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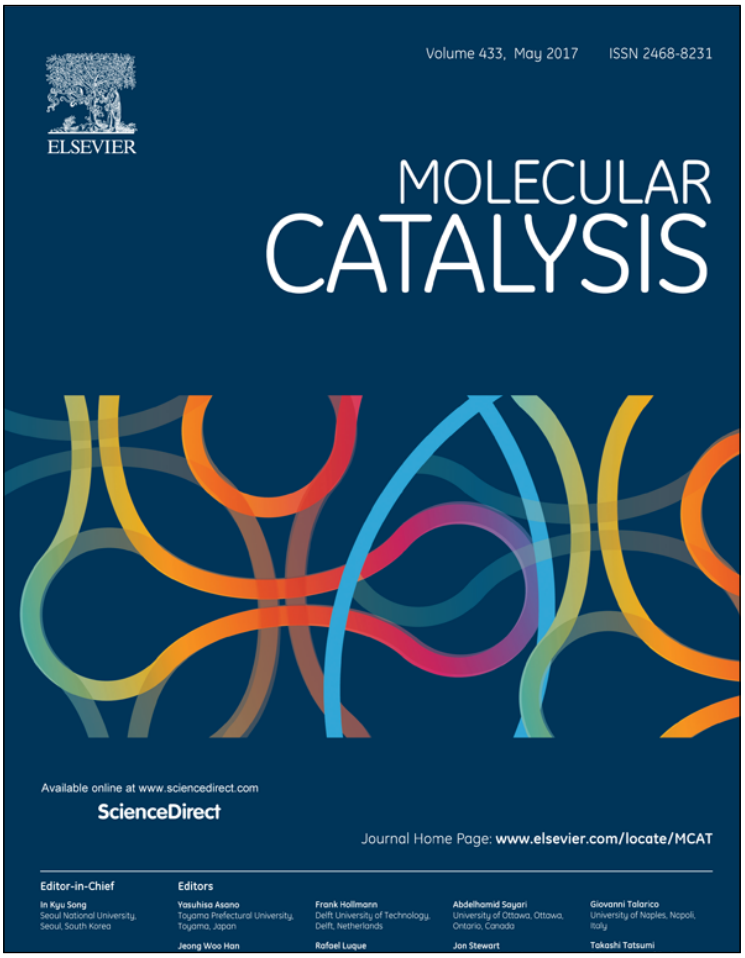

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Editor's choice paper

Comparative study of CO adsorption on planar and tetrahedral Pt nanoclusters supported on TiO_2(110) stoichiometric and reduced surfaces

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ABSTRACT

TiO_2 is a widely used material due to its electronic and catalytic properties, which are of interest for technological applications. In catalysis it is generally used as support for different catalyzers, such as for example Pt subnanoclusters given that they improve the efficiency of the material.

In this work we use an *ab initio DFT + U* modeling method to study the structure and energetic of Pt_4 clusters deposited on rutile TiO_2(110) stoichiometric and reduced surfaces. For the Pt-titania system we examine the relative stability between the flat versus 3D tetrahedral Pt_4 structures, and characterize the cluster/substrate interaction. We determine their equilibrium geometries, adsorption energies, charge transfer effects and electronic density of states to characterize different aspects of the metal-oxide interaction. For both, the stoichiometric and reduced rutile TiO_2(110), we find that the flat square configuration is preferred, as experiments indicate. In particular, we are interested in the potential activity of these cluster-supported systems for the oxidation of CO adsorbed on Pt. To examine this behavior we evaluate the structure, electronic DOS properties and charge transfer effects for the adsorption of CO on both the flat and tetrahedral Pt_4 isomers over the stoichiometric and reduced TiO_2 rutile surfaces. The results point to the planar cluster on the stoichiometric surface as the most stable configuration for CO adsorption, while for the CO conversion to CO_2 the tetrahedral Pt_4 cluster on the stoichiometric TiO_2 surface would be the most favorable catalytic substrate.

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1. Introduction

Metallic nanoclusters deposited over oxide supports play an important role for the design of model catalysts for heterogeneous catalysis applications. The oxide support contributes to stabilize the nanoparticles preventing their sintering. Noble metals (Pt, Au) supported on reducible oxides as for example TiO_2, have proven to be efficient catalysts for the water gas shift reaction (WGS, $CO + H_2O \rightarrow CO_2 + H_2$) at low temperature [1], reaction of great importance in several industrial processes. In particular, Pt-based catalysts are the ones that show more catalytic activity, compared to other noble metals, in relation to the WGS reaction [2]. Also, due to the strong metal-support interaction, the catalytic performance is highly dependent on the specific oxide support used [3]. Through experimental studies it is known that noble metals activate CO; the specific mechanism that takes place depends on the specific conditions of the reaction: the oxide support, the noble metal (its size and form), and the temperature and gas composition [4]. In order to get knowledge of how this factors influence on the performance of the active catalytic sites under specific reaction conditions, it is of fundamental importance to reach a microscopic atomic-scale understanding of the structure and nature of the metal-support interface interactions. In this sense, *ab initio* density functional theory (DFT) methods for electronic structure calculations are being commonly used for this task [5–7], therefore providing valuable information to interpret and complement experimental studies.

Several theoretical as well as experimental studies have been performed on Pt_n clusters deposited on the rutile TiO_2(110) surface. Size-selected Pt_n (n = 4, 7–10, 15) clusters soft-landed on TiO_2(110) – (1 × 1) surfaces could be visualized for the first

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time, using atomic resolution ultrahigh-vacuum scanning tunneling microscopy (STM) [8]. It was reported that clusters smaller than Pt_7 lay flat on the surface with planar structures, while a planar-to-three dimensional transition was observed for the Pt_8 cluster. In a later work, Watanabe et al. [9] confirmed this 2D-3D transition for a cluster size of n = 8 by applying similar STM observations. Moreover, the authors interestingly show that this structural 2D-3D transition correlates with a corresponding transition for the catalytic oxidation rate for CO on site-selected clusters; the reactivity increases up to Pt_8 at 572 K and 598 K, and then decreases for clusters of higher sizes. The decrease in the reactivity might be associated to a blocking effect of the reaction sites produced by the upper layer atoms of the 3D layered structures, leading to a decrease in the frequency of the CO oxidation reaction.

Motivated by these experimental results, theoretical studies based on the DFT were considered to treat the Pt/TiO_2 system, by modeling Pt_n clusters supported on both the stoichiometric [1,10] and the partially reduced rutile $TiO_2(110)$ [1]. In both works the projected augmented wave (PAW) method and the PBE approximation for the exchange correlation (XC) potential, were used. Ammal et al. [1] predicted that two-layer structures are the most stable geometries for Pt_n (n = 4–7) clusters over the oxide surface, while Jiang et al. [10] predicts that Pt_4 has a planar nearly square structure on $TiO_2(110)$, in agreement with the STM experiment [9], but two-layer structures for the Pt_5-Pt_8 clusters.

Oxygen vacancies in TiO_2 surfaces have an important role in the catalysis of WGS reactions. DFT results predict that the equilibrium configurations of Pt_n clusters are sensitive to the presence of oxygen vacancies. In fact, by comparing DFT results for the stoichiometric $TiO_2(110)$ surface against the reduced one, it is predicted that Pt atoms prefer to form a closed-packed structure with (111) facets near an oxygen vacancy of the TiO_2 support, as well as a less dense structure with (100) facets away from oxygen vacant sites. For the stoichiometric surface the preferred cluster geometric patterns found can be explained from the strong interaction of Pt atoms with both the surface oxygen atoms and the Ti_{5c} atoms. This behavior contrasts with that of Au_n clusters which interact weakly with the TiO_2 surface and for which the (111) facet is most stable [11,12]. The stronger interaction of Pt clusters with the $TiO_2(110)$ surface is also reflected through their adsorption energies that range from −1.8 to −4.3 eV, compared to Au_n clusters for which these energies range from −0.5 eV to −1.5 eV [12]. Similarly this is true for the binding mechanism of Pt_n clusters to a partially reduced rutile $TiO_2(110)$ surface; the Pt_n clusters bind more strongly with the reduced surface than Au_n clusters [12]. Pt clusters form mostly planar or two-layer structures whereas Au tends to form two or three-layer structures with fewer atoms interacting with the surface. The binding for the Pt clusters with the oxide support increases by about 0.8–0.9 eV in the presence of an oxygen vacancy in the oxide surface [5]. Also, for some cluster sizes coexistence between the (100) and (111) arrangements is also predicted, in agreement with experimental studies based on infrarred spectroscopy and adsorption calorimetry of adsorbed CO on Pt/TiO_2 catalyst on samples reduced at 473 and 773 K [13].

