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Lacaze-Dufaure, Corinne and Roques, Jérôme and Mijoule, Claude and Sicilia, E. and Russo, N. and Alexiev, V. and Mineva, T. *A DFT study of the NO adsorption on Pdn (n = 1–4) clusters.* (2011) Journal of Molecular Catalysis A: Chemical, vol. 341 (n° 1 - 2). pp. 28-34. ISSN 1381-1169

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A DFT study of the NO adsorption on Pd$_n$ ($n = 1$–4) clusters

C. Lacaze-Dufaure [a,*], J. Roques [b], C. Mijoule [a], E. Sicilia [c], N. Russo [c], V. Alexiev [d], T. Mineva [d,e]

[a] *Centre Interuniversitaire de Recherche et d'Ingénierie des MATériaux, Institut National Polytechnique de Toulouse, 4 allée Emile Monso, BP 44362, 31030 Toulouse Cedex 4, France*
[b] *Institut de Physique Nucléaire, Université Paris-Sud 11, 15 rue Georges Clemenceau, Bat 100, 91406 Orsay Cedex, France*
[c] *Dipartimento di Chimica and Centro di Calcolo ad Alte Prestazioni per Elaborazioni Parallele e Distribuite, Universita' della Calabria, I-87030 Arcavacata di Rende (CS), Italy*
[d] *Institute of Catalysis, BAS, G. Bonchev Str. 11, 1113 Sofia, Bulgaria*
[e] *Institut Gerhardt, Ecole de Chimie de Montpellier, UMR 5253 CNRS, 8 rue de l'Ecole Normale, 34296 Montpellier, Cedex 5, France*

ABSTRACT

We report a density-functional study of some properties of the adsorption process of the NO molecule on small palladium clusters ($n = 1$–4). The interaction between NO and the Pd$_n$ clusters is studied on various adsorption sites. Both, NO and Pd$_n$ geometrical relaxations are taken into account. The significant conformational reconstruction of the metallic cluster upon NO adsorption induces a large decrease of the NO adsorption energy. Nevertheless, the N–O binding energy is strongly weakened when the molecule is adsorbed on the small Pd$_n$ clusters due essentially to an electrostatic repulsion between both N and O atoms. The possible dissociation process of NO on Pd$_4$ cluster is then investigated within two processes: the NO molecule does not dissociate on Pd$_4$ with process (i) (dissociation of the isolated gas phase NO molecule followed by the adsorption of both nitrogen and oxygen atoms on the cluster). Process (ii) which presents three successive steps (adsorption of the NO molecule, dissociation of the NO molecule adsorbed on Pd$_4$, adsorption of the O atom on the cluster) is studied in details and we propose a reaction pathway locating transition states and intermediate species. The activation energy for process (ii) is high and the dissociation of the NO molecule on the Pd$_4$ cluster is thus highly improbable.

1. Introduction

The reduction of NO by CO on palladium is of practical interest because it is one of the reactions taking place in a three-way car exhaust catalyst. To understand the reaction process, it is necessary to study the interactions between the reactive molecules and the particles of catalyst and the first step in any heterogeneous catalytic reaction is the adsorption of the reactants. We thus studied the NO adsorption on small palladium clusters in the framework of the density functional theory (DFT). This method is based on the determination of the electronic density and is able to predict numerous properties related with the reactivity of such systems.

Early theoretical works dealing with NO adsorption on palladium were reviewed by Whitten and Yang [1]. These early computations were followed by DFT calculations for the adsorption of NO on a Pd atom, a Pd$_2$ cluster and a PdO system to examine the activity of metallic and oxidized metals in NO adsorption [2–4]. These studies showed that for the Pd$_2$ system, the bridge site is the more stable adsorption site. Finite cluster-model calculations were also made with frozen Pd$_n$ ($n = 4, 5, 8, 25$) clusters to model NO adsorption on the Pd(1 1 0) surface [3,4]. Jigato et al. pointed out

that the adsorption energy for NO on the eight-atoms cluster at the bridged site (1.66–1.92 eV) is higher than at the hollow (0.71 eV) and top (0.11–0.40 eV) sites [3]. Matsubara and co-workers found tilted structures for NO adsorbed on the fourfold site of the Pd$_5$ cluster [4]. Frozen Pd$_n$ ($n = 10, 13, 18$) clusters were also used to simulate the Pd(1 1 1) surface [5,6]. These studies show that the charge transfer is an electron donation–backdonation process between the metallic cluster and the adsorbate. The same results were found for the NO adsorption on Ni(1 1 1) [7].

