcal mol⁻¹ more stable than the bridge mode. These results indicate that anchoring a palladium atom on a single center at the (110D) surface of γ-alumina is not stable.

The natural bond orbital (NBO) analysis shows that the palladium atom assumes positive charge at Pd₁/Al₁₃O₂₃H₇ complexes, with values +0.194 ē, +0.192 ē and +0.190 ē for Pd(1), Pd(2) and Pd(3), respectively (Table S6). After relaxation (Table S7), an increase of the charge on the palladium atoms is observed (+0.282 ē, +0.255 ē, and +0.282 ē, respectively). These results show that the migration to sites with a greater coordination number leads to an increase of the acidity of a single palladium atom deposited on (110D) surface.

The energy decomposition analysis (EDA) was performed to characterize the contribution of the participating forces to the Pd—γ-alumina interaction energy. The LMOEDA method [82], which breaks up the interaction energy into five components: electrostatic, polarization (covalent contribution), repulsion, exchange, and dispersion was employed to the Pd₁/Al₁₃O₂₃H₇ complexes. At the sites involving Pd—O interactions, the electrostatic contribution is the largest one among the stabilizing components, corresponding to 19% of the total energy (Fig. 7a, b). The polarization term is the second largest, with a magnitude close to the first one (17%), followed by exchange (16%), and by a small dispersion effect (3%). Such behavior indicates that the type of oxygen anion coordination does not influence the nature of the Pd—O interaction in this system.

As for the Pd—Al₉ interaction, the polarization is the main stabilizing contribution, being two times greater than the electrostatic interaction (28% against 14%, Fig. 7c). The main covalent character of the Pd—Al bond is also pointed out in [118, 119]. The exchange component has the same value as the electrostatic, whereas the dispersion remains as the smallest one (5%). The destabilizing (positive) contribution of repulsion is (individually) the largest one, representing 45% (Pd—O) and 39% (Pd—Al₉). The total interaction energies and their components calculated with the LMOEDA method are shown in Fig. S3.

The NBO analysis points that, after adsorption of Pd₄ on the γ-alumina surface, the γ-alumina aggregate acquires a total negative charge of −0.298 ē (Fig. 8b). The NBO charge distribution on the sites directly involved in the anchoring of Pd₄ indicates a higher charge variation on
the Al₉ cations than on the oxygen anions. The Al₉ cations attenuate their positive charge by 0.218 ē (from +1.913 to +1.695 ē), whereas the oxygen anions undergo smoother charge modifications: +0.004 ē for O₉ (from −1.266 to −1.262 ē) and −0.015 ē for O₁₀ (from −1.291 to −1.306 ē).

In the lower layers of the γ-alumina model, slight changes in the atomic charges are observed. The aluminum ions (Alt and Alo) directly bonded to O₉ and O₁₀ can be highlighted. They lose electron density (0.071 ē and 0.051 ē, respectively) when Pd₄ adsorbs (Fig. 8a, b). This behavior is probably a consequence of charge redistribution between the ions and a compensation effect caused by the approximation of Pd₄. As reported by Guo and Zhang [5] in their theoretical study of non-reducible oxides, such as γ-alumina, the propagation of the effects promoted by the metal – support interaction is limited to the region close to the contact between these units, due to the low electronic and ionic conductivity of these types of oxides.

The complete charge distribution over the Pd₄/Al₁₃O₂₃H₇ complex, calculated with all models used in this work, is given in Table S3.

The total charge assumed by the adsorbed Pd₄ unit (+0.298 ē) is not equally distributed among the palladium atoms. The most positive charge is on Pd(1) (+0.173 ē), a palladium atom placed over O₉. The other palladium atoms, Pd(2) and Pd(3), maintain charges close to zero (+0.045 ē and +0.040 ē) and are situated over O₁₀ and Al₉, respectively. When this charge distribution is compared with the isolated boat Pd₄ arrangement (Fig. 8a, b), Pd(1) and Pd(2) lose electron density (Δq = +0.325 ē and +0.191 ē, respectively), whereas Pd(3) acquires charge density (Δq = −0.110 ē) upon adsorption.

