

Molecular adsorption of NO on a Pd₄ cluster: A density functional theory (DFT) study

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Abstract. In this work, theoretically adsorption of N, O, NO, as well as the possible spontaneous dissociation of NO on the small cluster of Pd₄ is studied. We used the theory of density functional. The main purpose is to have a reference for further study of these processes in larger clusters. It was determined the fundamental state, transition states, energies of adsorption, Mulliken transfers charges and vibration frequencies of the adsorbed species. The three species are adsorbed on Pd₄ vertices but with the bond inclined, between two atoms (bridged) and between three atoms (in a hole). Other types of energy capture presented lower adsorption, such as adsorption of NO with its bond parallel to a Pd-Pd edge. The NO dissociation in Pd₄ must be activated. The values of energies, frequency ranges and adsorption distances relate to the number of Pd atoms involved in the interaction. This work reproduced on Pd sheets results obtained by much more expensive procedures.

Keywords: NO, nanocluster, Pd₄, adsorption, DFT.

Introduction

Pd catalysts are being widely used to perform many important reactions in chemistry, and their study has been increased in the last decades due to the current need to eliminate some contaminants coming from vehicle emissions such as CO, NO_x, SO_x, etc. This need has prompted a series of theoretical and experimental studies in order to determine possible decontamination mechanisms [1]. Especially for the adsorption and reduction of NO, various mechanisms have been proposed [2-6]. In spite of the broad interest in these phenomena, there are just a few theoretical studies concerning catalyzed reactions on Pd nanoparticles. In fact, there are theoretical studies using methods for the study of periodic solids or by classic simulations on the adsorption of NO on surfaces, which are, in general, planar and without defects. In catalysis, adsorption sites such as vertices, edges, holes and defects are, in many reactions, the most active.

On the other hand, the best catalysts are those that are highly dispersed which means that very small particles have to prevail in them. To perform chemical reactions between two or more species, such particles have to be larger than tetramers. In this work, as a first stage, the study of sites and adsorption states of O, N and NO on palladium tetrahedrons was carried out, which despite their reduced size are useful to characterize the adsorption processes concerning these species. The adsorp-

Resumen. En este trabajo se estudió teóricamente la adsorción de N, O, NO, así como la posible disociación espontánea de NO sobre el pequeño cúmulo de Pd₄. Se utilizó la teoría de funcionales de la densidad. El objetivo del trabajo es tener una referencia para estudios posteriores de estos procesos en cúmulos mayores. Se determinó el estado basal, estados de transición, energías de adsorción, transferencias de cargas de Mulliken y frecuencias de vibración de la especie adsorbida. Las tres especies se adsorben en vértices de Pd₄ pero con el enlace inclinado, entre dos átomos (en puente) y entre tres átomos (en un hueco). Otros tipos de captura presentan energía de adsorción menor, como la adsorción de NO con su enlace paralelo a una arista. Los resultados muestran que la disociación de NO en Pd₄ debe ser activada. Los valores de las energías, frecuencias y distancias de adsorción se relacionan con el número de átomos de Pd involucrados en la interacción. Este trabajo reproduce resultados obtenidos sobre láminas de Pd por procedimientos mucho más costosos.

tion on the cluster is described as a local phenomenon. In addition, the NO dissociation mainly occurs on Pd sites that show low coordination numbers [5]. In a further work the results coming from studies that are being performed on Pd₁₀ and Pd₁₃ will be presented.

The NO catalytic reduction by hydrocarbons, H₂ and CO on gold and on rhodium [7,9] supported on several metal oxides, such as MgO, Al₂O₃, Fe₂O₃ and others show a good catalytic performance. Burch *et al.* [10] presented a review of different mechanisms for the NO reduction on the platinum group metal catalysts. These processes require bigger metal clusters than the tetrahedrons used here, as was reported by Worz *et al.* [5] in the case of small Pd_n clusters. Other studies are presented in Ref. [12-15].

Method

In this work the procedure stated in reference [2] was followed: the calculations were performed by using the density functional theory [16]. The B3LYP hybrid functional was used [17] by means of the Gaussian03 package calculation system [18]. The atomic orbitals for Pd atoms are gaussian type LANL2DZ basis sets of double- ζ quality [19] whereas those for O and N atoms were 6-311G** basis sets. The Pd external electrons (4s, 4p and 4d) were subjected to the LANL2

potential [19] created by the nucleus and the internal electrons, which includes relativist effects, except spin-orbital effects. The convergence criterion between SCF cycles was set to 10^{-6} . For these small clusters, the consistency of the calculated spin projections is assured. The major spin contaminations are 0.82 and 2.04 for the expectation value of the S^2 operator in doublets and triplets, respectively. The vibration frequencies for the adsorbed species were calculated; and those with only one negative frequency were also taken into account; the latter is accepted as a transition state in the adsorption process.