The interaction of NO with small Pd$_n$ clusters was also studied taking into account the full geometry optimization of the NO–Pd$_n$ systems. For the adsorption of NO on Pd$_4$ (Td), Endou et al. calculated an adsorption energy of 2.32 eV for the adsorption of NO on-top of one Pd atom. The adsorption energy of NO on the threefold site of the Pd$_4$ cluster was only 0.73 eV. For the two adsorption sites, the NO molecule has a bent geometry on the Pd$_4$ cluster [8]. A detailed investigation of the interaction of NO molecules with small Pd$_n$ clusters by Grybos et al. confirmed that adsorption is strong, with a binding energy ranging from 2 to 3 eV [9]. The authors described that the adsorption of NO on palladium clusters leads to large changes in geometry around the adsorption site because of the overlap of the Pd d-orbitals with the π* orbital of NO.

The interaction of NO with copper, silver and iron clusters is also reported in the literature [10–12]. It was shown that interaction of NO with copper and silver tetramers leads to an adsorption energy

* Corresponding author. Tel.: +33 5 34323412; fax: +33 5 34323498/99.
E-mail address: corinne.dufaure@ensiacet.fr (C. Lacaze-Dufaure).

Table 1

Most stable adsorption geometries for the adsorption of NO on Pd_n clusters (doublet state for the Pd_nNO systems) at the B3LYP level. Distances (d) are in Å, NO stretching frequencies (ν) in cm^{-1}, Mulliken and NBO net charges (q) in a.u. and binding energies E_b in eV.

System	Adsorpt. site	d_{NO}	d_{PdN}	ν_{NO}	$q_{N \text{ Mulliken (NBO)}}$	$q_{O \text{ Mulliken (NBO)}}$	Dipole moment (NBO)	E_b
Free NO								
Calc.	/	1.158	/	1991	0.11	−0.11	0.09	/
Exp[a]		1.150		1904			0.16	
PdNO Top	Top	1.175	1.920	1812	0.03	−0.13		1.30
Relaxed								
Pd_2NO relaxed	Top	1.165	1.853	1843	0.06	−0.12	0.50	1.34
	Bridge	1.201	1.990	1635	−0.08	−0.18	1.86	1.90
Others works	Bridge[b]	1.202	1.977					2.41
	Top[c]	1.164	1.781	1940				2.21
	Bridge[c]	1.199	1.876	1688				2.65
	Top[d]	1.18	1.87	1786				2.63
	Bridge[d]	1.21	1.95	1549				3.07
Pd_3NO	Top	1.163	1.850	1847	0.06	−0.10	0.10	1.47
Relaxed	Bridge	1.208	1.960	1572	−0.10	−0.17	1.09	1.65
	Threefold	1.215	2.007; 2.007; 2.023	1558	−0.21	−0.22	2.49	1.70
Others works	Top[d]	1.18	1.83	1764				2.44
	Bridge[d]	1.21	1.94	1570				2.52
	Threefold[d]	1.22	1.98/1.98/2.01	1475				2.49
Pd_4NO	Top	1.165	1.838	1846	0.07 (0..10)	−0.12 (−0.17)	0.27	1.36
Relaxed								
	Bridge	1.199	2.007	1604	−0.08 (−0.03)	−0.15 (−0.26)	0.72	1.32
Others works								
	Threefold	1.216	1.994; 1.994; 2.074	1508	−0.18 (−0.18)	−0.22 (−0.28)	0.84	0.95
	Top[d]	1.18	1.82					2.53
	Bridge[d]	1.23	2.00					2.50
	Threefold[d]	1.22	1.99/1.99/2.00					2.04
	Top[e]	1.149						2.32
	Bridge[e]	1.193						2.04
	Threefold[e]	1.200						0.73

[a] Ref. [47].
[b] Ref. [4].
[c] Ref. [2].
[d] Ref. [9].
[e] Ref. [8].

of 0.40–0.89 eV (bridge and top sites on Ag_4) and 0.90–1.50 eV (bridge and top sites on Cu_4) and an increase in the NO bond length [10]. Zhou et al. presented a systematic study of the interaction of NO with Ag_n clusters ($n = 1$–7) and pointed out that the NO bond is weakened and that there is an electronic transfer from the cluster to the NO molecule [11]. Gutsev et al. investigated dissociative and associative attachment of NO to Fe_n ($n = 1$–6) clusters [12].

The chemisorption of diatomic molecules on small Pd_n clusters was also the subject of many studies. In their study of the CO and CN^- adsorption on a Pd_{10} cluster, Ample et al. concluded that the CO bond is weakened whereas the CN^- one is strengthened upon chemisorption [13]. The CO chemisorption was also particularly investigated by Bertin et al. and Schultz et al. [14,15] that showed that the predominant bonding mechanism is a charge transfer.