These results indicate that charge redistributions occur within both metal and support units when Pd₄ anchors on the Al₁₃O₂₃H₇ model. The combined MSI/MMI effects induce an electronic flux that provides a positive charge on the palladium atoms bonded to the oxygen anions and an increase in the electron density on the metal atoms anchored on the Al₉ cations. Such behavior is probably due to the mostly electrostatic character of the Pd – O interaction, pointed by the LMOEDA calculation. This polarizes the charge towards the oxygen ions, turning these palladium atoms into acidic centers. In addition, anchorage on O₉ produces the most positive charge on the palladium atom, a consequence of the lower coordination of this oxygen anion when compared to O₁₀. However, the Pd – Al₉ electron transfer seems to be the most responsible for the positive charge on Pd(3), since Al₉ receives electron density after the Pd₄ adsorption.

To estimate the energetic contribution of the main metal – support electron transfer to the stability of the Pd₄/Al₁₃O₂₃H₇ complex, the calculation of deletion energy was performed through the NBOdel procedure [89, 90]. The average value per interaction, obtained by turning off the electronic delocalization at the Pd – γ-alumina sites, shows
investigated by the NBO procedure. The main backdonation face within the 69.3 kcal mol\(^{-1}\) is evaluated, the deletion energy points to a contribution higher than that obtained for the isolated energy of interactions, which are mostly attractive, become repulsive in opposite signals (Fig. 8a, b). Thus, the electrostatic Pd removed, however, the Pd atoms assume higher charges with atoms assume a positive charge. When the \(\gamma\)-alumina ions are removed, the \(\gamma\)-alumina model. Therefore, the direction which commands the electron transfer among the palladium atoms is evaluated, the deletion energy points to a contribution of 69.3 kcal mol\(^{-1}\) per atom. This value is 8.5 kcal mol\(^{-1}\) higher than that obtained for the isolated \(\text{Pd}_4\) boat cluster (60.8 kcal mol\(^{-1}\), Table 2). Although there is an increase in the energy related to the electron flux between the palladium atoms, it is reasonable to accept that the electrostatic component influencing the Pd–Pd interactions depends on the charges that they assume at the surface of the \(\gamma\)-alumina model. As shown above, after the adsorption of \(\text{Pd}_4\) on the (110D) surface, all palladium atoms assume a positive charge. When the \(\gamma\)-alumina ions are removed, however, the Pd atoms assume higher charges with opposite signals (Fig. 8a, b). Thus, the electrostatic Pd–Pd interactions, which are mostly attractive, become repulsive in the presence of the support. This significant change in the electrostatic component helps explain the decrease in the cohesive energy of \(\text{Pd}_4\) on the (110D) face \(E_{\text{coh(110D)}}\).

Table 2 Deletion energy \(E_{\text{del}}\)(kcal mol\(^{-1}\)) involved in donation (Don.) and backdonation (Back.) processes in MSl (values averaged per Pd – ion pair) in \(\text{Pd}_4/\text{Al}_{13}\text{O}_{23}\text{H}_7\) complex, in the absence and in the presence of the NO molecule (when adsorbed in the bridge mode), and in M MI (values averaged per Pd atom) in isolated (Iso.) and supported (Sup.) \(\text{Pd}_4\) clusters

| Interaction | \(E_{\text{del}}\)(kcal mol\(^{-1}\)) |
|------------|-------------------------------|
| MSI Don    | 36.76                         |
| MSI Back   | 44.48                         |
| MMI Iso    | 60.79                         |
| MMI Sup   | 69.30                         |

In the absence of the other palladium atoms, the intensity of \(E^2\) for this interaction increases by 11.0 kcal mol\(^{-1}\) (to 27.6 kcal mol\(^{-1}\)), without modification in the shape of the involved orbitals (Fig. 9b). These results are in line with the increase in the electron density on the \(\text{Al}_6\) cations at (110D) face, in both \(\text{Pd}_4/\text{Al}_{13}\text{O}_{23}\text{H}_7\) and \(\text{Pd}_4^{10p}/\text{Al}_{13}\text{O}_{23}\text{H}_7\) complexes, through the palladium anchoring (Fig. 8a, b and Table S6). Therefore, such behavior confers a Lewis acid character for the \(\text{Al}_6\) in the predominantly covalent Pd – Al\(_6\) interaction.