Three different types of NO approaches were considered:

- i) To a vertex, either aligned with the Pd_4 center or leaned; in the NO case it was also approached with its bond either perpendicular or parallel to the C_s symmetry plane;
- ii) To a Pd-Pd bond, through the axis towards the Pd_4 center; and as for NO, with its bond either parallel or perpendicular to the Pd-Pd bond;
- iii) Centered in a hole, with NO parallel and perpendicular to the C_s axis. The initial Pd-Pd distance considered is 2.75 Å [20] which corresponds to the Pd crystal (111) plane, which is the nearest neighboring distance and the most active in catalysis because small particles are formed with faces from these planes [5]. The initial bond distance in the NO was 1.15 Å [21, 22]. The optimization processes started with the species already close to Pd_4 , but still not adsorbed, by looking for the positions and capture geometries. Both the cluster and NO were also optimized.

The adsorption energy is calculated by the traditional equation:

$$E_{\text{ads}} = (E_A + E_{\text{cluster}}) - E_{A\text{-cluster}}$$

In this equation, A can be substituted by O, N or NO; and $(E_A + E_{\text{cluster}})$ is the energy of the separate fragments.

Results and Discussion

The theoretical results obtained here are compared with observed values reported in literature [4-6, 11-15, 22-30].

A. NO, N, O and Pd_4

Table 1 show the calculated energies obtained in the separate fragments. It can be noticed that the S^2 proper value, of the ground states for each specie, reproduces accurately the results obtained by other authors: doublet for NO, quadruplet for the N atom triplet for the O atom; and triplet for Pd_4 [25]. The optimization of the NO bond distance showed an increment of about 4.3 %, depending on the system, whereas in the Pd cluster, the bond lengths are shortened up to 6.2%.

The Pd-Pd bond distances are reduced to 6.6%, during the adsorption with related to the bond distance in the Pd bulk sheet. The calculated dipolar moment of the NO molecule is small in the ground state this value is almost half the observed value (0.15 D), such an effect can be due to the charge method used here through which are calculated and as it is well known, to the size of the basis used here. In the Pd_4 cluster appears a small dipolar moment due to the rupture of the tetrahedron symmetry, which is a characteristic of the optimization method, when a very symmetric geometry is considered. That is the reason to get Pd-Pd bonds not all equals.

In Table 1 the extreme d values are included: in the ground state the major difference is 5.5 %. In the excited state is 6.2 %, thus, the deformation is not so big. As for NO, the calculated E_{bond} value is 152.5 kcal/mol, differing from the observed value in 1.6 %, this is an acceptable difference considering the experimental variations. For the NO vibration frequency, the difference between the calculated and observed value was smaller than 1%.

B. $\text{Pd}_4 + \text{N}$

In Table 2, the results for the N adsorption on Pd_4 are shown. Three adsorption sites were found: N leaned on a Pd ver-

Table 1. Pd_4 , NO, N and O single species results.

Calculated values of the relative energies (ΔE_T), spin scalar operator ($\langle S^2 \rangle$), bond distances (d), dipolar moments (μ), highest frequencies (ν) with their corresponding force constant (k_F) and relative energies (ΔE_T) for the lowest states for each species.

Species	State	ΔE_T kcal/mol	$\langle S^2 \rangle$	d Å	μ D	ν cm^{-1}	k_F mdyne/Å
NO	2π	0.00	0.7500	1.158	0.08	1994	34.8
NO	4π	102.42	3.7500	1.425	0.23	1065	9.9
Pd_4	$3A_1$	0.00	2.0003	2.60, 2.71	0.04	233	3.4
Pd_4	$1A_1$	16.52	0.0000	2.58, 2.83	0.00	234	3.4
N	$4S_{3/2}$	0.00	3.7500	—	—	—	—
N	$2S_{3/2}$	66.09	0.7500	—	—	—	—
O	$3P_2$	0.00	2.0000	—	—	—	—
O	$1P_2$	64.73	0.0000	—	—	—	—

NO experimental values: $E_{\text{bond}} = 150.1$ kcal/mol, $d = 1.151$ Å, $\mu = 0.15$ D [21], $\nu = 2011$ cm^{-1} [26]. d Pd-Pd (111) = 2.75 Å [20].

