First principle studies of palladium nanoparticles on titanium dioxide surfaces for catalytic application

A F Mazibuko, R G Diale, H R Chauke and P E Ngoepe

Materials Modelling Centre, University of Limpopo, Private bag x1106, Sovenga,
0727, South Africa

E-mail: andile.mazibuko@ul.ac.za

Abstract. Palladium-based catalysts are being developed as an alternative to the commonly used high cost platinum catalyst due to similar electronic configurations and lattice constants. Pd catalysts are cheaper than platinum with a high methanol-tolerance. In this study, first principle density functional theory was used to study the catalytic properties of Pd/TiO_2, the interaction and the electronic behavior of palladium nano-clusters on a stable titanium dioxide surface using the plane-wave pseudo-potential method. Titanium dioxide is used as a metal support to develop the palladium catalyst and is the most important transition metal oxide since its photo-catalytic activity was discovered. This transition metal oxide is used in many catalytic processes in the industries such as metal catalysts, which include the platinum group metals such as Pd, Pt, and Rh. These metals are involved in processes such as fuel cells, methane oxidation, catalysis, and in emission control technology. Firstly, the stability of titanium dioxide polymorphs was deduced from elastic properties and are in good agreement with the experimental values to within 3%. The observation made was based on the shear modulus of rutile being higher and positive compared to that of the other polymorphs suggesting that rutile is more stable. The order of surface stabilities is given as (110)> (100)> (101)> (001)> (111), and in good agreement with previous work. Adsorption of water on the stable (110) surface showed that the (110) surface was more exothermic. Secondly, the interaction of palladium clusters with titanium dioxide surface showed that Pd_{13} prefers the top adsorption site due to the least negative adsorption energy. The findings of this work suggest that palladium-based catalysts may play a significant role in future developments and applications in emission control technologies.

1. Introduction

Palladium is found as a free metal that forms part of the platinum group metals (PGMs) but it is more reactive than the heavier platinum [1]. Pd nanoparticles are ideal for use in catalytic reactions because of their increased surface area compared to that of the bulk material and as such are an important material component in hydrogen storage and gas sensing applications [1]. The most important attribute of Pd is its high hydrogen adsorption capacity which is greater than for any other metal.

Titanium dioxide (TiO_2) is a semiconducting transition metal oxide that is alternatively used as a support material in catalysis because of its useful physical properties and applications in various technologies [1]. Metal nanoparticles supported on metal oxides are used in various industrial catalytic processes [2]. The most used catalysts are Pt and Pt-based catalysts. Recently, Pd-based catalysts are being developed since they have similar electronic configurations and lattice constants as Pt but cheaper [3]. Pd is used as an electrode material in fuel cell applications where a highly pure hydrogen production is important and gaseous hydrogen is the only gas that can pass this metal. Car exhaust fumes might be made less toxic by using Pd as a catalyst in the catalytic convertors of cars [3, 4].

The oxide supported metal catalysts are necessary to enhance catalytic activity and durability of catalysts during methane oxidation, photocatalysis and CO oxidation [5]. There has been a variety of experimental studies on supported palladium catalysts that raised an interest to this field of research [6,7]. However, the challenge is understanding the interaction between catalytic metals and the support materials. In recent studies, density functional theory (DFT) has been used to investigate surface properties and interactions of many systems including oxide supported metals [8,9].

In this paper, we use density functional theory to investigate the TiO_2 surface interaction with water and Pd nanoclusters on (110) TiO_2 surface and to study the catalytic properties of Pd/TiO_2. The Pd-based catalyst play a significant role in emission control technology, particularly as an automotive exhaust catalyst. The surface energies and effect on hydrated surfaces is important to establish the dominant surface of titanium. Firstly, TiO_2 surface and adsorption energies of H_2O/TiO_2 and Pd_{13}/TiO_2 were calculated. Secondly, a systematic investigation on the stability of Pd_n clusters (n=3-19) will be drawn from the binding energy and second order difference energy (D_2E). It will be established that the Pd_{13} nanocluster is more stable and may have a great potential for enhancing catalytic properties. Finally, the rest of the paper is arranged in the following manner: section 2 provides computational details; section 3 is the results and discussions on the two interacting Pd clusters and Pd/TiO_2 systems; and, lastly the conclusion.