Pd nucleation on \(\text{Pd}_4/\text{Al}_{13}\text{O}_{23}\text{H}_7\)

To investigate the affinity of the \(\text{Pd}_4\) agglomerate on the (110D) surface for one additional palladium atom, a fifth palladium was approximated to the supported \(\text{Pd}_4\) cluster. The most stable \(\text{Pd}_4/\text{Al}_{13}\text{O}_{23}\text{H}_7\) arrangement is shown in Fig. 10. Triplet is the most stable electronic spin state (Table S2). The preferential nucleation site for Pd(5) on \(\text{Pd}_4/\text{Al}_{13}\text{O}_{23}\text{H}_7\) is the bridge, involving Pd(1) and Pd(2), with Pd–Pd distances of 2.656 Å and 2.601 Å, respectively (Fig. 10a). It is interesting to note that these palladium atoms where Pd(5) anchors are the most positive centers of the \(\text{Pd}_4/\text{Al}_{13}\text{O}_{23}\text{H}_7\) complex. The Pd(5)–surface distance is reasonably long, 3.749 Å. After the nucleation process, most of the Pd – Pd distances involving the palladium atoms directly anchored on the \(\gamma\)-alumina surface are elongated. The greatest increase is observed in Pd(1)–Pd(2), the position where Pd(5) anchors \(\Delta d_{\text{Pd-Pd}}=+0.309\) Å, Fig. 2 and Table S8). In addition, Pd(1) and Pd(4) migrate from ontop to the bridge and hollow sites, respectively. The final geometric coordinates characterize a square pyramidal arrangement for \(\text{Pd}_5\), as shown in Fig. 10a, c).

The origin of the metal – support charge transfer was also investigated by the NBO procedure. The main backdonation contribution is the Pd(3)→ Al\(_6\) transfer, which occurs via overlapping between 4\(d^2\) (99%, occ. = 0.916 ē) and 3\(sp^{0.23}\) (81% s, 18% p, occ. = 0.283 ē) orbitals, respectively, with stabilization energy \(E^2\) Eq. (3)) of 16.6 kcal mol\(^{-1}\) (Fig. 9a).
of 2.6 kcal mol\(^{-1}\) (Eq. (10) [120], \(E_{\text{nuc(iso)}} = -57.5\) kcal mol\(^{-1}\)), showing that the synergistic MSI/MMI effect slightly favors the metal cluster growth. Thus, the role played by MSI/MMI effect on the sintering control, neglecting the influence of temperature, could be expected to be only moderate.

Upon the formation of the Pd\(_5\)/Al\(_{13}\)O\(_{23}\)H\(_7\) complex, the \(\gamma\)-alumina moiety remains negatively charged, with an increase in the charge magnitude (from \(-0.298\) to \(-0.423\) \(\varepsilon\)). A small change in the charges of the palladium atoms is observed, except for Pd(3) (bonded to Al\(_3\)), whose positive charge increases by 0.193 \(\varepsilon\) (from +0.040 to +0.233 \(\varepsilon\)). In addition, when the \(\gamma\)-alumina coordinates are removed, Pd(3) keeps a small positive charge of +0.092 \(\varepsilon\), showing that the most positive value assumed by this atom in Pd\(_5\)/Al\(_{13}\)O\(_{23}\)H\(_7\) must be a consequence of the MSI. This result reinforces the Lewis acid behavior of the Al\(_3\) at the (110D) surface. The complete charge distribution in Pd\(_5\)/Al\(_{13}\)O\(_{23}\)H\(_7\) and Pd\(_5\) agglomerates is shown in Tables S3 and S9.

**NO adsorption on Pd\(_4\)/Al\(_{13}\)O\(_{23}\)H\(_7\)**

To evaluate the effect of the metal–support interactions (MSI) in the catalytic step of anchoring an adsorbate, a nitric oxide (NO) molecule was adsorbed and optimized on the palladium atoms in the Pd\(_4\)/Al\(_{13}\)O\(_{23}\)H\(_7\) complex in different modes (atop (linear), bridge, hollow, \(di-\sigma\), and \(\pi\)). For the resulting NO/Pd\(_4\)/Al\(_{13}\)O\(_{23}\)H\(_7\) structures, the doublet electronic spin state \((S = 1/2)\) was obtained as the most stable (Table S10).