In most of the mechanisms proposed for the WGS reaction on Pt-supported systems, one of the steps is the oxidation of carbon monoxide adsorbed on Pt [4]. In fact, CO was found to be the most abundant reagent in the WGS reaction catalyzed by supported Pt nanoparticles. The dynamics of adsorption of CO on Pt nanoparticles, for different CO coverages, was also modeled by the DFT study of Ammal et al. [1] for the rutile surface. Their results suggest that surface Pt atoms will be covered by CO under WGS reaction conditions; only the interfacial Pt atoms will be available for catalysis. The Pt sites away from the metal oxide interface would possibly act as a CO reservoir.

It is important to note that in these previously mentioned DFT works involving Pt clusters adsorbed on the rutile surface [5,10] no Hubbard coefficient was taken into account to include corrections for the Coulomb interactions of the Ti *d* electrons. It has been shown that this correction, as included in the DFT + U approximation, is needed to correctly account for the band gap of TiO_2, usually overestimated by typical hybrid XC functionals [14]. The interaction between the metal cluster and support can strongly influence the final chemisorption and catalytic properties of the system. The metal cluster-oxide support interaction is expected to be better represented by the use of the Hubbard correction [6]. This type of approximation has been applied to describe the atomic and electronic structures of Pt_n (n = 1,4) clusters on stoichiometric, reduced and reconstructed $TiO_2(110)$ surfaces [15]. In this work, the authors found that the clusters geometries on the ideal stoichiometric surface look like their gas phase ground state structures, indicating that metal–metal interaction within the cluster would be stronger than the cluster-substrate interaction. Their predicted geometries are significantly distorted on the partially reduced surfaces. Significant band gap narrowing occurs upon adsorbate-surface interaction; however no metallization arises even for Pt_4 on rutile. More recently the DFT + U approximation was successfully applied to model the CO adsorption properties on Pt-supported systems for the less studied anatasa surface [6]. The dynamics of the CO adsorption on Pt nanoparticles deposited on the anatasa $TiO_2(101)$ (pure, N-doped and/or reduced) were investigated using UV–visible diffuse reflectance spectroscopy, diffuse reflectance infrared Fourier transform spectroscopy and the DFT calculation method. The authors reported experimental and theoretical information to help understanding how the presence of nitrogen in both, stoichiometric and reduced conditions, affects the electronic and magnetic structures of $Pt/TiO_2(101)$ system, and its influence on the adsorption of CO and its oxidation to CO_2 as possible step in the WGS or other reactions which involve CO_2 formation from CO.

In this work we use an *ab initio* DFT + U modeling method to study the structure and energetic of Pt_4 clusters deposited on the rutile $TiO_2(110)$ surface. For the Pt-supported system we examine the relative stability between the flat versus 3D tetrahedral Pt_4 structures, and characterize different aspects of the cluster/substrate interaction such as: equilibrium geometries, adsorption energies, charge transfer effects and electronic density of states (DOS). In particular, we are interested in the potential activity of these cluster-supported systems for the oxidation of CO adsorbed on Pt. To examine this behavior we model the adsorption of CO on Pt atom of the supported Pt_4 cluster, and characterize their equilibrium geometries, adsorption energies, charge transfer effects and electronic density of states (DOS). Comparison will be made with previously reported DFT [1,10] and DFT + U [15] results for the Pt/TiO_2 system.

2. Computational details and surface models

Spin polarized total energy DFT calculations were carried out using the Vienna Ab-Initio Simulation Package (VASP) [16–18] and the Projector Augmented-Wave (PAW) pseudopotentials [19] was used to reproduce the atomic core effects in the electronic density of the valence electrons. In the standard mode, VASP code performs a fully relativistic calculation for the core-electrons and treats valence electrons in a scalar relativistic approximation. Spin-orbit coupling (SOC) of the valence electrons may be included using the second-variation method [20] using the scalar-relativistic eigenfunctions of the valence states. The inclusion of spin-orbit coupling [21] allows a calculation of orbital moments, the determination of the easy axis of magnetization, and the calculation of magnetic

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anisotropy energies. In our case SOC calculations, not shown in this work, for Pt_2 (dimer) and Pt_4 (nanoclusters) show that energy value corresponding to SOC range from 0.58 eV to 0.97 eV depending on the direction of the applied magnetic field (SAXIS), over total energies of around −6 and −15 eV for Pt_2 and Pt_4 clusters, respectively. This situation change when the Pt cluster is deposited on the surface, in which SO effects, allocated in the Pt atoms, are expected to contribute similarly in the isolated and supported cluster, and therefore will tend to cancel out when defining adsorption properties of the system. In our case, the Pt-substrate interaction is of the order at −6 eV which makes the SO interactions negligible.

For electron exchange and correlation effects we adopted the Generalized Gradient Approximation due to Perdew and Wang (GGA-PW91) [22,23]. The plane wave basis was generated considering 4 valence electrons for Ti ($3d^3 4s^1$), 6 valence electrons for O ($2s^2 p^4$), 4 valence electrons for C ($2s^2 p^2$) and 10 electrons for Pt ($5d^9 6s^1$). The kinetic energy cut-off for the plane wave expansion of the electronic wave function was 400 eV. The Brillouin zone (BZ) integration was performed on well-converged Monkhorst-Pack k-point meshes [24] of $(7 \times 1 \times 5)$ for rutile (110). The energy convergence criterion used was 0.1 meV and the value of Hubbard coefficient [25] for corrections of the Coulomb interactions of the Ti *d* electrons was optimized to a value of 8 eV [26]. In this work, we use the Dudarev's approach [27] implemented in the VASP through careful selection of U, achieving excellent matches with the experimental band gap (BG) and bulk modulus measured for the systems investigated.

Some electronic characteristics as the local density of orbital states (LDOS) and the charges of the ions using Bader's analysis [28] were evaluated.

The TiO_2(110) rutile surface was represented by a slab containing three layers of titanium and oxygen atoms and a vacuum of 12.9 Å along the [110] direction, included in a periodic $(2 \times 1 \times 2)$ supercell (Fig. 1a). During the structural optimization, the bottom two layers were fixed at their bulk positions, whereas the top layer was allowed to relax together with the Pt_4 cluster. The optimized values of the cell parameters are:

a = 3.10 Å, b = 26.25 Å (include the vacuum gap) and c = 6.69 Å. The partially reduced TiO_2(110) surface was obtained by removing a bi-coordinated oxygen atom from the surface (identified as TiO_2(110) + Vo), shown in Fig. 1b.

The metal-oxide interaction was modeled by placing four Pt atoms on (110) rutile surface considering two initial configurations: the planar Pt_4 (P) and the tetrahedral Pt_4 (T) clusters (Fig. 2(a–b)). The final structures obtained in both cases after relaxation, are illustrated in the corresponding sections. The analysis was completed studying the two clusters configurations deposited on the partially reduced surface named as Pt_4/TiO_2(110) +Vo.

The corresponding Pt_4 adsorption energies were computed from the respective total energies using the following equation:

$$E_{ads=}E_{PT_{4/surface}} - (E_{pt_4} + E_{surface}) \quad (1)$$

where E_{ads} is the Pt_4 adsorption energy; $E_{Pt4/surface}$ and $E_{surface}$ are the total energy of stoichiometric (S) or reduced (R) TiO_2(110) surface, with and without the Pt_4 adsorbed on it; E_{Pt4} is the total energy of the cluster in its isolated equilibrium configuration.