Table 2. Pd₄-N results (multiplicity = 4).

Adsorption energies (E_{ADS}), geometries, highest frequencies (ν) of the adsorbed N with its corresponding force constant (k_F), capture distance ($d_{\text{Pd-N}}$), Mulliken charge transfers and dipolar moments (μ).

Initial site <i>N</i>	Final site <i>N</i>	E_{ADS} kcal/mol	$N \nu$ cm ⁻¹	k_F mdyne/Å ⁻¹	$d_{\text{Pd-N}}$ Å	Charge Transfer (Δq)					$I\mu I$ D
						Pd ₁ a.u.	Pd ₂ a.u.	Pd ₃ a.u.	Pd ₄ a.u.	<i>N</i> a.u.	
on Pd and vertical	on Pd and vertical	—	2n < 0	—	—	—	—	—	—	—	—
on Pd and tilted	on Pd and tilted	-25.79	708.3	4.7	1.79	0.04	0.04	0.04	0.14	-0.26	2.56
on hole	on hole	-70.93	514.9	2.5	2.02	0.14	0.14	0.14	0.05	-0.47	1.42
on bridge	on bridge	-69.98	549.4	2.8	1.88	0.19	0.01	0.01	0.19	-0.40	2.70

tex, with respect to the central axis, N captured on bridge between two Pd atoms, and on a hollow interacting with three Pd atoms. The stability of the capture increases in the same order. The ground state is a quadruplet. The frequency presented in this table is the calculated value for the highest Force Constant, which corresponds to the adsorbed N vibration energy. Our calculated adsorption energies represent, all of them, exothermic processes, whereas the Hammer's results [6] represent endothermic processes, but this author does not report the spin values of his calculated systems and their adsorptions are calculated on stepped surfaces; the capture sites are similar with his results. On a Pd atom the N adsorbed is tilted.

As for the charge transfer (Δq), from the results it can be seen that when the N atom interacts directly with many Pd atoms, the charge transference towards the N atom increases as it can be seen in the adsorption of the N atom in a hole, where each of the three Pd atoms forming the hole transfer the same charge quantity. It can also be noticed that as Δq increases, the bond length between Pd and N increases. When the N atom presents a symmetric interaction with a Pd₄ vertex, it is not adsorbed due to the fact that there is not enough charge transfer; but if the N atom is bent with respect to the principal axis, a higher overlapped orbital is obtained which increases the charge transfer.

As was indicated, the deepest well occurs when the N atom interacts with three Pd atoms (a hollow). The capture of N on bridge, with two Pd atoms, presents a minor energy depth well of 5.1 kcal/mol. In this case the total charge transfer is smaller than in a hollow capture. On the other hand, the dipolar moment, as a trend, shows an inverse relationship with the charge transfer.

Thus, the Pd-N bond formation, the geometry of the Pd-N and the value of the adsorption energy depend on the charge transfer value towards the Pd atoms directly interacting with the N atom.

C. Pd₄ + O

Table 3 shows the interaction results between the metallic cluster and the O atom. The ground state of the Pd₄-O is a triplet.

The O atom can be adsorbed on vertices, holes or edges (on a bridge). As was also obtained for the N atom, the adsorption of this atom on a bridge prevents further reaction with other systems. Comparing with Hammer's [6] results the adsorption sites are newly similar, but his adsorption energies are much minor.

From the calculations, it is also observed that when the number of Pd atoms in contact with O increases, the vibration frequency and the dipolar moment of the O diminish, on the other hand, the adsorption energy, capture distance and charge received by oxygen tend to increase. According to the aforementioned results, the characteristics of the different interactions of O with Pd₄, i.e. its adsorption on Pd₄ is similar to the N adsorption on Pd₄.

D. Pd₄ + NO

The results of this section are compared with works presented in references [22, 26-30]

In the Pd₄ cluster, the NO molecule is adsorbed by the N side. If the approach starts by the O side, in general, the NO molecule turn during the geometric optimization or various negative frequencies appear in the system vibrations.