After geometry optimization, the only stable arrangements for NO adsorbed on the Pd\(_4\) supported cluster model are ontop and bridge adsorption modes (Fig. 11 and Table 3). When approaching NO in a linear mode, it converges to angular (ontop mode), a result also reported by Viñes and coworkers [121], who showed that this mode is energetically favorable, stabilized by an interaction between a \(\pi^*\) molecular orbital of NO and the \(dz^2\) atomic orbital of palladium. The NO molecule anchors more strongly in the bridge mode involving Pd(1) and Pd(2), with an energy of \(-29.8\) kcal mol\(^{-1}\). However, this mode is only 1.3 kcal mol\(^{-1}\) more stable than adsorption in the ontop mode on Pd(2) \((-28.5\) kcal mol\(^{-1}\)). Both values are close to the experimental heat of adsorption of NO on palladium supported on \(\gamma\)-alumina (\(-27.2 \pm 1.4\) kcal mol\(^{-1}\)) [122], which gives support to the employed model. Ontop adsorption modes on Pd(1) and Pd(3) occur with adsorption energies of \(-23.1\) kcal mol\(^{-1}\) and \(-14.7\) kcal mol\(^{-1}\), respectively. The Pd–N bond distances are shorter in the ontop than in the bridge mode (Table 3). The Pd–N bond distances are shorter in the ontop than in the bridge mode (Table 3). In the latter, the Pd–N bond distance shows values of 2.030 \(\AA\) (Pd(1)) and 2.084 \(\AA\) (Pd(2)), against 1.909 \(\AA\), 1.901 \(\AA\), and 1.969 \(\AA\), for Pd(1), Pd(2), and Pd(3), respectively. The N–O distance is elongated to 1.197 \(\AA\) for adsorption in the bridge mode, in relation to the calculated (1.148 \(\AA\)) and experimental (1.150 \(\AA\)) values for the isolated molecule. In the ontop mode, however, this elongation is smaller, 1.163 \(\AA\) (Pd(1) and Pd(2)) and 1.161 \(\AA\) (Pd(3)). The Pd–N–O bond angle is in the range of 133.2 – 138.3\(^\circ\), values in good agreement with theoretical results (between 115 and 143\(^\circ\)) found in the literature for the adsorption of NO.
on isolated \((n = 1 \text{–} 6)\) \cite{124, 125} and supported on mordenite zeolite \cite{126} Pd\(_n\) clusters. The NBO calculation shows that the NO molecule acquires the highest electronic density when it is adsorbed in the bridge mode \((\Delta q_{\text{NO}} = \Delta q_{\text{NO}}) = –0.370 \, \text{e}^{-}\). Consequently, the total charge on the Pd\(_4\) cluster reaches its highest positive value in the supported NO/Pd\(_4\) complex. In comparison to the bare Pd\(_4/\text{Al}_{13}\text{O}_{23}\text{H}_{7}\) complex, the \(\Sigma q_{\text{Pd}_4}\) increases by \(+0.311 \, \text{e}^{-}\) (from \(+0.298\) to \(+0.609 \, \text{e}^{-}\), Fig. 8b and Table 3). The \(\gamma\)-alumina unit compensates the positive charge on Pd\(_4\) by \(0.059 \, \text{e}^{-}\) (15\%). This behavior suggests that the adsorption of NO in the bridge mode induces at least a small electronic flux from the support to the metal atoms and promotes backdonation from Pd\(_4\) to NO moieties. The complete charge distribution in NO/Pd\(_4/\text{Al}_{13}\text{O}_{23}\text{H}_{7}\) is given in Table S11.

The NBO stabilization energy points to Pd\(\rightarrow\text{NO}_{\text{bridge}}\) backdonation as the main electron flux, involving a total energy of \(37.0 \, \text{kcal mol}^{-1}\) (Table 4). The Pd\(\rightarrow\text{NO}\) backdonation process occurs via an overlap between the \(4d_-^2\) orbitals of the palladium atoms and a \(2\pi^*\) orbital in the NO molecule (65% polarized to the nitrogen atom, Fig. 12). This is in line with the electronic occupancy in the NO molecule \((0.433 \, \text{e}^{-}\)) and the N\(\rightarrow\text{O}\) bond stretching after the adsorption in the bridge mode \((1.197 \, \text{Å} \text{ against } 1.148 \, \text{Å})\).