2. Computational details

First principle density functional theory (DFT) calculations were performed using the generalized gradient approximation (GGA) refined by Perdew, Burke and Ernzerhof (PBE) [10] as implemented in the CASTEP [11] and VASP codes [12]. The plane wave cut-off energy of 500 eV was used for all structures and the Brillouin zone sampling scheme of Monkhorst-Pack [13] with 6x6x1 k-point mesh for all TiO_2 surfaces and 3x3x1 for the palladium nanoclusters. All surface calculations were performed within a (2X2) supercell, using a 12-layer slab with the vacuum slab of 15 Å to avoid an interaction of the adsorbate with the repeating upper slab. The palladium nanoclusters (n=3-19) were constructed using KLMC and optimized using CASTEP. Convergence was achieved when the maximum component of the residual forces was less than 0.01 eV/Å. After adsorption, the 6 bottom layers were frozen while the top layers could interact with the palladium cluster. Density functional tight binding theory ($DFTB^+$) was used to parametrize TiO_2 at different radii and to derive the potentials for Ti-O, O-O, O-Ti, Ti-Ti interactions. The surface stabilities for different terminations are determined by their surface energy, calculated as:

$$\mathrm{E_{surface}} = \left(\frac{1}{2A}\right)[\mathrm{E_{slab}} - (\mathrm{n_{slab}})(\mathrm{E_{bulk}})] \tag{1}$$

where $\mathrm{E_{slab}}$ is the total energy of the cell containing the surface slab, $\mathrm{n_{slab}}$ is the number of atoms in the slab, $\mathrm{E_{bulk}}$ is the total energy per atom of the bulk and A is the surface area. A low positive value of $\mathrm{E_{surface}}$ indicates stability of the surface termination. The strength of the interaction of the surface with the adsorbate is shown by the adsorption energy, as:

$$\mathrm{E_{adsorption}} = [\mathrm{E_{system}} - (\mathrm{E_{slab}} + \mathrm{E}_{palladium})] \tag{2}$$

where $\mathrm{E_{system}}$ is the energy of the surface slab with collector, $\mathrm{E_{slab}}$ is the energy of the surface slab (Equation 1), n is the number of adsorbates adsorbed on the surface and $\mathrm{E}_{palladium}$ is the energy of the isolated palladium clusters. A negative value reveals a strong interaction between the adsorbate and the surface, whereas a positive value reveals the opposite.

3. Results and discussion

3.1. Structural properties of TiO_2.

It was observed from the parameterization of TiO_2, that the lattice parameters and bond lengths obtained are in good agreement with that of the standard DFT and experimental data. In Table 1, the calculated lattice parameters and bond lengths for TiO_2 are presented. The Slater-Koster files for TiO_2 were refined by varying the radius and the best fit was obtained with lattice parameters (a=4.566, c=3.168) which compare very well with experimental values (a=4.567, c=2.932).

Table 1. Lattice parameters and bond lengths for TiO_2.

Structure		Lattice parameters			Bond length
	Atom	a (Å)	b (Å)	c (Å)	(Å)
	Exp. [14]	4.567	4.567	2.932	2.025
TiO_2	Calc.	4.566±0.12	4.566±0.12	3.168±0.08	2.055±0.11

3.1.1. Mechanical properties of the TiO_2 polymorphs.

The elastic properties provide an estimate of the mechanical stability, strength and indirectly the melting temperature**.** We observe that all three TiO_2 polymorphs (rutile, anatase and brookite) are mechanically stable since they display positive shear modulus (C' >0). The shear modulus is higher for rutile compared to the other polymorphs which implies that rutile is the most stable. The calculated (Calc.) values accord well with experimental (Exp.) data. Furthermore, the ratio of brittleness/ductility (B/G) as proposed by Pugh [15], reveal that the polymorphs are ductile (since B/G >1.75).

Table 2. Elastic constants C_{ij}, bulk B (GPa), shear G (GPa), Young moduli E (GPa) and ratio of brittleness/ductility (B/G) of TiO_2.