The interaction of the NO molecule with palladium surfaces was also investigated by DFT periodic calculations. For instance, Sautet et al. studied the reactivity of the Pd(1 1 1) and Pd (1 0 0) surfaces with NO [16–18]. At low coverage, the threefold fcc and hcp hollow sites are the most stable with a binding energy of 2.0 eV on Pd(1 1 1) while the bridge site is favoured on Pd(1 0 0) with a binding energy of 1.54 eV. The binding energies decrease with the coverage and the NO dissociation is found to be endothermic on palladium. Gajdos et al. also demonstrated that the threefold sites are the most stable adsorption sites on Pd(1 1 1) but they showed that NO dissociates on Pd(1 1 1) [19,20]. Hammer found that MgO(1 0 0) supported Pd monolayer films are more reactive in regard to NO adsorption than thicker ones or pure palladium [21,22]. The adsorption of NO at high coverage was examined experimentally and theoretically by Stensgaard et al. who identified various adsorption structures with a tilted geometry for the NO molecule [23,24]. During the adsorption process, the work function of the metal is increased as a conse-

quence of the electronic transfer from the metal to the NO molecule. Jelic et al. performed DFT calculations combined with a thermodynamic approach to investigate the composition and structure of Pd(1 0 0) and Pd(1 1 1) surfaces for NO oxidation over a wide range of temperatures and pressures [25]. Vines et al. present results of a combined experimental and theoretical study on the adsorption of NO on Pd nanoparticles modelled by unsupported cuboctahedral Pd_n clusters cut from Pd bulk and containing up to 140 atoms [26]; the adsorption of the NO molecules is favoured on the hollow sites on the (1 1 1) facets of Pd_n clusters, closely followed by the NO adsorption on the bridge sites at the edges between adjacent (1 1 1) facets.

In this paper, we present a study of the interaction between small palladium clusters (Pd_n: $n = 1$–4) and the NO molecule. The study of the adsorption process is followed by a study of the possible dissociation process of NO on Pd_n clusters that to our knowledge is not available in the literature. The electronic properties of various adsorption sites of NO on Pd_n are first studied, including adsorption energies, electron transfer process and full geometrical relaxations. Secondly, the adsorption energies of the O and N atoms on Pd_4 are determined taking into account the structural relaxation of the systems. Two cases are considered: a separate adsorption of each atom or a simultaneous co-adsorption of both atoms allowing describing the nature of the N/O electronic interaction. Finally, the possible dissociation process of NO on Pd_4 is discussed.

2. Computational methods

The calculations were performed in the framework of the density functional theory using the GAUSSIAN03 packages [27]. In this

Table 2
Most stable adsorption geometries for the adsorption of NO on Pd_4 clusters at the B3LYP level. Distances (d) are in Å, NO stretching frequencies (ν) in cm^{-1}, Mulliken net charges (q) in a.u. and binding energies binding energies E_b in eV.

Systems	Pd_4NO^a Pd$_4$ frozen	Pd_4NO^b Pd$_4$ relaxed
Site	Threefold	Threefold
Multiplicity	2	2
Geometry	Bent	Bent
d_{N-O}	1.209	1.216
d_{Pd-N}	2.014	1.994; 1.994; 2.074
ν_{NO}	1546	1509
q_N	−0.16	−0.18
q_O	−0.22	−0.22
E_b	1.91	0.95

[a] Partial relaxation: the Pd$_4$ cluster is frozen and the NO molecule is allowed to relax.
[b] Fully relaxed Pd$_4$NO system.

study, the exchange part of the functional was treated with the Becke's three parameters functional (B3) [28] while the correlation part was described by the Lee, Yang and Parr (LYP) functional [29]. The so-called B3LYP functional has proved to be suitable to describe such kind of systems [30–34]. Los Alamos National Laboratory effective core potentials as well as a DZ atomic basis set were used for Pd taking into account explicitly 18 electrons [35–37]. The N and O atoms were treated with the 6-31G* basis set.

Spin polarized calculations were performed and the results presented here concern the systems in their more stable spin states. The spin multiplicity of the systems is given in Tables 1–4. The bare Pd_n clusters were allowed to relax (Fig. 1). For the optimization of the geometry, we stated the convergence setup for forces on atoms and for calculated displacement between two steps at cutoff values of 0.00045 a.u. and of 0.0018 a.u. respectively.

The NO molecule was initially adsorbed on the on-top, twofold bridge or threefold sites of the Pd_n ($n=1–4$) clusters (see Fig. 2). The NO–Pd_n systems were therefore allowed to relax without constrain. The geometry optimization was followed by a vibrational analysis in order to characterize the stationary points. Finally, in order to evaluate the charge transfer arising between the cluster and the chemisorbed NO molecule, a charge analysis was done by two different approaches: the classical Mulliken net charge analysis (all studied systems) and the Natural Bond Orbital (NBO) method (Pd_4NO).