The NBO results also show NO\(\rightarrow\text{Pd}\) electron flux, occurring via overlap between a \(2s_{\text{Pd}}\) orbital, centered on nitrogen, and the \(5 \, \text{s}\) orbital on the palladium atom. However, the energy gap between the orbitals for donation is much larger than for backdonation \((17.2 \, \text{eV} \text{ against } 2.7 \, \text{eV})\), indicating that the former is a less favored process. In addition, the calculation of the deletion energy (NBOdel, Table 2) indicates that NO anchoring in the bridge mode modifies only slightly the magnitude of the electron transfer in the Pd\(_4\)\(\rightarrow\gamma\)-alumina interface, with changes of only \(-0.1 \, \text{kcal mol}^{-1}\) for donation and \(-1.0 \, \text{kcal mol}^{-1}\) for backdonation. However, the presence of NO in this bridge mode increases by three times the interaction between the palladium atoms \((69.3 \, \text{kcal mol}^{-1} \text{ against } 209.2 \, \text{kcal mol}^{-1})\).

\begin{table}[h]
\begin{center}
\caption{Adsorption energy \((E_{\text{ad}})\) for NO molecule on Pd\(_4/\text{Al}_{13}\text{O}_{23}\text{H}_{7}\) and Pd\(_4/(\text{boat})\) aggregates, geometric parameters (bond distance \((d)\) and bond angle \((a)\)) and NBO charge \((q)\) on \(\gamma\)-alumina, Pd\(_4\), Pd atom bonded to NO and NO moieties.}
\begin{tabular}{cccccccc}
\hline
\textbf{Model} & \multicolumn{3}{c}{NO/Pd\(_4/(110D)\)} & \multicolumn{3}{c}{NO/Pd\(_4/(\text{boat})\)} \\
\hline
\textbf{Mode} & \textbf{Site} & \textbf{Ontop} & \textbf{Bridge} & \textbf{Ontop} & \textbf{Bridge} \\
\hline
\textbf{Ions} & O\(_{\text{di}}\) & O\(_{\text{tr}}\) & Al\(_{\text{o}}\) & O\(_{\text{di}}\) & O\(_{\text{tr}}\) & O\(_{\text{di}}\) & O\(_{\text{tr}}\) \\
\textbf{E\(_{\text{ad}}\)} (kcal mol\(^{-1}\)) & \(-23.09\) & \(-28.46\) & \(-14.74\) & \(-29.79\) & \(-26.86\) & \(-27.03\) & \(-31.07\) & \(-28.81\) \\
\textbf{dPd\(\rightarrow\text{N}\)} (Å) & \textbf{dN\(\rightarrow\text{O}\)} (Å) & \textbf{dPd\(\rightarrow\text{N}\)} (Å) & \textbf{dN\(\rightarrow\text{O}\)} (Å) & \textbf{dPd\(\rightarrow\text{N}\)} (Å) & \textbf{dN\(\rightarrow\text{O}\)} (Å) & \textbf{dPd\(\rightarrow\text{N}\)} (Å) & \textbf{dN\(\rightarrow\text{O}\)} (Å) \\
\textbf{0.1} & \textbf{1.163} & \textbf{1.163} & \textbf{1.161} & \textbf{1.197} & \textbf{1.160} & \textbf{1.160} & \textbf{1.153} & \textbf{1.206} \\
\textbf{0.2} & \textbf{133.41} & \textbf{134.48} & \textbf{138.30} & \textbf{137.81} & \textbf{133.20} & \textbf{132.89} \\
\textbf{q\(_{\text{Alumina}}\)} (e\(^{-}\)) & \textbf{q\(_{\text{Pd}_4\text{a}}\)} (e\(^{-}\)) & \textbf{q\(_{\text{Pd}_4\text{b}}\)} (e\(^{-}\)) & \textbf{q\(_{\text{Pd}_4\text{c}}\)} (e\(^{-}\)) & \textbf{q\(_{\text{Pd}_4\text{d}}\)} (e\(^{-}\)) & \textbf{q\(_{\text{Pd}_4\text{e}}\)} (e\(^{-}\)) & \textbf{q\(_{\text{Pd}}\)} (e\(^{-}\)) & \textbf{q\(_{\text{NO}}\)} (e\(^{-}\)) \\
\textbf{q\(_{\text{Alumina}}\)} (e\(^{-}\)) & \textbf{q\(_{\text{Pd}_4\text{a}}\)} (e\(^{-}\)) & \textbf{q\(_{\text{Pd}_4\text{b}}\)} (e\(^{-}\)) & \textbf{q\(_{\text{Pd}_4\text{c}}\)} (e\(^{-}\)) & \textbf{q\(_{\text{Pd}_4\text{d}}\)} (e\(^{-}\)) & \textbf{q\(_{\text{Pd}_4\text{e}}\)} (e\(^{-}\)) & \textbf{q\(_{\text{Pd}}\)} (e\(^{-}\)) & \textbf{q\(_{\text{NO}}\)} (e\(^{-}\)) \\
\hline
\textbf{1} & \textbf{–0.315} & \textbf{–0.262} & \textbf{–0.232} & \textbf{–0.239} & \textbf{+0.317} & \textbf{+0.283} & \textbf{+0.271} & \textbf{+0.609} & \textbf{–0.019} & \textbf{+0.018} & \textbf{–0.011} & \textbf{+0.467} \\
\textbf{1} & \textbf{+0.053} & \textbf{–0.077} & \textbf{–0.030} & \textbf{+0.238} & \textbf{+0.123} & \textbf{–0.157} & \textbf{–0.151} & \textbf{+0.086} & \textbf{+0.165} & \textbf{+0.167} & \textbf{+0.167} \\
\textbf{2} & \textbf{–0.002} & \textbf{–0.021} & \textbf{–0.039} & \textbf{–0.370} & \textbf{–0.019} & \textbf{–0.018} & \textbf{+0.011} & \textbf{–0.467} \\
\hline
\end{tabular}
\end{center}
\end{table}