Structure	**Rutile**		**Anatase**	**Brookite**
C_{ij}	Calc.	Exp. [16]	Calc.	Calc.
C_{11}	260.237	268	354.339	287.658
C_{12}	160.323	175	116.550	148.716
C_{13}	150.253	147	136.398	148.610
C_{21}	160.323	-	116.550	148.716
C_{22}	260.237	-	354.339	296.769
C_{23}	150.253	-	136.398	125.080
C_{31}	150.253	-	136.398	148.610
C_{32}	150.253	-	136.398	125.080
C_{33}	467.803	484	207.011	291.593
C_{44}	120.806	124	81.435	95.083
C_{55}	120.806	-	81.435	90.681
C_{66}	211.497	190	60.354	77.682
C'	49.957	-	118.895	69.471

Structure	**Rutile**		**Anatase**		**Brookite**
	Calc.	Exp. [16]	Calc.	Exp. [16]	
Bulk modulus	206.476	212	182.943	178	191.943
Shear modulus	113.194	113	76.805	-	82.272
Young modulus	287.114	-	201.379	-	215.845
B/G	1.82	-	2.4	-	2.3

3.1.2. Surface energies of rutile.

The TiO_2 surfaces and energies of the rutile surfaces are shown in Figure 1. The surfaces were cleaved from the optimized bulk rutile with spacegroup P4_2/mnm. The surface with the smallest surface energy is considered stable [17]. The slab models in Figure 1 show the order of stability of the surfaces taken before relaxation. We note that the most stable surface is the (110) surface with a surface energy of 0.083 eV/Å^2, 12 layers and 24 atoms.

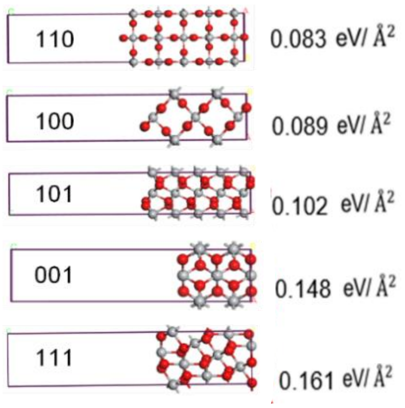


Figure 1. Rutile (TiO_2) surfaces in the order of stability (110)> (100)> (101)> (001)> (111).

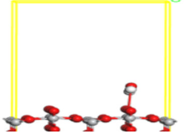
3.1.3. Adsorption of water onto rutile surfaces.

Table 3 lists the adsorption energies of the five surfaces and their adsorption sites ((b)-top and (in)-in plane as indicated on the right of Table 3). We found that the (110) TiO_2 surface is stable as shown by a more negative E_{ads} value. This suggest that the surface is more exothermic, and the reaction is spontaneous. These results accord well with the surface energies (Figure 1). We also found that the more negative value is on the oxygen adsorption site which is in the plane.

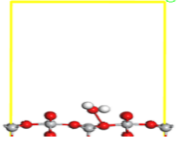
Table 3. The calculated adsorption energies of H_2O molecule adsorbed on different adsorption sites on the five stable TiO_2 surfaces. The adsorption sites are indicated on the right.

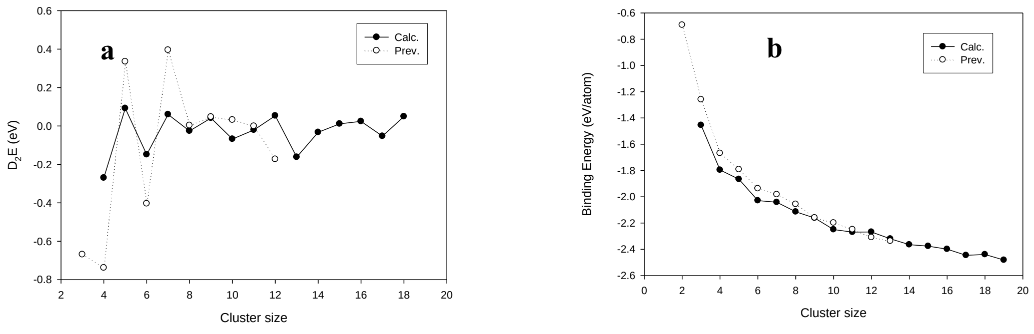
Surface	Adsorption site	E_{ads} (eV)
100	H_2O on O site	-1.765
100	H_2O on Ti site	-1.934
101	H_2O on O(in)site	-4.309
101	H_2O on O(b) site	-4.242
101	H_2O on Ti site	-5.028
110	H_2O on O(b) site	-9.592
110	H_2O on O(in)site	-10.562
110	H_2O on Ti site	-10.426
001	H_2O on O site	-3.748
001	H_2O on Ti site	-4.904
111	H_2O on O(b) site	6.282
111	H_2O on Ti(in)site	6.073
111	H_2O on O(in)site	-3.212
111	H_2O on Ti(b) site	6.930