The study of the carbon monoxide adsorption on stoichiometric and reduced Pt_4/TiO_2(110) systems was done by placing the adsorbate over the optimized Pt_4 cluster already deposited on the rutile surface. The possible CO adsorption site was chosen starting from the Bader's charge analysis of the previously optimized surfaces, by placing the CO molecule over the most reduced Pt atom. After that, the total geometry was allowed to optimize completely together with the Pt cluster and the top layer of the surface; the other two layers of the slab were left fixed in the position of the pre-optimized surface.

The corresponding CO adsorption energy was calculated using the following equation:

$$E_{ads=}E_{CO-Pt_4/TiO_2} - (E_{CO} + E_{Pt_4/TiO_2}) \quad (2)$$

where E_{CO-Pt_4/TiO_2} is the total energy of the stoichiometric or reduced system with CO adsorbed, E_{Pt_4/TiO_2} is the corresponding total energy of: Pt_4/TiO_2(110) and Pt_4/TiO_2(110)+Vo, respectively, with Pt_4 evaluated in both P and T configurations. E_{CO} is the total energy of the isolated carbon monoxide gas.

3. Results and discussion

In this section we present the salient features of the Pt_4 cluster deposited on stoichiometric and reduced TiO_2(110) (i.e. presence of an oxygen vacancy, V_O) in their two possible geometrical configurations P and T. We evaluate their adsorption energies, charge transfer effects and the electronic density of states. The analysis is completed with the study of CO adsorption on Pt for the above mentioned systems. The main results are discussed in the following subsections, and are summarized in Tables 1–4 .

3.1. The Pt_4 cluster on the stoichiometric TiO_2(110) surface

First we considered the Pt_4 cluster deposited over TiO_2(110) in the P and T geometries; we get that the adsorption energy is lower for the P than for the T cluster, by 0.44 eV. This effect is correlated with a strong interaction of Pt atoms with the TiO_2 surface atoms, also evidenced by the high adsorption energies obtained, which are −6.42 eV and −5.98 eV for the P and T clusters, respectively. We note however that when SO interactions are taken into account, planar geometries are in fact predicted as ground state for the isolated Pt_4 cluster [29]; for the supported clusters as modeled here, in which SOC can be neglected, it is the strong interaction between the cluster and surface that makes the planar geometry favorable. Our prediction is in agreement with the experimental findings of Watanabe et al. [9] according to which 2D configurations for Pt_n clusters of up to n = 7 are observed. Such pattern is consistent with a strong interaction of the Pt atoms with the Ti and O atoms of the surface; note that for the planar cluster the average Pt–Pt distances are 2.51 Å, whereas the Pt-O ones are smaller, 2.14 Å (Table 1). This behavior contrasts with that of Au clusters which tend to form two-three layer Pt cluster structures with few atoms interacting with the surface with energies ranging from −0.4 to −1.5 eV [12].

In Fig. 3 we show the lowest energy configurations obtained for Pt_4 adsorbed on rutile surface. There are previous DFT predictions on this topic, most of them consider conventional XC potentials; to our knowledge only few works can be mentioned using the type of approximation of the present work (DFT + U), which represent more closely the experimentally measured TiO_2 band gap see Ref. [30] and references cited therein]. Our result concerning the relative stability between the P and T isomers for the rutile surface supports a previous *ab initio* DFT prediction based on the PW91 GGA XC potential [10] but disagrees with that of Ammal et al. [1] who predicts a distorted pyramid by using the GGA PBE XC potential. By using the DFT + U approximation, with the PBE XC potential, and U = 4.5 eV, for the Pt_n/TiO_2(110) system, Celik et al. [15] predict that metal–metal interactions would be stronger than cluster-substrate. In particular, for the Pt_4 cluster, a distorted bent rhombus configuration is predicted, with one of the Pt atoms lying above the other three and making no contact with the surface. This result differs with ours, which points to a strong metal-substrate interaction and which are found to reproduce better the behavior deduced from experiments by predicting a planar configuration for the Pt_4 cluster. Also to note is hat their adsorption energies for the Pt clusters

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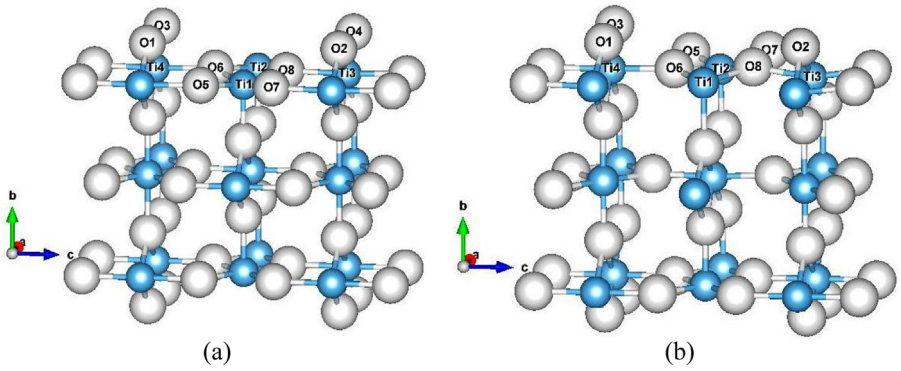

Fig. 1. (Color online) Rutile TiO_2(110) (a) and TiO_2(110) + Vo (b). Only part of the surface atoms is shown. Ti atoms on the surface consist of 5-fold (Ti1, Ti2) and 6-fold (Ti3, Ti4), whereas the surface O atoms comprise 2-fold (O1, O2, O3, O4) and 3-fold (O5, O6, O7, O8). Blue and white balls represent the Ti and O atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

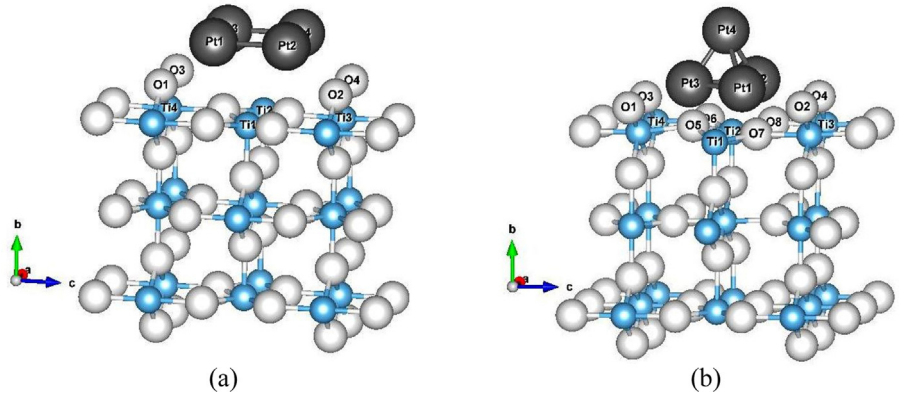

Fig. 2. (Color online) Side view of rutile Pt_4/TiO_2(110) planar (a) and tetrahedral (b). Only two of all cases studied are depicted here as examples. Dark grey balls represent the Pt atoms.

Table 1
Calculated Bader charges and principal distances between atoms for the Pt_4 cluster adsorbed on the stoichiometric (S) TiO_2 surface. ΔQ is net charge of Pt cluster. The corresponding atoms numbers are indicated in Fig. 2. (P): planar and (T) tetrahedral Pt_4 configurations. The corresponding adsorption energies have been added in italics in the first column.