\(a\)Palladium atom at the adsorption site (1, 2, or 3).

---

\footnote{This value is in the same order of magnitude as the HOMO \textendash\text{LUMO} gap for NO/Pd\(_n\) clusters \((n = 1 \text{–} 6)\) \((1.6 \text{–} 2.3 \, \text{eV})\) \cite{127}.}

---

\textbf{Fig. 11} Side views of NO/Pd\(_4/\text{Al}_{13}\text{O}_{23}\text{H}_{7}\) complexes.
NO adsorption on Pd₄

To better rationalize the influence of MSI on the NO adsorption process on the Pd₄/Al₁₃O₂₃H₇ complex, the γ-alumina moiety was removed, and the NO molecule was optimized on the bare boat Pd₄. A set of NO/Pd₄ aggregates was obtained, which is shown in Fig. S4. For all the calculated configurations, the doublet electronic state was found as the one of lowest energy (Table S10).

In the absence of the γ-alumina atoms a significant increase of 16.4 kcal mol⁻¹ in the adsorption energy was observed for NO anchored ontop on Pd(3) (from –14.7 to –31.1 kcal mol⁻¹, Table 3). For the other ontop sites, the changes are much lower: 3.8 kcal mol⁻¹ for Pd(1) (from –23.1 to –26.9 kcal mol⁻¹) and 1.5 kcal mol⁻¹ for Pd(2) (from –28.5 to –27.0 kcal mol⁻¹). The smallest change was observed for NO adsorbed in the bridge mode, Pd(1) – (2) – (3) (−33.4 kcal mol⁻¹), were observed only in the absence of γ-alumina (Fig. S4 and Table S12).

Small modifications were observed in the geometric parameters, with exception of the Pd–N distance, which undergoes a more pronounced shortening in two cases: in ontop (Pd(3)) of 0.139 Å (from 1.969 to 1.830 Å) and bridge mode (Pd(1) – Pd(2)) of 0.061 Å and 0.113 Å (from 2.030 to 1.969 Å and from 2.084 to 1.971 Å, Table 3).

The variation in the NO adsorption energy due to the MSI (ΔEₜₚₑₜRAL) was then fragmented into two effects: electronic (ΔEₑₑₜ) and geometric (ΔEₜₚₑₘ). The first one is caused by the modification in the electronic structure of the metal aggregates promoted by electron flux at the metal/support interface. The second one is due to the change in the geometry in which the molecule adsorbs.