(b)-top



(in)-in plane





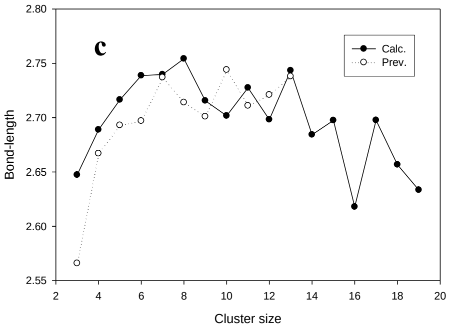


Figure 2. (a) Second order energy difference, D_2E, (b) Binding energy and (c) Bond length with respect to cluster size for Pd_n nanoclusters (n=3-19). The current work (Calc.) is compared with previous theoretical (Prev.) findings [18].

3.2. Palladium nanoparticles

The second order difference energy (D_2E) is a stability function and stable structures can be identified from the lowest peaks as shown in Figure 2a. We note from Figure 2a that n=4, 6, 8, 10, 13 and 17 are in local minima. These structures are referred to as the stable clusters or magic clusters. The predicted magic number clusters assigned n=4, 6 and 13 are most preferred and agrees with previous theoretical studies [18], while cluster 10 was only found in the current work. The magic clusters behavior was also investigated using the binding energies and are plotted in Figure 2b.

We obtained that the binding energies and the D_2E energy agree well with experimental and theoretical data. It was observed from the binding energy results that the clusters are far from converging, which can only be achieved when clusters are increased to larger sizes. Furthermore, the Pd_{13} cluster is used for further adsorption calculations since it has an enhanced stability for large clusters under consideration. It was observed from Figure 2c that the bond lengths of the palladium nanoclusters used are in good agreement with the experimental values to within 3%. It was noted that the cluster size increases as the binding energy per atom decreases and this is a common behavior for all metal clusters in this paper.

3.3. Pd adsorption on (110) TiO_2

The effect of Pd/TiO_2 is determined by examining the adsorption energies and bond lengths of Pd on (110) TiO_2. In this work Pd_{13} was adsorbed on various sites of (110) TiO_2 surface and optimized (relaxing top layers and fixed 6 bottom layers) as shown in Figure 3. The preferred adsorption sites, adsorption energies and bond lengths are listed in Table 4. The Pd_{13} is adsorbed at a distance of 2.053 from the (110) surface as shown in Figure 3(a) and we note that Pd_{13} is likely to adsorb on the top oxygen as shown on Figure 3(b).

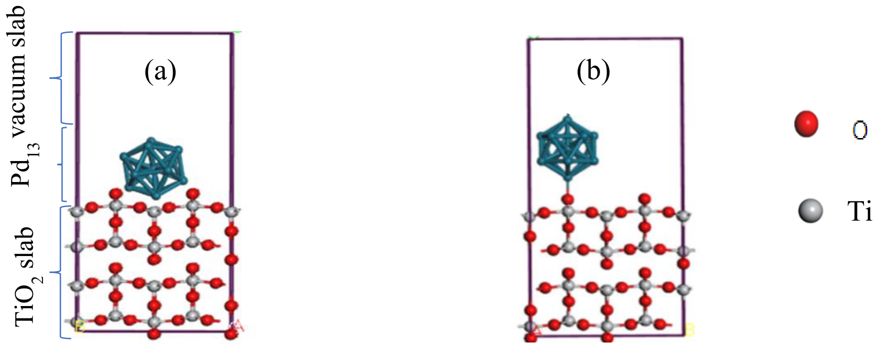


Figure 3. The geometries of Pd_{13} adsorption on a (110) TiO_2 surface: (a) Pd_{13}/TiO_2 and (b) Pd_{13}-O/TiO_2.

We observe from Table 4 that in terms of relaxed bond lengths, the preferred adsorption site is the one with the lowest Pd-O bond length which is where Pd_{13} is bonded to three top oxygen (3b) atoms, with a Pd-O bond length of 2.054 Å. The adsorption strength of the interaction of Pd_{13} with (110) TiO_2 was calculated using Equation 2.

Table 4. The calculated Pd-O bond length and adsorption energies of the Pd_{13}/TiO_2 (110) system.