In Table 4, some of the performed approaches are shown. The system multiplicity is not such exact as was for the adsorbed N and O atoms, it varies 5 % as a maximum, but this problem is a characteristic of the method employed. The adsorption sites (holes, edges and vertices) in the metallic cluster are shown in Figure 1.

There is an observed result which is reproduced in very small Pd clusters: Pd clusters up to 4 atoms, with NO coadsorbed with CO [5], do not dissociate the NO molecule under normal conditions. Moreover, it has been reported that the NO adsorption on Pd is only dissociative if a reducing agent is present [14]. In order to succeed in the NO rupture, this molecule has to be approached in a perpendicular position towards an edge and with the bond already relaxed; the minimum of this relaxed bond was 1.50 Å. In this case the optimization of the geometry does not lead to the restitution of the bond length, but to its rupture. In Table 4, it can be seen the need to surpass a potential energy barrier otherwise the NO bond is not activated.

Table 3. Pd₄-O results (multiplicity = 3).

*N adsorption energies (E_{ADS}), cluster geometries, highest frequencies (ν) of the adsorbed N with its corresponding force constant (k_F), average capture distance ($d_{\text{Pd-N}}$), Mulliken charge transfers and dipolar moments (μ).

Initial Site O	Final Site O	E_{ADS} kcal/mol	O ν cm ⁻¹	k_F mdyne/Å ⁻¹	$d_{\text{Pd-O}}$ Å	Charge Transfers (Δq)					
						Pd ₁ a.u.	Pd ₂ a.u.	Pd ₃ a.u.	Pd ₄ a.u.	O a.u.	$I\mu I$ D
on a vertex	almost tilted	-57.21	828.6	7.5	1.81	0.04	0.08	0.08	0.20	-0.40	3.64
tilted	tilted	-58.35	581.9	3.6	2.01	0.08	0.08	0.08	0.12	-0.36	3.50
on a hole	on a hole	-87.98	446.9	2.2	2.02	0.19	0.19	0.19	-0.01	-0.56	1.53
on bridge	on bridge	-82.90	552.3	3.3	1.93	0.22	0.05	0.05	0.22	-0.54	3.15

*The same symbols are used as in Table 2.

Table 4. Pd₄-NO results (close to 2 spin multiplicity).

*O adsorption energies (E_{ADS}), cluster geometries, highest frequencies (ν) of the adsorbed O with its corresponding force constant (k_F), average capture distance ($d_{\text{Pd-N}}$), Mulliken charge transfers and dipolar moments (μ).

N ^o	Initial Site NO	Final Site NO	E_{ADS} kcal/mol	NO ν cm ⁻¹	k_F mdyne/Å ⁻¹	$d_{\text{N-O}}$ Å	$d_{\text{Pd-N}}$ Å
1	Vertical on Pd	Vertical on Pd	—	$\nu < 0$	—	—	—
2	N-O on Pd \perp to C _s	on Pd and tilted	-35.57	1751	29.6	1.19	1.98
3	**N-O on Pd, \parallel C _s	on Pd and tilted	-47.44	1842	30.0	1.20	1.84
4 [#]	N-O \perp to Pd-Pd	N & O on holes	-6.63	—	—	2.95 ¹	1.96
5	N-O \perp to Pd-Pd	N on bridge Pd-Pd	-53.72	1590	21.2	1.19	2.01
6	**N-O \parallel Pd-Pd	N-O \parallel Pd-Pd	-18.63	1375	17.0	1.20	1.85
7	N on bridge Pd-Pd	N \perp on bridge Pd-Pd	-56.25	1591	22.4	1.19	2.02
8	N on bridge Pd-Pd	on Pd and tilted	-47.48	1792	19.5	1.19	2.01
9	N-O \perp to a hole	N-O to a hole	-30.79	1317	15.1	1.18	2.05
10	N-O \parallel to a hole \parallel a C _s	on Pd and tilted	-40.85	1500	19.5	1.20	2.03
11	N-O \parallel to a hole \perp C _s	N-O \perp to a hole	-46.37	1401	19.1	1.20	2.01
12	NO \perp to Pd-Pd and \parallel z axis	N on a hole, O on bridge	+16.34	—	—	2.54	1.96

*The same symbols of Table 2 are used and besides: "C_s" = reflection plane in Pd₄, " \perp " = perpendicular, " \parallel " = parallel Experimental Values: ν values of NO (ads) in Pd_n/MgO: ~1720 cm⁻¹ if NO is on an atom, ~1620 cm⁻¹ if it is on bridge, and minor values in holes, ~1580 [4].