The electronic effect is calculated by the difference between the NO adsorption energies in isolated boat Pd₄, with geometry fixed in the same arrangement of the supported system (Eₜₚₑₜ), and hollow mode, Pd(1) – (2) – (3) (−39.2 kcal mol⁻¹), and hollow mode, Pd(1) – (2) – (3) (−33.4 kcal mol⁻¹), were observed only in the absence of γ-alumina (Fig. S4 and Table S12).

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between the NO adsorption energy in isolated boat Pd₄, with relaxed geometry (E_{\text{ad(III)}}), and the term E_{\text{ad(II)}} (Eq. (14)). Finally, the total effect promoted by MSI (ΔE_{\text{total}}) is the sum of the electronic and geometric effects (Eq. (12)). These contributions are illustrated in Fig. 13.

The percentage of participation of the electronic and geometric effects in the NO adsorption energy on the Pd₄/Al₁₃O₂₃H₇ systems is shown in Fig. 14. The result indicates that these effects act in opposite directions at the sites where oxygen ions are involved (Pd(1), Pd(2), and Pd(1) − (2)). While the electronic contribution intensifies the adsorption energy, the geometric contribution weakens it. Because of this compensation, the total effect is small, in the range of 1.0–3.8 kcal mol⁻¹ (Table 5). The exception to this behavior occurs for the adsorption in the ontop mode on Pd(3), where the palladium atom is coordinated to an Al₀ ion. In this site, both contributions are of the same signal and similar magnitudes (ΔE_{\text{elec}} = −8.0 kcal mol⁻¹, 49%, and ΔE_{\text{geom}} = −8.4 kcal mol⁻¹, 51%), producing an expressive total weakening of 16.4 kcal mol⁻¹ in the NO adsorption energy.

The NBO charge distribution analysis reinforces that the adsorption in the ontop mode does not lead to a considerable electron density on the NO molecule, which is independent of the presence of the support. However, in the bridge mode, the negative charge produced on NO increases by 26% (from −0.370 to −0.467 ē, Table 3). The charge values calculated by the other models are shown in Table S13.

The NBO analysis also shows an increase of 40% in the total stabilization energy involved in the orbital overlapping in the

![Fig. 13 Illustration of the total (ΔE_{\text{total}}), electronic (ΔE_{\text{elec}}), and geometric (ΔE_{\text{geom}}) MSI effects involved in the adsorption of the NO molecule on Pd₄/Al₁₃O₂₃H₇](image)

![Fig. 14 Contribution, in percentage (%), of electronic and geometric MSI effects to the adsorption energy of the NO molecule on Pd₄/Al₁₃O₂₃H₇ complex: positive and negative values were adopted to illustrate the increasing and decreasing contributions of the adsorption energy, respectively](image)

| Mode | Ontop | Bridge |
|------|-------|--------|
| Ions | Oₐₙ | Oₓ | Alₓ | Oₐₙ−Oₓ |
| ΔE_{\text{total}} (kcal mol⁻¹) | −3.77 | +1.43 | −16.33 | +0.98 |
| ΔE_{\text{elec}} (kcal mol⁻¹) | +8.55 | +7.03 | −7.95 | +3.81 |
| ΔE_{\text{geom}} (kcal mol⁻¹) | −12.32 | −5.60 | −8.38 | −2.83 |

Pd → NO backdonation at the Pd(1) − (2) site, after removal of the γ-alumina moiety (from 37.0 to 52.0 kcal mol⁻¹, Table 4).
This result points to the same direction as the increase in the negative charge in NO adsorbed on this site. Additionally, the NBOdel calculation points to an increase of 2.7 times in the contribution of Pd–Pd interactions to the stability of the system without γ-alumina, after the NO adsorption in bridge mode (from 60.8 to 163.2 kcal mol\(^{-1}\), Table 2). This increase is similar to the observed in the presence of support, indicating that the effect of the NO adsorption on the MMI is independent of γ-alumina.