Adsorption site	Pd-O bond length (Å) Calc.	Exp. [19]	E_{ads} (eV)
O(b)	2.063	2.036	-1.746
Ti(in)	2.278	2.264	-1.438
O(in)	2.109	2.096	-2.259
O(2b)	2.083	-	-2.842
O(3b)	2.054	-	-1.815

Interestingly, compared to the bond lengths, the adsorption energies show that the preferred adsorption site is the Pd bonded to two top oxygens (2b) with an adsorption energy of -2.842 eV. This suggests that the reaction is spontaneous and exothermic.

4. Conclusion

Calculations on the lattice parameters of TiO_2 polymorphs were performed using first principles method and the results were found to be in good agreement with the available experimental data. The mechanical properties suggested that rutile is the most stable polymorph. The surface energies for the five crystallographic planes showed the (110) surface as the most stable surface with the smallest surface energy of 0.083 $eV/Å^2$. The interaction between water and the surfaces of rutile (TiO_2) was investigated, it was found that the (110) surface with water adsorbed on the oxygen site because of the most negative adsorption energy. Furthermore, the order of stability accords well with previous surface work done [17]. We have also calculated the binding energies and second difference energy of the palladium clusters and found good agreement with the experimental data [18].

The Pd_{13}/TiO_2 (110) interactions were determined by adsorbing palladium (Pd_{13}) at different adsorption sites and we observed the effect on the bond lengths and adsorption energies of the system. The adsorption energy for the $Pd_{13}/TiO_2(110)$ suggested that the reaction is spontaneous (negative, $E_{ads}<0$). Furthermore, the Pd-Ti bond distances are comparable before and after adsorption with a slight increase from 2.057 Å to 2.278 Å. This may suggest a good catalytic reactivity of the $Pd_{13}/TiO_2(110)$. The findings of this research may suggest that the interactions of $Pd_{13}/TiO_2(110)$ are favorable and may be used in catalytic convertors.

Acknowledgements

The work was carried out at the Materials Modelling Centre (MMC), University of Limpopo. We acknowledge the Centre for High Performance Computing (CHPC) for computing resources and the National Research Foundation for financial assistance. The authors also wish to recognize the support of the South African Research Chair initiative of the Department of Science and Technology.

References

[1] Wang M, Guo D and Li H 2005 *J. Solid State Chem.* **178** 1996
[2] Chen J, Arandiya H, Gao x and Li J 2015 *Catal. Surv. Asia* **19** 140
[3] Zhang C and He H 2007 *Catal. Today* **126** 345
[4] Youngku S 2010 *Appl. Surf. Sci.* **257** 1692
[5] Shao Y, Liu J, Wang Y and Lin Y 2009 *J. Mater. Chem.* **19** 46
[6] Rao C R K and Trivedi D C 2005 *Coord. Chem. Rev.* **249** 613
[7] Yui T, Kan A, Saitoh C, Koike K, Ibusuki T and Ishitani O 2011 *ACS Appl. Mater. Interfaces* **3** 2594

[8] Wanbayor R and Ruangpornvisuti 2012 *Appl. Surf. Sci.* **258** 3298
[9] Dianat A, Seriani N , Ciacchi L C, Pompe W, Cuniberti G and Bobeth M " 2009 *J. Phys. Chem.* C **113** 21097
[10] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 38
[11] Segall M D, Lindan P J D, Probert M J, Pickard C J, Hasnip P J, Clark S J and Payne M C 2002 *J. Phys. Cond. Matter.* **14** 2717
[12] Kresse G and Furthmüller J 1996 *Phys. Rev.* **154** 11169
[13] Monkhorst H F and Park J D 1976 *Phys. Rev.* B **13** 5188
[14] Rezaee M, Khoie S M and Liu K H 2011 *Cryst. Eng. Com.* **13** 5055
[15] Pugh S F 1954 *Philos. Mag.* **45** 823
[16] Isaak D G, Carnes J D, Anderson O L, Cynn H and Hake E 1998 *Phys. Chem. Miner.* **26** 31
[17] Mellan T A and Grau-Crespo 2012 *J. Chem. Phys.* **137** 154706
[18] Chattaraj D, Parida S C, Dash S and Majumder C 2014 *Eur. Phys. J. D.* **68** 302
[19] Sanz J F and Ma´rquez A 2007 *J. Phys. Chem.* C **111** 3949