The chemisorption of the NO molecule on the threefold site of a frozen Pd$_4$ cluster is also reported in order to determine the influence of the cluster relaxation on the NO adsorption process.

For all the considered systems, the binding energy $E_b(X/Y)$ between a X and a Y species is calculated as the difference between the absolute energy of the XY system and the sum of the energies of the isolated X and Y species: $E_b(X/Y) = E(X) + E(Y) + E(X/Y)$.

Table 3
Characteristics of the N–O bond in the free NO molecule or in the Pd$_4$-adsorbed NO molecule. Distances (d) are in Å, NO stretching frequencies (ν) in cm^{-1}, Mulliken net charges in a.u. and the dissociation energies E_{dis} in eV.

System	E_{dis}	d_{NO}	ν_{NO}	q_N	q_O
NO gas phase	6.61	1.158	1991	0.11	−0.11
NO adsorbed on Pd$_4$	4.84[a]	1.165	1846	0.07	−0.12
	4.43[b]	1.216	1508	−0.18	−0.22
	6.24[c]	1.165	1846	0.07	−0.12

[a] NO on top site, N on threefold site.
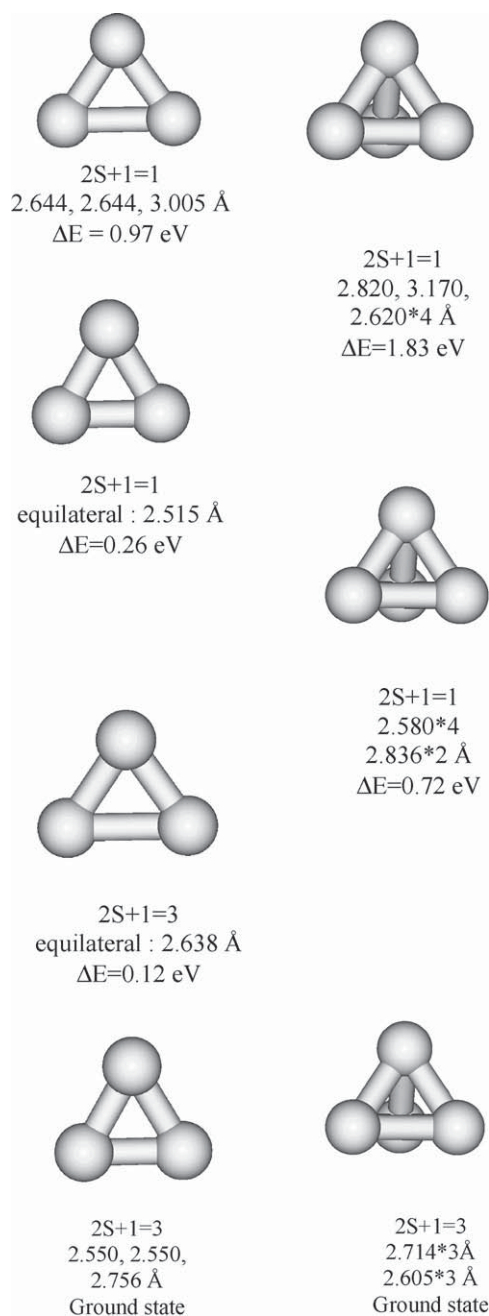[b] NO and N on threefold sites.
[c] NO and N on top sites.

Fig. 1. Stable structures for the Pd_n ($n=3$ and 4) clusters (B3LYP/LanL2DZ level). The spin multiplicity and the bond length are also indicated. ΔE represents the energy of the cluster relatively to the ground state.

3. Results and discussion

3.1. Structure of Pd_n clusters

We present and discuss in this section the energetic, geometrical and electronic properties of relaxed Pd_n ($n=1–4$) clusters. We first study the multidimensional potential energy surface of the bare palladium clusters. We performed spin polarized computations on the electronic ground state and the spin multiplicity of the systems is given in Fig. 1. All the clusters were fully optimized. Atomization energies are calculated. The stable structures of the Pd$_3$ and Pd$_4$ clusters are displayed in Fig. 1. For the Pd atom, the calculated energy difference between the $^1S(d^{10})$ ground state and the $^3D(s^1d^9)$ state of the palladium single atom is esti-

X	Adsorpt. site on Pd_4	Multiplicity	d_{PdX}	q_N	q_O	$E_b(X)$
N	Threefold	2	1.914; 1.925; 1.925	−0.52	/	3.13
O	Threefold	3	2.011; 2.011; 2.011	/	−0.57	3.23
N et O[a]	N threefold	2	1.913; 1.941; 1.958	−0.52	−0.54	5.94
	O threefold		1.948; 2.114; 2.211			
NO	Top	2	1.994; 1.994; 2.074	0.07	−0.12	1.36