The distortion in the geometry of Pd\(_4\) from the planar to the boat arrangement modifies neither the preferential adsorption mode nor the charge of the NO molecule (Pd(1)−(3))=−0.190 e, Tables S12 and S14 and Fig. S4 and S6). However, it promotes a decrease of 10.8 kcal mol\(^{-1}\) in the adsorption energy (from −50.0 to −39.2 kcal mol\(^{-1}\)). For the other sites, the decrease is in the range of 21−31% (8.6−15.1 kcal mol\(^{-1}\)). When compared to adsorption in the tetrahedral arrangement, the adsorption energies for the boat form are higher (2.0−18.4 kcal mol\(^{-1}\)). Thus, in general, the intensity of NO adsorption on the boat form is intermediate between the planar and the tetrahedral arrangements. Such a result could be interesting for the catalysis, as a catalyst must interact with the adsorbate at intermediate intensity, neither so weakly that it cannot activate the species, nor so strongly that the catalytic sites are inactivated due to the molecule can't desorb (Sabatier's principle).

Finally, the results of this work reveal information which can contribute to the understanding of the nature of the interactions occurring at the metal support interface in Pd/γ-Al\(_2\)O\(_3\) system and, consequently, collaborate to the development of more efficient catalysts, a field that has been widely explored in the last decades [7–9, 13, 21, 23]. Through using the Pd\(_4\)/Al\(_{13}\)O\(_23\)H\(_7\) model, employing the DFT/NBO/LMOEDA methodology, it was possible to evaluate the behavior, individually as well as synergistically, of the EMSI and MMI effects at the Pd/γ-Al\(_2\)O\(_3\)(110D) interface, face to palladium nucleation and NO adsorption processes. Nevertheless, it is important to emphasize that this behavior and the magnitude of these effects will depend on the topology of surface of the support and the nature of the deposited metal [24, 27, 31, 33–35, 37, 40, 41]. Some changes in these effects in Pd\(_4\)/γ-Al\(_2\)O\(_3\) are verified when the (110D) and (110C) [30] surfaces are compared, being mainly in the arrangement adopted by the Pd\(_4\) cluster (boat versus butterfly, respectively) and the preferential adsorption mode for NO molecule (bridge versus ontop, respectively).

**Conclusions**

In this work, a detailed evaluation of the behavior of the MSI and MMI effects into two processes of great importance in controlling the catalyst performance — nucleation and molecular adsorption — was performed on a Pd\(_4\)/γ-Al\(_2\)O\(_3\)(110D) agglomerate. The deposition of planar Pd\(_4\) on the (110D) termination of an Al\(_{13}\)O\(_23\)H\(_7\) agglomerate results in a boat-shaped cluster with cohesion energy value intermediate to those of the planar and tetrahedral arrangements. Nevertheless, the presence of an electronic effect in the metal–oxide interface (EMSI) weakens the interactions among the palladium atoms (MMI), decreasing the cohesion energy in 25.5 kcal mol\(^{-1}\). This effect is governed by Pd\(_4\)→γ-Al\(_2\)O\(_3\) electron transfers, mainly via Pd–Al bonds, leading to charge redistribution in both palladium and oxide units. The redistribution generates positive centers on the palladium atoms bonded to oxygen anions. These palladium atoms act as acidic centers which are the preferential sites for the anchoring of an additional palladium atom as well as the NO molecule. In accordance with LMOEDA, the Pd–O bonds are mainly electrostatic in nature, whereas Pd–Al has a predominantly covalent character. The nucleation of a fifth palladium atom on Pd\(_4\)/Al\(_{13}\)O\(_23\)H\(_7\) produces a distorted square pyramidal arrangement for Pd\(_5\).

Therefore, the results suggest a role played by synergistic MSI/MMI effect on Pd\(_4\)/γ-Al\(_2\)O\(_3\)(110D) interface, a crucial issue to understand the behavior of heterogeneous catalysts, which has been widely discussed in literature. This effect favors very slightly the nucleation and, consequently, its influence on the sintering process (neglecting the influence of temperature) could be expected to be only moderate. However, on the NO anchoring, this effect depends on γ-Al\(_2\)O\(_3\)(110D) site: weakening the NO adsorption energy on Pd–Al sites and presenting little influence on Pd–O sites. In addition, it provides the NO adsorption mode that most favors the Pd→NO (4d\(_z^2\)→2π\(^*\)) backdonation (bridge) and, consequently, the elongation of the N–O bond length, benefiting the catalytic process.

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Data availability The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

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