Systems	Atoms	Dist. (Å)	Charge (*e*)		
			Pt	Ti	O
(P-S)	<Pt-Pt>	2.506	Pt1: 0.03	Ti1: 2.66	O1: −1.22
	Pt1-O1	2.139	Pt2: −0.09	(*2.72*)	(*−1.28*)
	Pt2-O2	2.144	Pt3: 0.14	Ti2: 2.66	O2: −1.22
	Pt3-O3	2.140	Pt4: 0.02	(*2.72*)	(*−1.28*)
	Pt4-O4	2.145			O3: −1.22
-6.42 eV	Pt1-Ti1	2.824	ΔQ = 0.10		(*−1.28*)
	Pt2-Ti1	2.793			O4: −1.22
	Pt3-Ti2	2.822			(*−1.28*)
	Pt4-Ti2	2.792			
(T-S)	Pt1-Pt2	2.628	Pt1: 0.14	Ti1: 2.67	O5: −1.29
	Pt2-Pt4	2.619	Pt2: 0.08	(*2.72*)	(*−1.40*)
	Pt3-Pt4	2.473	Pt3: 0.23	Ti2: 2.69	O8: −1.42
	Pt1-Pt3	2.727	Pt4: −0.10	(*2.72*)	(*−1.36*)
	Pt2-Pt3	2.722			O7: −1.39
-5.98 eV	Pt1-Pt4	2.604	ΔQ = 0.35		(*−1.36*)
	Pt1-O2	2.061			O1: −1.23
	Pt1-O7	5.255			(*−1.28*)
	Pt2-O4	2.081			O2: −1.22
	Pt3-O5	2.082			(*−1.28*)
	Pt3-O1	2.573			O3: −1.27
	Pt3-O8	3.294			(*−1.28*)
	Pt3-Ti1	2.768			O4: −1.21
	Pt3-Ti2	2.949			(*−1.28*)
	Pt2-Ti2	2.853			
	Pt1-Ti1	2.945			

#Charge values of corresponding atoms in the Pt-free surface are indicated in italics.

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Table 2
Bader charges and principal distances between atoms calculated for the $Pt_4/TiO_2(110)$+Vo (R) systems. ΔQ is net charge of Pt cluster. The corresponding atoms numbers are indicated in Fig. 3. (P): planar and (T) tetrahedral Pt_4 configurations. The corresponding adsorption energies have been added in italics in the first column.

Systems	Atoms	Dist. (Å)	Charge (*e*)		
			Pt	Ti	O
(P-R)	Pt1-Pt2	2.563	Pt1: 0.20	Ti1: 2.66	O2:−1.21
	Pt2-Pt4	2.694	Pt2: −0.02	(*2.73*)	(*−1.31*)
	Pt3-Pt4	2.480	Pt3: −0.13	Ti2: 2.67	O1: −1.20
	Pt1-Pt3	2.460	Pt4: −0.01	(*2.35*)	(*−1.29*)
	Pt1-O1	2.045		Ti4: 2.53	O4: −1.21
-5.72 eV	Pt2-O2	2.152	ΔQ = 0.04	(2.73)	(*−1.31*)
	Pt4-O4	2.108			
	Pt1-Ti1	3.216			
	Pt2-Ti1	2.565			
	Pt3-Ti2	3.670			
	Pt4-Ti2	2.613			
(T-R)	Pt1-Pt2	4.106	Pt1: 0.36	Ti3: 2.32	O8: −1.35
	Pt2-Pt4	2.526	Pt2: 0.01	(*2.73*)	(*−1.46*)
	Pt3-Pt4	2.555	Pt3: −0.01	Ti5: 2.30	O2: −1.15
	Pt1-Pt3	2.529	Pt4: −0.04	(*2.73*)	(*−1.29*)
-5.75 eV	Pt2-Pt3	2.520	ΔQ = 0.32	Ti1: 2.72	O7: −1.43
	Pt1-Pt4	2.575		(*2.35*)	*(−1.45)*
	Pt1-O2	1.932		Ti2: 2.68	
	Pt1-O7	3.648		(*2.73*)	
	Pt3-O8	2.099			
	Pt3-Ti2	2.927			

Table 3
Bader charges and principal distances between atoms calculated for the CO molecule adsorbed on the $Pt_4/TiO_2(110)$ (S) and $Pt_4/TiO_2(110)$+Vo (R) systems. The corresponding atoms numbers are indicated in Fig. 3. (P): planar and (T) tetrahedral Pt_4 configurations.

SystemsCO/	E_{ads} (eV)	Atoms	Dist. (Å)	Charge (*e*)			
				CO	Pt	Ti	O
(P-S)	−2.85	C-O	1.179	C: 1.58	Pt1:0.20	Ti1:2.62	O2:−1.25
		Pt1-C	2.009	(*1.80*)	Pt2:0.24	(*2.66*)	(*−1.22*)
		Pt2-C	1.952	O:−1.83	Pt3:−0.13		
		Pt1-Pt3	2.943	(*−1.80*)	Pt4: 0.13		
		Pt2-Pt4	2.914		ΔQ = 0.44		
		Pt1-Pt2	2.631				
(P-R)	−2.19	C-O	1.162	C: 1.72	Pt1: 0.14	Ti4:2.34	O1:−1.23
		Pt1-C	2.830	O:−1.88	Pt2: 0.46	(*2.53*)	(*−1.20*)
		Pt2-C	1.838		Pt3:−0.21		O2:−1.25
		Pt1-Pt3	2.539		Pt4:−0.01		(*−1.21*)
		Pt2-Pt4	2.916		ΔQ = 0.38		O6:−1.40
		Pt1-Pt2	2.708				*(−1.44)*
		Pt2-O2	2.025				
(T-S)	−1.41	C-O	1.156	C: 1.71	Pt1: 0.25	Ti1:2.63	O1:−1.29
		Pt4-C	1.869	O:−1.86	Pt2: 0.29	(*2.67*)	(*−1.23*)
		Pt3-O7	2.227		Pt3:−0.23	Ti2:2.69	O7:−1.35
		Pt3-Ti1	2.691		Pt4: 0.24	(*2.63*)	(*−1.39*)
		Pt3-Ti2	2.690		ΔQ = 0.55		
		Pt2-O4	1.997				
		Pt1-O2	1.998c				
(T-R)	−2.33	C-O	1.156	C: 1.70	Pt1: 0.29	Ti2: 2.66	O2:−1.18
		Pt4-C	1.858	O:−1.86	Pt2:−0.07	(*2.68*)	(*−1.15*)
		Pt3-O7	3.660		Pt3:−0.21	Ti3:2.29	O6:−1.45
		Pt3-Ti1	3.833		Pt4: 0.23	(*2.32*)	(*−1.48*)
		Pt3-Ti2	2.876		ΔQ = 0.24	Ti5:2.28	O7:−1.40
		Pt3-O7	2.174			(*2.30*)	(*−1.43*)
		Pt1-O2	1.925				

Table 4
Bader charges after CO adsorption on $Pt_4/TiO_2(110)$ for stoichiometric (S) and reduced (R) systems. (P) planar and (T) tetrahedral Pt_4 configurations. The total charges of titania, Pt_4 cluster, substrate ($TiO_2(110)$ surface and Pt_4 cluster) and CO molecule are indicated.

Charges	(P-S)	(P-R)	(T-S)	(T-R)
$TiO_2(110)$	−0.180	−0.225	−0.402	−0.087
Pt_4	0.435	0.380	0.550	0.241
substrate	0.255	0.155	0.148	0.154
CO	−0.255	−0.155	−0.149	−0.154

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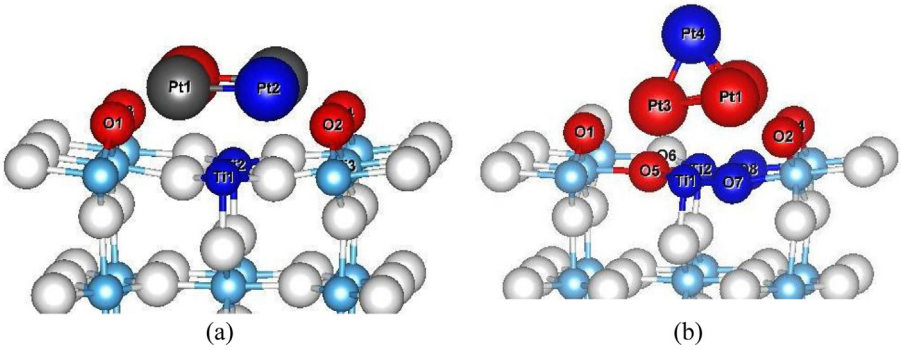