**First Negative Frequency, Transition State.

[#]NO is perturbed, with an Initial Bond Distance of 1.50 Å

The results obtained for a Pd₄ cluster adsorption of NO keep the same tendencies and similarities to the ones obtained for N and O single atoms respectively: when the adsorption energy increases, the vibration frequency diminishes, in this case, the NO bond frequency. The NO capture distances for the different sites are similar. The charge transfers (Table 5) are not so clearly related with the adsorption energy, as it occurs in the atoms.

The NO adsorption with N bridged on a Pd-Pd bond is the most stable; it is so stable that it can prevent further reaction of NO with other species. Hammer [6] found that adsorptions on the Pd-edge and Pd-step sites are favored over other adsorption sites. The low coordination of the aforementioned configurations (step and edge) in the Pd crystals explains the high reactivity of these sites. The NO bond is tilted to a principal

symmetry axis or to an edge normal axis, when is adsorbed on top or on bridge sites respectively. The aforementioned configuration has also been proposed by other authors but in bigger Pd clusters or on flat Pd surfaces.

The reaction number 4 of Table 4 presents a very small E_{ADS} because most of the work to relax the bond was done before approaching the NO molecule to the cluster and thus it is activated towards an edge. The optimized adsorption leads to the NO bond expansion from 1.15 Å to 1.20 Å. This effect occurs even in the absence of the cluster (Table 1); and it is a result that can be attributed to the method used. The capture distance slightly changes according to the adsorption site but it is maintained around 2.00 Å. In general, as it was expected, this distance is reduced as the adsorption energy increases.

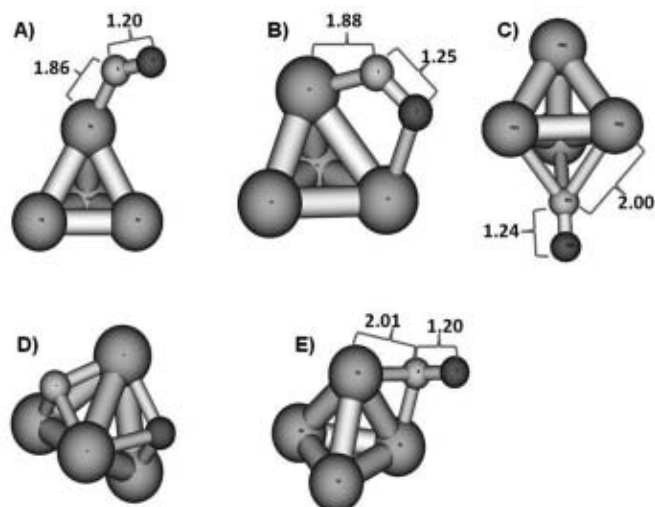


Fig. 1. Final NO adsorption sites on Pd₄. Average bond distances in Å.

As it is expected, the position and the allocation of the vibration bands of adsorbed NO on Pd surfaces depend on the temperature and pressure because their changes modify the NO coverage. So in the literature there is controversy with respect of its assignment [26]. Højrup *et al.* [29] in a Scanning Tunneling Microscopy (STM) study and DFT calculations found that with coverage of 1/6 of monolayer (ML), the calculated adsorption energy (E_{ADS}) in hollows was 41.5 kcal/mol and on bridge sites was 33.4 kcal/mol. By increasing the coverage to 1/2 ML the E_{ADS} diminishes to 32.3 and 30.4 kcal/mol, respectively, in the $c(4 \times 2)$ structure or still more in the $p(2 \times 2)$ structure, where the tilted-atop sites appear. So, in all the cases the NO adsorption in hollows is

the most stable configuration for these authors. Hammer's [6] and our results are different, for he and us, the more stable configuration is the adsorption on a bridge site. By using Infrared Reflected Absorption Spectroscopy (IRAS) and DFT calculations, Ozensoy *et al.* [27] observe that the wave number increases with the NO pressure and the lowering of temperature. At 550 K and 1×10^{-6} mbar, the frequency is 1525 cm^{-1} . At 250 K, two bands are measured, one at 1592 cm^{-1} and other at 1736 cm^{-1} , being the second more intense. At 150 K the positions are 1549 and 1755 cm^{-1} respectively. The vibrational bands at 1593 and 1742 cm^{-1} were assigned to NO adsorption on three-fold hollow and atop sites respectively. Similar results are obtained by Pérez Jigato *et al.* [26]. Besides P. Granger *et al.* [28] reports that in situ infrared spectra of the CO + NO reaction present frequencies of 1770 and 1790 cm^{-1} for different adsorption sites. Loffreda *et al.* present similar vibrational frequencies and NO adsorption sites assignment [30].