[a] Coadsorption of N and O atoms are adsorbed on different facets of the tetragonal cluster.

mated to a mean value of 0.87 eV corresponding to a mixing of the J = 1, 2, 3 atomic eigenstates; the corresponding experimental value is 0.82 eV [38]. The inter-atomic Pd–Pd bond length in Pd_2 ground state (triplet state) is 2.526 Å with a dissociation energy of 0.96 eV (experimental value: 0.73–1.13 eV). The corresponding singlet state is less stable of 0.34 eV and has an inter-atomic distance of 2.762 Å. The triangular structure of Pd_3 was fully optimized without any symmetry constrain. The most stable state has a spin multiplicity of 3 and corresponds to a distorted triangular conformation. In this state, the atomization energy is 2.56 eV. Concerning the Pd_4 cluster, the full geometry optimization starting from a regular tetrahedral structure leads to a C_{2v} tetrahedral geometry in agreement with previous results [30–34,39–43]. Bond lengths are considerably contracted compared with the nearest neighbour distance in fcc massive palladium of 2.75 Å. The atomization energy for the ground state (triplet state) is 5.0 eV. The lowest excited state is a singlet distorted tetrahedron, which lays 0.72 eV higher in energy than the ground state.

3.2. Interaction of NO with Pd_n clusters

The results for the free molecule and the Pd_nNO system are reported in Table 1. The NO/Pd_n binding energies are given together with the Mulliken net charges on N and O, the dipole moment and the NO stretching frequency. The Pd_nNO systems were fully optimized. For the free NO molecule, the B3LYP functional is adapted to the description of the geometric and spectrometric parameters. The use of the 6-31G** basis does not give further improvement (i.e. ν_{N-O} = 1991.0 cm^{-1}). We started from various geometries for each system, allowing an extensive study of the potential energy surface. The most stable conformations are presented in Fig. 2. The NO molecule always chemisorbs in a bent geometry and significant changes of the conformational structure of the Pd_n clusters are observed. Globally, the binding energy calculated for the adsorption of NO on the Pd_n clusters are in the range of the experimental value of 1.86 eV measured in thermal desorption by Ramsier et al. [44]. Concerning the polarization of the species, clean Pd_n clus-
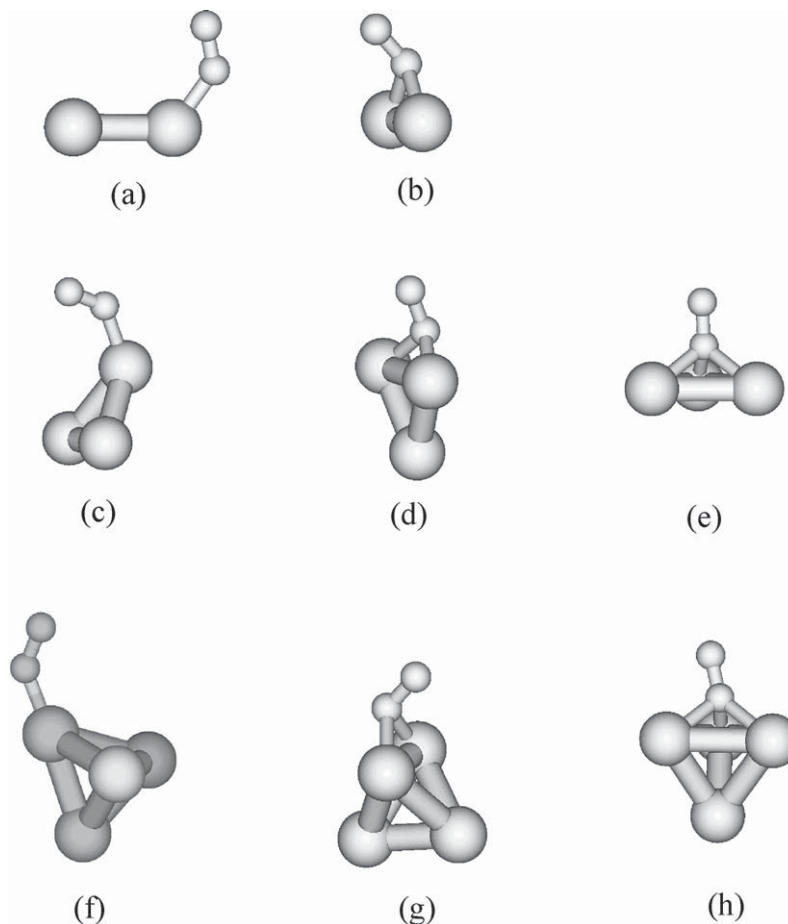

Fig. 2. Adsorption of the NO molecule on Pd_n clusters – doublet spin state. (a) and (b) Pd_2NO systems (top and bridge sites). (c)–(e) Pd_3NO systems (top, bridge, threefold sites) (f)–(h) Pd_4NO systems (top, bridge and threefold sites).

ters have no dipole moment and the NO molecule has a low dipole moment. The adsorption of NO on Pd_n clusters leads to significative polarization of the systems.