Fig. 3. Most stable configurations for $Pt_4/TiO_2(110)$ for the a) planar and b) tetrahedral Pt_4 cluster isomers. The atoms with higher degree of oxidation or reduction higher degree of oxidation and reduction "with respect to the free surface and free cluster" are highlighted in red and blue, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

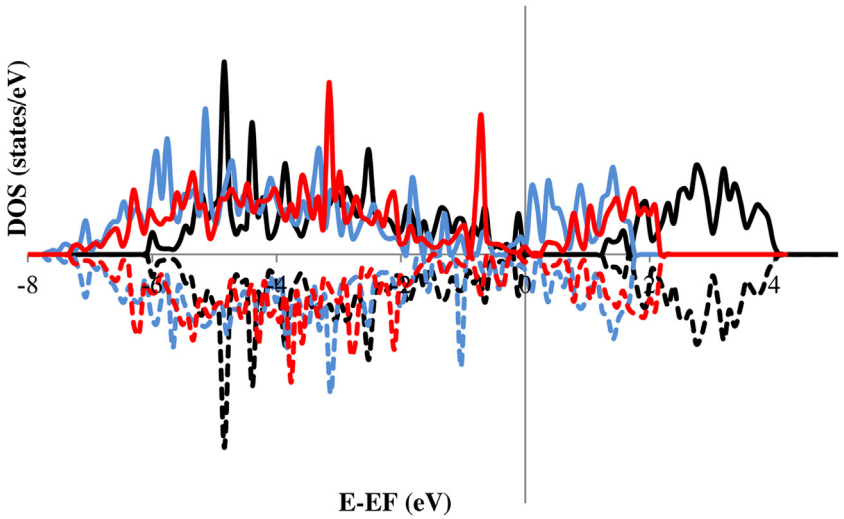

Fig. 4. DOS curves of pure rutile surface (black curve), $Pt_4/TiO_2(110)$ with planar (blue curve) and tetrahedral Pt_4 cluster adsorbed (red curve). The spin-down cases were plotted as negative values (dotted line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article). The vertical line (0 eV) corresponds to the Fermi level (EF).

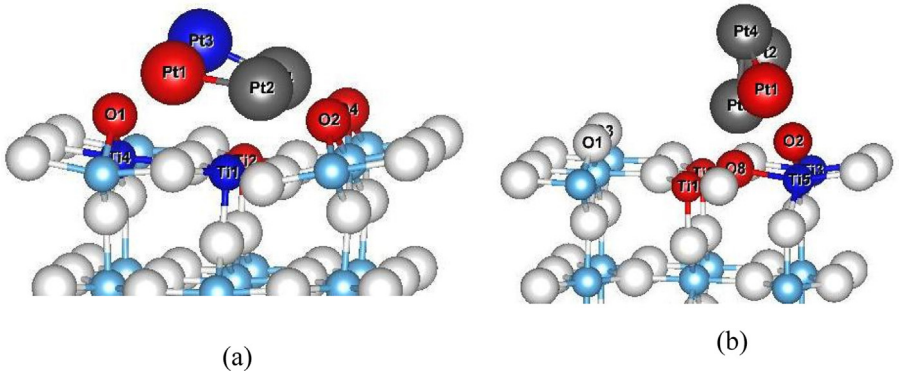

Fig. 5. Most stable configurations for $Pt_4/TiO_2(110)+V_O$ for the (a) planar and (b) tetrahedral Pt_4 cluster isomers.

on the surface are much lower (~3 eV) than the ones obtained in this work (~6 eV).

The results of the Bader's charge analysis performed are included in Table 1. We report the total charge difference of the Pt_4 when adsorbed to the surface; a positive value of $\Delta Q\,[Pt_4]$ means that the cluster is depleted of electronic charge, that is, electrons are transferred from the cluster to the surface, and therefore the cluster is oxidized getting a net positive charge. From Table 1 it can be seen that for Pt_4 (both P and T) clusters adsorbed on the stoichiometric $TiO_2(110)$ surface, the Pt_4 clusters are positively charged or oxidized, with 0.10*e* and 0.35*e* transferred to the support, respectively. This charge transfer is higher for the (T) than for the (P) configuration. Concerning the (P) isomer, not all Pt atoms behave symmetrically with respect to the charge transfer; Bader's charge analysis reveals however that one of the Pt atoms (Pt3) in the cluster get a positive charge, while another is negatively charged (Pt2); the other two Pt atoms have almost no net charge. The bi-coordinated oxygen atoms (O1 to O4) close to the Pt cluster (Fig. 2) have negative

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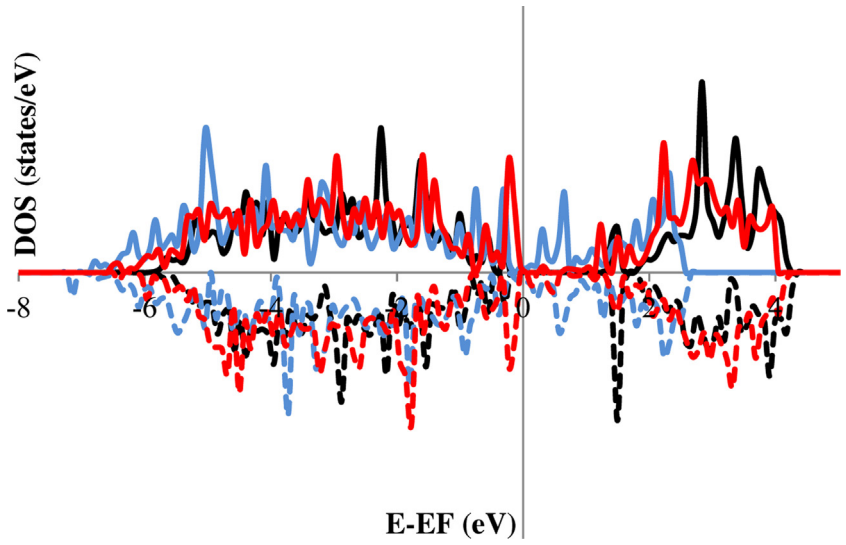

Fig. 6. DOS curves of the reduced rutile surface (black curve), $Pt_4/TiO_2(110)+Vo$ with planar (blue curve) and tetrahedral Pt_4 cluster adsorbed (red curve). The spin-down cases were plotted as negative values (dotted line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article). The vertical line (0 eV) corresponds to EF.

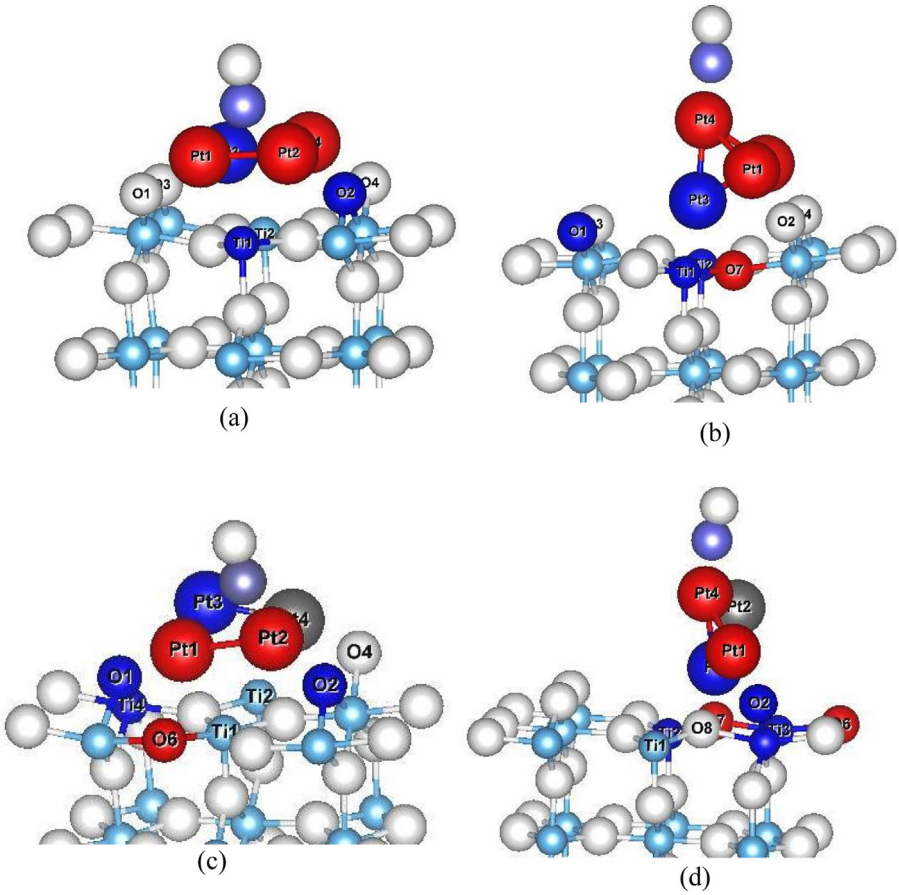

Fig. 7. CO adsorbed on $Pt/TiO_2(110)$ for (a) P and (b) T configurations and on $Pt/TiO_2(110)+Vo$ for the same configurations (c and d). C in lilac, O in white, Ti en blue, Pt in gray. The atoms with higher degree of oxidation or reduction are highlighted in red and blue, respectively. Atoms numbers correspond to Table 3. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