According to other studies on the (111) surface, the NO adsorption on holes shows the deepest well energy, either with low or high coverages [7], but if the coating is very low, the on bridge site is the most stable. In Figure 1, the three most frequent NO adsorption sites in Pd₄ (A, C and E) as well as the not very frequent site (B) and the NO activated rupture (D), are shown.

The (A) geometry is obtained in the approaches numbered 2, 3, 8 y 10 in the aforementioned table. The (C) geometry is obtained in the approaches 9 and 11. In case 11, the approach started with NO parallel to the hole; after the optimization, it turned and ended up perpendicular to the whole plane. The (E) configuration, bridged, corresponds to the final geometry in the various approach modes; in fact, it is the only one that is formed and obtained if the initial distance is 6 Å or higher. In this case, the N atom is bridged between two Pd atoms and

Table 5. Pd₄ - NO charge transfers. Mulliken charge transfers and dipolar moments.

N°	Final Site NO	Charge Transfers (Δq)						
		Pd ₁ a.u.	Pd ₂ a.u.	Pd ₃ a.u.	Pd ₄ a.u.	N a.u.	O a.u.	μ I D
1	Vertical on Pd	—	—	—	—	—	—	—
2	on Pd and tilted	0.04	0.03	0.04	0.00	-0.01	-0.10	1.89
3**	on Pd and tilted	0.03	0.02	0.02	-0.01	0.07	-0.13	0.33
4	N & O on holes	0.30	0.16	0.15	0.27	-0.40	-0.48	2.56
5	N on bridge Pd-Pd	0.12	-0.01	0.00	0.12	-0.08	-0.15	0.72
6**	NO bond II Pd-Pd	0.07	0.00	0.00	0.09	0.00	-0.16	1.01
7	N on bridge Pd-Pd	0.11	0.01	0.01	0.11	-0.08	-0.16	1.95
8	on Pd and tilted	0.01	0.00	0.02	0.02	0.07	-0.12	0.27
9	⊥ to a hole	0.02	0.02	0.02	-0.01	-0.02	-0.03	2.04
10	on Pd and tilted	0.05	0.00	0.04	0.03	-0.02	-0.10	1.94
11	⊥ to a hole	0.03	0.03	0.02	-0.02	0.02	-0.08	2.54
12	N on a hole, O on bridge	0.05	0.40	0.40	0.16	-0.48	-0.48	4.01

**First Negative Frequency, Transition State.

the O atom is bent, where the N-O bond form an angle with respect to the Pd bond (cases 5 and 7 in Table 4). The (B) configuration is only obtained if, at the starting point, the NO bond is parallel to an edge which corresponds to a transition state (case 6, Table 4). The (D) configuration represents the rupture of the NO bond which is not possible to be obtained by the optimized initial bond distance present in the other cases (1.16 Å as it can be seen in Table 1). As was mentioned before it was only obtained activating the bond.

It can be observed in the charge transfers, as in the previous cases, that Δq is correlated with the number of Pd atoms directly associated with the NO molecule during the interaction; it can be observed that when the NO dissociation occurs, the charge transfer is very big.

Conclusions

From our results and after very careful studies of the different N, O, NO interactions with the many Pd₄ cluster adsorption sites, it was shown that the adsorption of these species on very small metallic clusters provides useful information to determine and characterize both the sites and reaction modes without the need to use bigger clusters, which are more difficult to be theoretically studied. In addition, the results of adsorption calculations with clusters gave more alike results with stepped surfaces calculation from literature than with flat ones, because the steps present Pd atoms with a lower coordination. The need of a reducing agent was found for our small cluster. Without such agent, neither activation nor dissociation of the NO molecule is possible. In the work was reproduced the bending or inclination of the NO molecule related to the main axes of the cluster when the adsorption occurs on a Pd atom or on a Pd-Pd bond. The adsorption of O and N atoms on Pd₄ cluster sites result to be selective due to the fact that it depends on the number of atoms that interact directly with them. This dependence limits not only the charge transfer but also the adsorption energy amount.

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