For the Pd–NO system, the NO molecule is bent with a Pd–N–O angle of 127.8° in agreement with previous works [3,4,9,45,46]. We calculated a binding energy of 1.30 eV. It is in a good agreement with the B3LYP calculations of Krim et al. (adsorption energy: 1.30 eV) [46]. Upon adsorption on the Pd atom, the N–O bond length is increased and we observed a redshift for the N–O stretching frequency ($\Delta \nu = 179$ cm^{-1} upon adsorption). The population analysis reveals a weak electronic transfer from the metallic atom to the NO molecule (0.10 au). The calculated shift of the N–O stretching mode is lower then the experimental shift $\Delta \nu = 211$ cm^{-1} observed upon adsorption of NO on a Pd atom in excess argon [45,46]. The calculations (using PW functional) of Grybos et al. also predict a larger redshift of the N–O stretching frequency ($\Delta \nu = 201$ cm^{-1} upon adsorption) and a stronger binding energy (2.16 eV). We also found a linear geometry that is a transition state.

For the Pd_2NO species, we found several minima on the potential energy surface. The bridge site is energetically the most stable in agreement with previous works [2,9]. We calculated a binding energy of 1.90 eV. Due to the Pd_2/NO interaction, the Pd–Pd and N–O distances are increased. Both the increase of the NO bond and the shift of the stretching NO frequency are directly correlated to a weakening of the NO bond energy. The redshift of the N–O stretching mode upon adsorption on the bridge site ($\Delta \nu = 364$ cm^{-1}) agrees well with the value calculated by Grybos et al. ($\Delta \nu = 366$ cm^{-1}) [9] and observed experimentally by Citra et al. ($\Delta \nu = 368$ cm^{-1}) [45].

Concerning the Pd_3NO system, three structures lie in the same range of energy. The threefold site is energetically favoured with a binding energy of NO of 1.70 eV; the binding energy for the adsorption of NO on the bridge site is 0.05 eV lower and the top site is the less stable one with a binding energy of 1.47 eV. The redshifts of the NO stretching frequency upon adsorption are in the range of 143–432 cm^{-1}. The same small energetic differences were reported by Grybos et al. who found that the adsorption on the bridge site is preferred by 49 meV [9]. Their PW91 calculations predicted strong binding energy (2.44–2.54 eV) and shifts of $\Delta \nu = 151–440$ cm^{-1} for the adsorption of NO on the Pd_3 cluster.

For the adsorption of NO on Pd_4 with a fully optimized structure, we found three stable adsorption sites on a tetrahedral Pd_4, namely a threefold, bridge and top sites. The top site is the most stable adsorption site with $E_b = 1.36$ eV, followed by the bridge site and the threefold one with a binding energy of 1.32 eV and 0.95 eV respectively. The comparison is good with the experimental value of 1.38 eV determined by Piccolo et al. for NO adsorption on Pd clusters supported on MgO [48]. Our results show that when going from the top to the threefold site, the electron transfer increases from 0.07 to 0.4 a.u. Both the Mulliken and NBO approaches give similar charges on the atoms. This is in good agreement with the theoretical results of Endou et al., who also found that the top site is the most stable one [8]. Nevertheless, the binding energies (0.73–2.32 eV) are larger than the values we calculated due to different computational conditions for the optimization of the structures (LDA level). The GGA calculations of Grybos et al. confirmed that the top site is preferred [9]. The binding energy of NO on Pd_n clusters is significantly smaller on clusters than on an infinite Pd(1 1 1) surface, i.e. 2.0–2.30 eV on threefold sites [16,17,19,20]. Two explanations may be advanced: firstly, the size of the cluster lowers the electron transfer between the adsorbate and the substrate. It thus does not take into account the long range interactions between the molecule and the bulk that are well described by the periodic computations [16,17]. Secondly, in order to increase its cohesion energy, there is a strong relaxation of the palladium cluster during the adsorption process. To demonstrate this evidence, we also studied the adsorp-
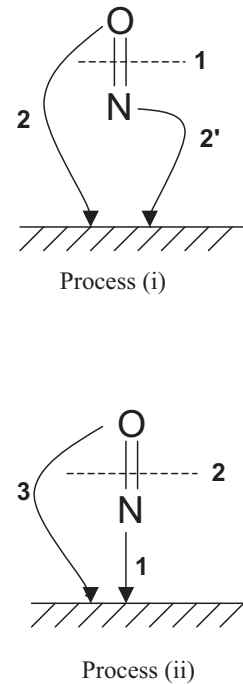