charges: −1.22*e*. They get oxidized when the cluster is adsorbed by experiencing a net charge transfer effect of +0.06*e* in average, with respect to their charges at the free surface. The Ti atoms (Ti1 and Ti2) located below the cluster, at an average distance Pt-Ti of 2.8 Å, have positive charge: +2.66*e*, getting reduced when the cluster is adsorbed on the surface, with a net charge transfer of −0.06*e*. Charge depletion of the Pt_4 cluster over the rutile surface have also been obtained by previous DFT-GGA studies of Ammal et al. [1] and Jiang et al. [10]. In the T configuration, the Pt atoms that are closer to the surface (Pt1–Pt3) get positive charge, while the one on top

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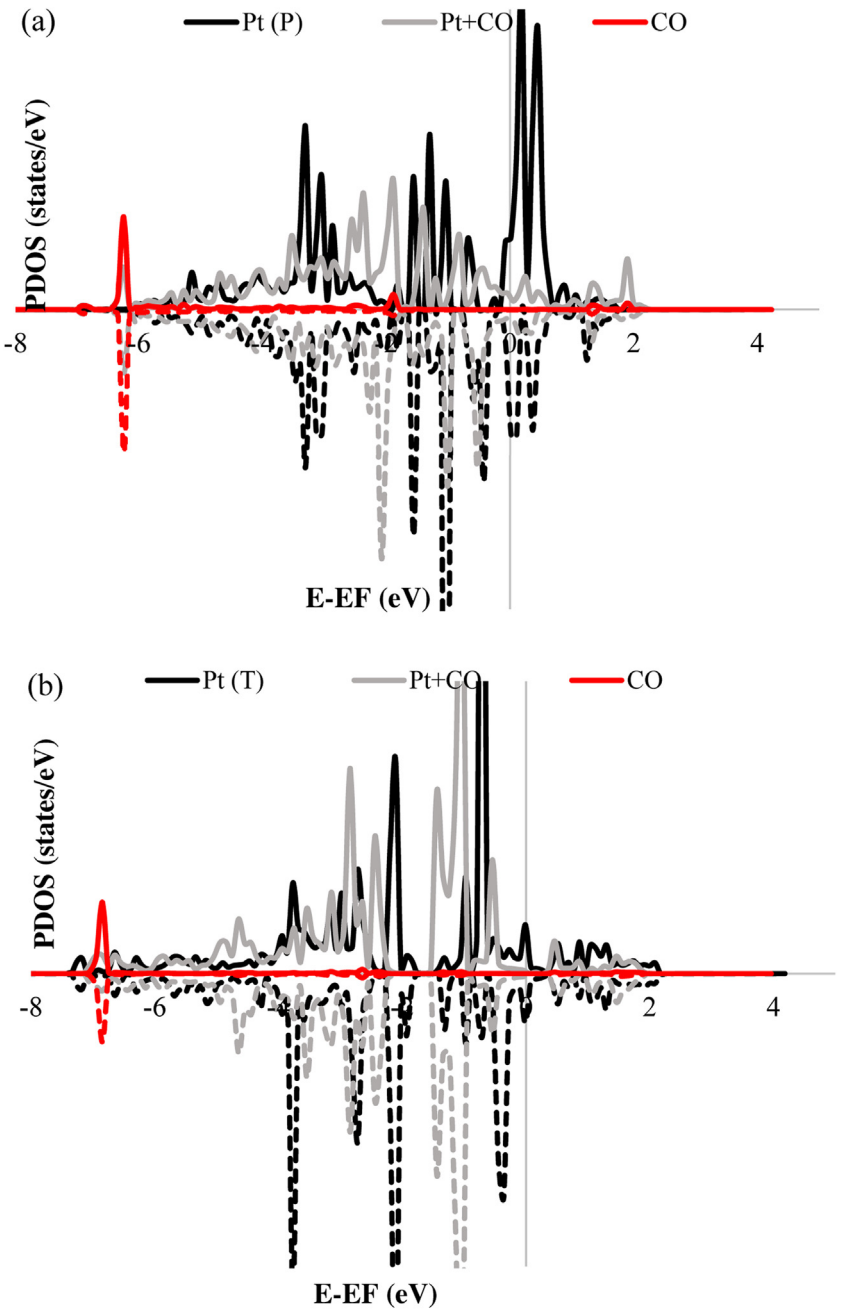

Fig. 8. Partial site-projected DOS for S-CO/Pt_4/TiO_2(110) with the Pt_4 cluster in the P (a) and T (b) configurations. The partial contribution of CO (red line) and Pt (grey line) electronic states are shown. For comparison the partial contribution of Pt atoms to the DOS of Pt_4/TiO_2(110) is also indicated (black line). The vertical line (0 eV) corresponds to EF. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

of the tetrahedral (Pt4) gets negatively charged with −0.10*e*. The Ti atoms (Ti1 and Ti2) below the cluster, have an average positive charge of +2.68*e*, getting reduced when the cluster is adsorbed on the surface, with an average charge transfer of −0.04*e*. The bi-coordinated oxygen atoms (O1 to O4) close to the Pt cluster (Fig. 2) have negative charges ranging from −1.21*e* to −1.27*e*, all of them get oxidized with a charge variation with respect to the free surface of +0.03*e* in average. The oxygen atoms below the cluster, O7 and O8, show a reduction which is not observed in the P configuration where all oxygen atoms are oxidized.

From the relationship between atoms charge analysis and the corresponding cluster-surface adsorption energies, it can be inferred that the lower energy of the tetrahedral geometry may be due to a higher repulsion between the five-coordinated Ti atoms and the Pt atoms of the cluster base (indicated in red in Fig. 3b).

In Fig. 4 we plot the total DOS for the T and P isomers Pt_4 on TiO_2(110). The calculated BG obtained for the rutile free surface is 1.6 eV. In both systems for both isomers it can be observed a vanishing of the BG by the appearance of metal-induced states in the BG of the clean surface; these states are mainly due to Pt *d* states mixed with a contribution from O 2*p* and Ti 3*d* orbitals (not shown here). By comparing with the DFT+U study of Celik et al. [15], we note that the Pt cluster that for the Pt4 cluster adsorption, adsorption, they get a band narrowing effect on the DOS, but not metallization of the system as found from our results. It is worth mentioning that the concentration of Pt in the present work is approximately twice that obtained by Celik et al. Also a general shift of the energy bands

