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Oxidation of small gas phase Pd clusters: A density functional study

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Abstract

The adsorption sites of O_2 on neutral Pd_N clusters ($N = 1$–4) were studied using spin density functional theory. Only for Pd_1O_2 molecular adsorption is found to be favorable. For $Pd_{2-4}O_2$ dissociative adsorption with the oxygen sitting on Pd bridge sites is preferred. Most Pd clusters remain in the same high spin states found for pure gas phase Pd clusters. Only the ground state of Pd_4O_2 increase its spin from a triplet to a quintet state. For molecular adsorption the O–O bond gets activated to a superoxo-like state.

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1. Introduction

Pd clusters are known to catalyse many important reactions in chemistry [1,2] e.g. the CO-oxidation in car catalytic converters or cycloaddition processes in organic chemistry. Although the broad interest in the catalytic properties of Pd triggered several pioneering ab initio studies of Pd surfaces catalysis [3–5] only little details are known concerning the structure of the intermediate products and the pathways of catalysed reactions on supported Pd nano-clusters. In this context a deeper theoretical understanding is surely useful and could provide additional information for chemists and technicians assisting them in their attempts to improve existing catalytic components or to design new catalysts.

Of course, reliable quantum mechanical calculations of industrially used catalytic transition metal particles still exceed the capacities of modern super computers by several orders of magnitude but already in our days it is possible to study metal–oxide supported transition metal clusters [6,7] and the catalytic properties [8,9] of nano-catalysts consisting of a moderate number of atoms.

Catalyst-assisted oxidation is of importance for environmental processes like exhaust gas cleaning. A first step towards an understanding of the relevant chemical mechanisms requires the knowledge of the energetically most favourable oxygen adsorption sites on the clusters as well as the nature (molecular or dissociative) of the O_2 adsorption [10]. Here we report on a systematic density functional investigation of the O_2 adsorption on neutral gas phase Pd_{1-4} clusters. The findings and trends obtained with this study will be useful for the setup and understanding of future simulations of supported Pd_NO_2.

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2. Methods

The adsorption sites were determined using the Born-Oppenheimer local spin density molecular dynamics method [11] including self-consistent generalized gradient corrections (GGA) [12] with nonlocal normconserving pseudopotentials [13] for the $4d^{10}$ and $2s^2 2p^4$ valence electrons of palladium and oxygen, respectively. The Kohn–Sham orbitals are expanded in a plane-wave basis with a 62 Ry energy cutoff, ensuring convergence of the calculated values. The cluster geometries were determined via symmetry-unrestricted structural optimizations for several possible isomers obtained by decorating the Pd_N gas phase ground state [14] with two oxygen atoms. For each structure spin-restricted optimizations were performed covering all energetically important spin multiplicities.

3. Results

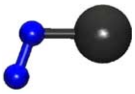
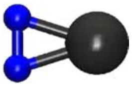
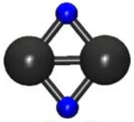
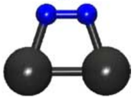
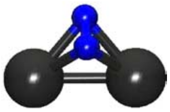
Tables 1 and 2 display structural and energetic information for the lowest energy isomers of $Pd_{1-4}O_2$ clusters. In the following we will describe adsorption sites and relevant spin states for the clusters considered in this article.

Pd_1O_2. The Pd monomer was the only species where O_2 molecular adsorption (MA) was energetically favoured (see structure Ia in Table 1). The oxygen dimer and the Pd atom form a elbow-shaped structure (bond angle O–O–Pd = 109.6°) with an adsorption energy $E_{ad} = E(Pd_NO_2) - E(Pd_N) - E(O_2)$ (i.e. the energy release upon adsorption of the dimer) of 1.104 eV. While the symmetric C_{2v} molecularly adsorbed oxygen (Ib) has 62 meV lower adsorption energy, the linear dissociated configuration Ic is energetically very unfavourable with $E_{ad} = 0.078$ eV, only. The O–O bond in the triplet ground state ($d = 1.31$ Å) is elongated compared to the bond of the gas phase dimer ($d = 1.25$ Å) indicating a superoxo type state.

Pd_2O_2. Already for the Pd dimer dissociative adsorption (DA) is preferred (see structure IIa in Table 2) although an MA isomer (IIb) is only 120 meV lower in adsorption energy. In the ground state the oxygen atoms sit on the Pd–Pd bridge sites. Note, that a dissociated linear isomer O–Pd–Pd–O (not shown) exhibit a 2.8 eV lower E_{ad}. Remarkably, the gas phase Pd_N as well as all the isomers (IIa–c) are triplet states. Based on the O–O bond length, the energetically best MA isomer (IIb) is again a superoxo state. The relaxation in Pd–Pd bond length (Δd_{Pd} in Table 1) upon O_2 adsorption is only small for the ground state and the best MA isomer.