Fig. 3. Dissociation process of the NO molecule on Pd_4 cluster – process (i) and process (ii).

tion of the NO molecule on a frozen Pd_4 cluster; the structure of the metallic system has the geometrical characteristics of the bulk (i.e. fcc structure, Pd–Pd distance = 2.75 Å). We studied the threefold adsorption site. The results of both approaches are compared in Table 2. They show that the geometry relaxation affects essentially the NO–Pd_4 binding energy. Conformational relaxation is thus required for such a study. Furthermore, when Pd_4 is frozen, there is a net electronic transfer of 0.38 a.u. from the cluster to the NO molecule, of the same order of the transfer observed when the full relaxation is allowed (0.40 a.u.).

3.3. Dissociative process of NO on Pd_4

In this section, we study the possibility for the NO molecule to dissociate when it is adsorbed on a Pd_4 cluster. Two processes (i and ii) may be involved in order to obtain the dissociative chemisorption energy ΔE_{chdis}. The zero of energy corresponds to the case where the NO–Pd_4 distance is infinite. The two processes (i) and (ii) are shown in Fig. 3.

(i) The isolated (gas phase) NO molecule is first dissociated (step 1 Fig. 3a) and then both nitrogen and oxygen atoms adsorb on the cluster (steps 2 and 2′ Fig. 3a).In that case, the calculated dissociative chemisorption energy of the NO dissociation process (i) is given by:

$$\Delta E_{chdis} = -E_{dis}(NO_{gp}) + E_b(N\ et\ O/Pd_4)$$

where $E_b(N\ et\ O/Pd_4)$ is the binding energy of the N and O species coadsorbed on the Pd_4 cluster respectively; $E_{dis}(NO_{gp})$ is the N–O dissociation energy for the free NO molecule.

(ii) Firstly the NO molecule is adsorbed on the cluster (step 1 in Fig. 3b); secondly Pd_4NO dissociates to give $Pd_4N + O$ (step 2 in Fig. 3b); finally O adsorbs on the Pd_4N system (step 3 in Fig. 3b). The first step corresponds to the binding energy of the NO molecule on the Pd_4 cluster $E_b(NO/Pd_4)$; the second step leads to the NO dissociation energy of the adsorbed NO molecule
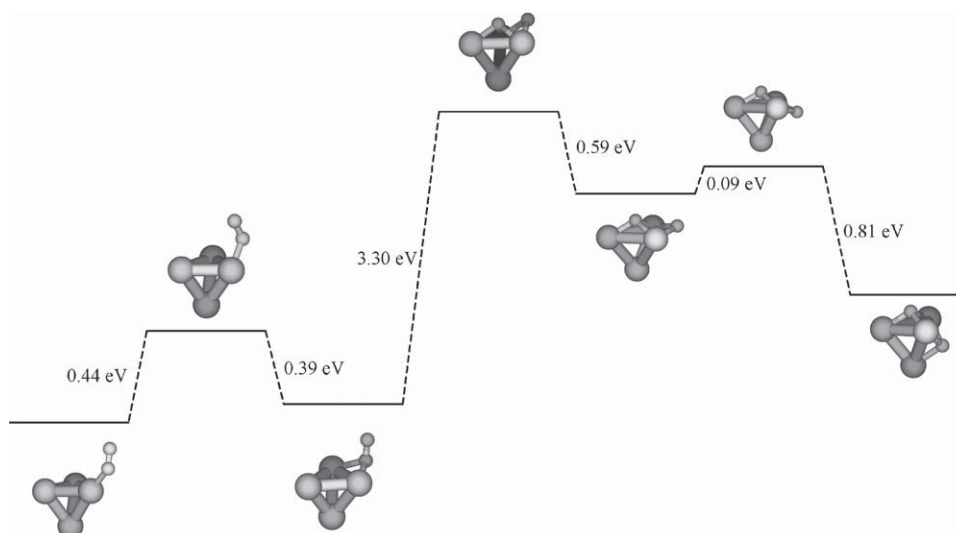
Fig. 4. Reaction pathway describing the dissociation of the NO molecule on Pd_4 cluster (process (ii)).