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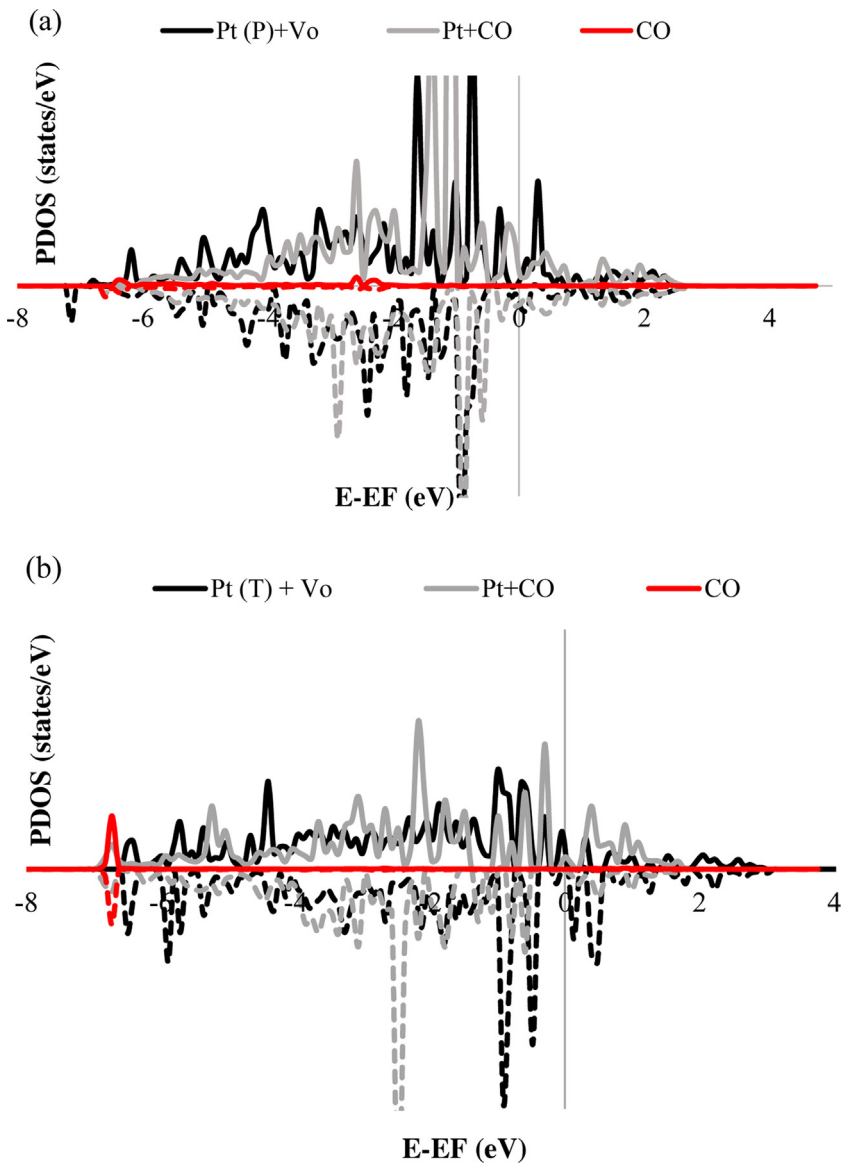

Fig. 9. Partial site-projected DOS for R-CO/Pt_4/TiO_2(110) with the Pt_4 cluster in the P (a) and T (b) configurations. The partial contribution of CO (red line) and Pt (grey line) electronic states are shown. For comparison the partial contribution of Pt atoms to the DOS of R-Pt_4/TiO_2(110) is also indicated (black line). The vertical line (0 eV) corresponds to EF. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

as a whole can be observed to lower energies, with an increase in the occupied band width from around 6 eV in the free surface, to 7.5 eV in the Pt-doped surfaces.

From the atomic projected PDOS (not shown here) it can be concluded that the hybridization between the states of tri-coordinated oxygen and platinum is higher for the planar configuration than for the tetrahedral one. The T isomer shows higher overlap than the P one between the states of bi-coordinated oxygen and platinum, and also between the Pt and Ti electronic states.

3.2. The Pt_4 cluster on the reduced TiO_2(110) surface

When the Pt_4 cluster is adsorbed on the rutile TiO_2(110) surface, the removal of a surface bi-coordinated O atom, (O3) next to Pt3 atom in the P cluster and (O4) next to Pt2 atom in the T cluster, produces a net repulsive effect, as evidenced by the equilibrium configuration of these systems, shown in Fig. 5. This is also reflected in the decrease of the corresponding adsorption energies, by 0.008 and 0.002 eV/atom, for the P and T respectively. Results reported in previous works indicate that the Pt clusters tend to bind more strongly to the reduced surface [5,15]. The (originally) P and T configurations becomes almost degenerate, with an energy difference of 0.03 eV, favoring the T one. For the T configuration a stronger geometrical distortion is observed, in a way that Pt1 is more strongly bonded to O2 in the surface; the bond length is reduced from 2.06 Å in the stoichiometric surface, to 1.93 Å in the reduced one (Tables 2 and 3). O7, together with O8, moves outwards of the surface increasing their interaction with Pt1 and Pt3 respectively. Here the distance Pt-O decreases in the reduced rutile surface with respect to the stoichiometric one, for Pt3-O8 and for Pt1-O7. The net charge of the cluster remains positive with most of its charge located in Pt1.

On the other side the (originally) P structure gets almost neutral in charge: +0.03*e*; most of the charge is located now in Pt1 bonded to O1 (-1.21*e*), and Pt3, which had a positive charge in the absence of the vacancy, now gets negatively charge (-0.13*e*), and is found displaced upwards from the surface.

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The previous analysis of charges, distances (between the oxygen atoms of the surface and the platinum ones), the corresponding adsorption energies of the metal cluster on S and R surfaces, and the geometric distortion observed in the Pt cluster (Fig. 5) can be explained by the different degree of attraction between a neutral metal cluster and the stoichiometric surface (S) or the surface with excess electrons (R). In particular, for the reduced surface (Fig. 5b), the cluster deforms as a consequence of the fact that Pt3, originally very positive (0.23*e* – Table 1), is attracted to the place where the oxygen vacancy occurred, recovering negative charge until it reaches the value of −0.01*e* (Table 2). There is experimental evidence of this type of deformation when the TiO_2(110) surface is reduced [31].

It should be noted that for both P and T configurations, an unexpected behavior is observed given that both, platinum and oxygen closest to the vacancy, are oxidized; the excess of charge due to deficiency of O, is located on the surface Ti atoms.

Concerning the DOS, we can first comment the changes on the DOS originated by an oxygen removal from the TiO_2 surface. It has been reported before [14] a shift of the conduction band minimum (CBM) of 0.18 eV to lower values of energies for the oxygen-deficient surface in comparison with the stoichiometric one. This effect has been explained by the equations of charge carriers for extrinsic semiconductors that predict such displacement [14]. Regarding the study of the reduced surface, the analysis of the corresponding DOS curves shows a band gap of 2.23 eV and two states located in the BG at 0.36 eV and 2.14 eV relative to the bottom of the CB.

Now we consider the Pt_4 cluster adsorbed on the R-TiO_2(110) system. In Fig. 6 we compare the corresponding total DOS, for both T and P isomers; we also include the DOS of the free R-TiO_2(110) surface for comparison. As for the stoichiometric surface case, the Pt_4 absorption leads to the disappearance of the BG due to metal-induced states in the BG energy region; these states are mainly due to Pt *d* states mixed with a contribution from O 2*p* and Ti 3*d* orbitals (not shown here). Resonant peaks at the band gap region can be observed particularly for the planar cluster configuration. Compared with Pt_4 absorbed on the stoichiometric surface, a global shift to higher energies can be observed for the energy bands as a whole, with a relative decrease in the occupied bandwidth (P: from 7.6 to 7.1 eV for the S and R surfaces, respectively: T: from 7.35 to 6.5 eV for the S and R surfaces, respectively). This might be correlated with the lower interaction of the Pt_4 cluster in the reduced TiO_2 surface as reflected from their lower adsorption energies.

3.3. CO adsorption on Pt_4/TiO_2(110) and Pt_4/TiO_2(110) + Vo (P and T)

The oxidation of CO to CO_2 is an intermediate step in many catalytic reactions as it happens in the important case of the WGS reaction. In most of the mechanisms proposed for Pt supported clusters on reducible and non-reducible oxides acting as catalysts [3], the CO molecule is always adsorbed on Pt. In particular, the Pt/TiO_2 system act as a bifunctional catalyst at low temperatures, where the reaction develops at its highest performance, because the Pt adsorbs/activate CO while the oxide support actives H_2O. Specifically, in one of the most viable redox route the CO is adsorbed on the Pt being oxidized to CO_2 by O atoms of the support surface [4]. In order to favor CO oxidation, it is therefore advantageous that the catalyst (Pt/TiO_2) keeps on in a reducible state as much as possible.