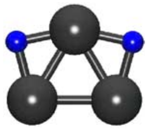
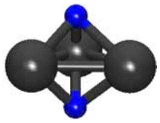
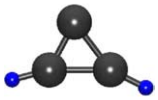
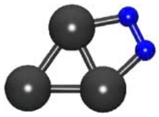
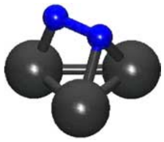
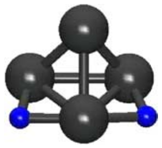
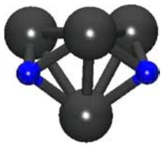
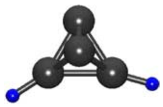
Pd_3O_2. As already observed for Pd_2O_2 the ground state IIIa of Pd_3O_2 exhibits bridge bonded dissociated oxygen and is also a triplet state. A Pd_3 with dissociated O on both hollow sites (IIIb) is 0.7 eV higher in potential energy followed by the best MA state (IIId) which has

Table 1
Lowest energy isomers of $Pd_{1-2}O_2$ and the corresponding spin state, adsorption energy E_{ad}, O–O bond distance d_{O-O} and the mean value difference of the Pd–Pd bond length in comparison to the bare Pd cluster value Δd_{Pd}

	Iso	S_z	E_{ad} (eV)	ΔE_{ad} (eV)	d_{O-O} (Å)	Δd_{Pd} (Å)
	Ia	0	0.934	0.170	1.31	
		1	1.104	0.000	1.31	
		2 Not stable				
	Ib	1	1.042	0.061	1.34	
	Ic	0	0.078	1.026	3.64	
		1	0.016	1.087	3.67	
	IIa	0	1.505	0.088	3.15	−0.02
		1	1.593	0.000	3.15	−0.03
		2	1.318	0.275	3.17	+0.10
	IIb	0	1.328	0.265	1.40	+0.10
		1	1.472	0.121	1.37	+0.14
		2	0.684	0.909	1.33	+0.00
	IIc	1	0.931	0.662	1.42	+0.30

Note, the results for different S_z values are only given for the best MA and DA isomer. For the other structures, the results for the optimum S_z is displayed.

Table 2
Lowest energy isomers of $Pd_{3-4}O_2$

	Iso	S_z	E_{ad} (eV)	ΔE_{ad} (eV)	d_{O-O} (Å)	Δd_{Pd} (Å)
	IIIa	0	2.072	0.041	3.79	+0.14
		1	2.113	0.000	3.80	+0.13
		2	1.750	0.363	3.94	+0.18
	IIIb	1	1.328	0.785	2.67	+0.29
	IIIc	Not stable → IIIa				
	IIId	0	1.023	1.090	1.34	+0.03
		1	1.050	1.063	1.35	+0.03
		2	0.821	1.292	1.36	+0.09
	IIIe	1	0.824	1.289	1.46	+0.15
	IVa	0	1.444	0.035	3.82	+0.10
		1	1.479	0.000	3.81	+0.10
		2	1.450	0.029	3.84	+0.07
		3	0.644	0.836	3.90	+0.06
	IVb	0	1.247	0.232	3.15	+0.20
	IVc	Not stable → IVa				
	IVd	0	0.970	0.509	1.34	+0.01
		1	1.027	0.453	1.35	+0.00
		2	0.906	0.573	1.34	+0.00
		3	−0.439[a]	1.919	1.35	+0.09

[a] Due to the restriction to $S_z = 3$ we get a stable isomer with negative adsorption energy.

once more superoxo character. Note, that the DA configuration with mono-coordinated (top-site) oxygen (IIIc) was not stable and relaxed into the ground state.

Pd_4O_2. This is the most interesting case. Although the ground state is again a DA isomer with bridge bonded O (structure IVa in Table 2), here the spin of the Pd cluster has increase from triplet to quinted upon oxygen adsorption. The same happened to the best MA isomer (IVd). The spin polarization, shown in Fig. 1, extends over the whole cluster with localised magnetic moments

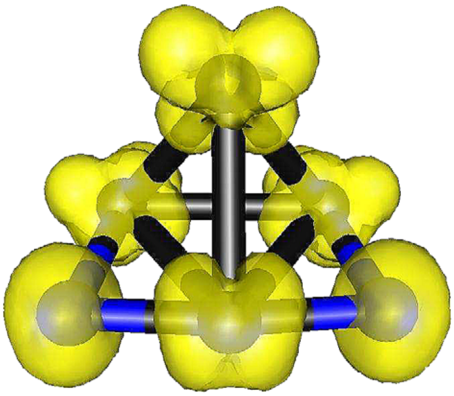


Fig. 1. Structure of the ground state Pd_4O_2 and isosurfaces of the spin polarization density ($S_z = 2$).

on both the palladium and the oxygen. Similar to the Pd trimer, dissociated hollow site adsorption (isomer IVb) is less favorable than the Pd–Pd bridge site and an isomer with oxygen bonded on top-sites (IVc) relaxed into the ground state.

4. Summary and conclusion

As a first step towards an understanding of the catalysed oxidation mechanism of supported Pd clusters we have presented a systematic study of the adsorption sites of O_2 on small gas phase Pd clusters. We found the following trends. The oxygen tends to dissociate on the Pd cluster. Only for Pd_1O_2 molecular adsorption is energetically favorable. We observed in all cases, that the bond of molecularly adsorped O_2 is elongated indicating activation of the superoxo state, while the adsorption-induced relaxation of the supporting Pd_N cluster was small. All ground state isomers are spin triplets, except Pd_4O_2 which turned out to be even a quintet state. Atomic O on bridge position was more stable than binding on hollow sites. Binding on top of a Pd corner site was not stable.

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