$E_{dis}(NO_{ads})$; the third step corresponds to the chemisorption energy of O on the Pd_4N cluster, $E_b(O/Pd_4N)$. Thus the calculated dissociative chemisorption energy of the NO dissociation process (ii) may be written as:

$$\Delta Echdis = Eb(NO/Pd4) - Edis(NOads) + Eb(O/Pd4N)$$

where $E_b(NO/Pd_4)$ is the binding energy of the NO molecule on the Pd_4 cluster and $E_b(O/Pd_4N)$ is the binding energy of the O atom on the Pd_4N system. $E_{dis}(NO_{ads})$ is the dissociation energy of NO adsorbed on Pd_4. It is given by: $\Delta E_{dis}(NO_{ads}) = E(Pd_4N) + E(O) - E(Pd_4NO)$ where E is the absolute energy of the systems in their most stable spin states.

The dissociation energy of free NO ($E_{dis}(NO_{gp})$) and of NO on Pd_4 ($E_{dis}(NO_{ads})$) are given in Table 3. Several processes are examined as the NO molecule and the N atom can be adsorbed on-top or threefold sites. Clearly the NO bond is strongly weakened when the NO molecule is adsorbed on Pd_4. The vibrational energy redshift as well as the increase in the N–O bond length are directly correlated to this energy decrease.

The results of the dissociation process are given in Table 4. The N and O atoms adsorb independently on the threefold site of the cluster with a binding energy of 3.13 and 3.23 eV respectively. The co-adsorbed N and O are nearly localized on these sites with a small repulsion between N and O due to the electrostatic interaction between both atoms (see the net charges). The total adsorption energy (5.94 eV) is thus slightly smaller that the sum of the individual adsorptions. We choose the most stable site i.e. the on-top site for the NO adsorption.

We calculated a dissociative chemisorption energy ΔE_{chdis} for process (i) of −0.67 eV. Clearly, this result shows that the NO molecule does not dissociate on Pd_4 through process (i) because the gas phase dissociation energy is larger than the binding energy of the N and O atoms co-adsorbed on Pd_4 (5.94 eV); we note that this is true even if we consider the sum of the individual adsorption of the N and O atoms on the cluster (6.36 eV).

For process (ii), the dissociative chemisorption energy ΔE_{chdis} has a value of −0.67 eV. The dissociation of the NO molecule is thus also endothermic. Moreover, the energy required for the dissociation of NO adsorbed on Pd_4 (4.84 eV) is larger than the energy released by the adsorption of O on the Pd_4N system (2.81 eV). To complete this result, we also made calculations to seek for the tran-

sition states (TS_i in Fig. 4) and intermediate species (I_i in Fig. 4) describing the dissociation of the NO molecule on the Pd_4 cluster according to process (ii). In Fig. 4, we propose a reaction pathway from the most stable Pd_4NO system (NO adsorbed on-top of the Pd_4 cluster) to the most stable final product (N and O adsorbed on threefold sites of the Pd_4 cluster). The barrier energy to TS1 is low (0.44 eV) and leads to I1 that is the Pd_4NO system with NO in bridge position. The I1-TS2 activation barrier energy is the highest activation barrier with a value of 3.30 eV. In the I2 species, the NO molecule is dissociated and the N (O) atoms are chemisorbed in the threefold (bridge) positions. In the final product, the N and O atoms are finally adsorbed on two threefold sites. This conformation is the most stable one as the N/O repulsive electronic interaction is reduced compared to the I2 conformation. The highest activation barrier for the dissociation process has a value of 3.30 eV. We can thus conclude that process (ii) is highly improbable. On the contrary, if we look to the reverse pathway (from the system with N and O co-adsorbed on Pd_4 to the NO molecule adsorbed on Pd_4) the results show that the recombination of the N and O atoms to form the NO molecule is favoured because of the low activation barriers (<0.8 eV).

4. Conclusion

A study of the interaction between small palladium clusters (Pd_n: $n = 1$–4) and the NO molecule is presented in this paper. The adsorption process is first investigated. We summarize our results:

- The adsorption of NO on small Pd_n clusters ($n = 1$–4) leads to a significant conformational reconstruction of Pd_n clusters accompanied by a polarization of the systems.
- The relaxation of the metallic clusters induces a large decrease of the chemisorption binding energy of NO.
- The N–O binding energy is strongly weakened when the molecule is adsorbed on the small Pd_n clusters due essentially to an electrostatic repulsion between both N and O atoms.

The possible dissociation process of NO on Pd_4 cluster is then investigated:

- The results show that the NO molecule does not dissociate on Pd_4 with process (i) (dissociation of the isolated gas phase NO

molecule followed by the adsorption of both nitrogen and oxygen atoms on the cluster).

- Process (ii) which presents three successive steps (adsorption of the NO molecule, dissociation of the NO molecule adsorbed on Pd_4, adsorption of the O atom on the cluster) has been studied in details and we propose a reaction pathway.
- The activation energy for process (ii) is high and the dissociation of the NO molecule on the Pd_4 cluster is thus highly improbable.

Acknowledgments

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