In this section we describe the results obtained when a CO molecule is adsorbed on the different Pt_4/TiO_2 systems considered in the previous sections. In Table 3 we summarize the main results including the adsorption energies, distances, and charges for all the cases studied.

The most stable configuration corresponds to the CO deposited over the planar cluster configuration as shown in Fig. 7, which is the case that will be discussed here in more detail. After optimization, for the (P) Pt_4/TiO_2(110), the CO molecule is vertically located between Pt1 and Pt2 with the carbon atom being closer to the surface. It can be seen from the evaluated charges, that the CO molecule as a whole is reduced, gaining electronic charge (-0.25*e*) from the Pt_4/TiO_2(110) system. This electronic charge might be thought as coming in part from the neighbouring Pt_4 cluster which as a whole loses charge (the exception is Pt3 that gains −0.13*e*). As a whole the Pt cluster oxides, with a net charge transfer of +0.34*e*, by the adsorption of CO. Considering CO adsorbed on Pt_4/TiO_2(110) + Vo, the relative stability between P and T isomers is slightly reversed, being most stable the configuration corresponding to CO adsorbed on the tetrahedral Pt_4 cluster. The difference in adsorption energy of 0.1 eV is negligible compared to that observed for the stoichiometric systems. This is the only case where the Pt_4 cluster is reduced after CO adsorption getting a net electronic charge of −0.07*e*.

The site projected DOS curves for the most stable CO adsorbed configuration, (P) Pt_4/TiO_2(110) are shown in Fig. 8a. The black line corresponds to the contribution of the Pt atoms to the DOS of the Pt_4/TiO_2(110) system, while the dark grey line, indicated as Pt + CO, corresponds to the same contribution but for the CO/Pt_4/TiO_2(110) system. The partial contribution of the CO states is indicated in red line.

It can be seen that by the CO adsorption the whole valence and conduction bandwidth shifts slightly to higher energies compared to the Pt_4/TiO_2(110) system without CO; a slight contraction of the occupied bandwidth is also obtained (not shown here). At energies around −6.2 eV, there is an important contribution of CO states, which hybridize with the Pt atomic states a fact that might be associated with the stability of the CO adsorbed system. As far as the CO chemisorption is concerned, the fundamental concept of back-donation introduced by Blyholder which invokes a donor-acceptor mechanism should be mentioned [32]. It was largely confirmed by other studies on various transition metal substrates that the bonding occurs through a concerted electron transfer from the highest filled (5σ) molecular orbital of CO to unoccupied metal orbitals (essentially d orbitals), with back-donation occurring from occupied metal d orbitals to the lowest unfilled $2\pi^*$ orbital of CO. In our case, back-donation implies a movement of electrons from Pt atomic orbital 5d to CO $2\pi^*$ antibonding orbital of CO. This causes that the charge on the Pt, particularly Pt2 (in P configuration) and Pt4 in T geometry become positive accompanied by a shortening at distances C-Pt (see Table 3). The PDOS curves show that for the P configuration there is more overlap between Pt atoms and titania. This is observed in the shape of the peaks, which are wider and of lower intensity. For the (T) Pt_4/TiO_2(110) case (Fig. 8b), which is the least stable configuration for the CO adsorption, the whole valence and conduction bandwidth is narrower than for the Pt_4/TiO_2(110) system, an indication of less interaction between the CO and the cluster-surface system. The CO peak is also present but shifted to lower energies, −7 eV approximately. A lower degree of hybridization can also be deduced from the site projected DOS (PDOS) plot. In complement, the electronic PDOS for the reduced cases studied are shown in Fig. 9. In general terms, the shape of the electronic structure does not change considering the presence of an oxygen vacancy on the surface. In particular, a relative displacement of the bands, compared to the stoichiometric systems, towards higher energies is observed. In the P case with Vo, the least stable case for CO adsorption, the CO molecule has an unfolded interaction with the Pt atoms which is not observed in the T configuration; also, the CO peaks are of much lower intensity.

In Table 4 we summarize the Bader's charges obtained for the four cases studied, indicating by separate the surface charges with and without the Pt_4 cluster deposited on it, indicated as substrate

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and TiO_2(110), respectively. By analyzing the variations of the charges the following can be concluded:

1- For the CO adsorbed systems, if the S and R cases are compared, we can see that the charge variation of the platinum atoms induced by the vacancy formation, is lower for the planar configuration than for the corresponding tetrahedral one (0.055*e* vs 0.309*e*, respectively). For the P-S case an almost equal charge transfer is produced from the Pt atoms to the CO molecule (0.255*e*) as to the surface (0.180*e*); this trend is reversed in the P-R case for which a larger charge transfer is produced to the surface (0.225*e*) instead than to the CO molecule (0.155*e*).

2- Instead, for the T-S case, where the Pt_4 cluster gets the most positive charge among the four cases studied, more oxidation of the Pt atoms is produced with charges being transferred mostly to the TiO_2(110) (0.402*e*), and less to the CO (0.149*e*). However, in the reduced T-R case, the Pt_4 cluster is the least charged, however similar charge transfer is produced towards the CO (0.154*e*) compared to the T-S case, and in less amount to the TiO_2(110) (0.087*e*). In this way, it could be thought that the Pt atoms recuperate negative charge from the neighbouring oxygen vacancy.

In summary, the previous analysis lead us predict that the most favorable case for the oxidation of CO would the T-S one. Besides, for this case the adsorption energy, in absolute value, is the least one; that is, for this configuration the CO molecule is the least bonded to the Pt_4 cluster. To complete this reasoning, we calculate the oxygen vacancy formation energy, for the P and T configurations, by using the following equation:

$$E_{for_V o} = E_{R-Pt_{4/TiO_2}} - E_{s-Pt_{4/TiO_2}} + \frac{1}{2}E_{O_2} \quad (3)$$

where $E_{R-Pt_{4/TiO_2}}$ is the total energy of the reduced system (P or T), $E_{s-Pt_{4/TiO_2}}$ is the total energy of the stoichiometric system (P or T), and E_{O_2} is the total energy of the isolated oxygen molecule gas.

The values obtained let us affirm that, it is energetically more favorable for the system to form an oxygen vacancy when the Pt is in the T configuration (2.13 eV) compared to the P configuration (2.60 eV). This result also supports the idea that the T-Pt/TiO_2 system would be the most favorable configuration towards CO oxidation from an oxygen surface and therefore expected to have better performance in the water gas shift reaction.

4. Conclusions

The structure and energetics of flat and 3D tetrahedral Pt_4 clusters deposited on rutile TiO_2(110) stoichiometric and reduced surfaces, were analyzed using an *ab initio DFT + U* modeling method to characterize the cluster/substrate interaction. For both, the stoichiometric and reduced rutile TiO_2(110), we find that the flat square configuration is preferred, as experiments indicate.

However, we also are interested in the potential activity of these cluster-supported systems for the oxidation of CO adsorbed on Pt. It is for this reason that the target was focused on studying the feasibility, or not, of this catalyst to be able to oxidize CO emphasizing the study of their specific properties. In particular, the structure, electronic DOS properties and charge transfer effects for the adsorption of CO on both Pt_4 isomers over the stoichiometric and reduced TiO_2 rutile surfaces were evaluated. From the analysis of the theoretical results associated with the CO adsorption energies, the charges and the geometry of the atoms involved, it can be concluded that the possible CO oxidation to CO_2 by oxygen atoms of support surface is enhanced if the Pt_n clusters adopt a pyramidal geometry suggesting the deposition of clusters with sized n > 4. Besides it is therefore desirable that the catalyst (Pt/TiO_2) abides in a reducible state as much as possible in order to favor CO conversion with the assistance of O atoms of the support surface.

Acknowledgments

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