



Virginia Commonwealth University  
VCU Scholars Compass

Physics Publications

Dept. of Physics

2014

# Potential of ZrO clusters as replacement Pd catalyst

Swayamprabha Behera

*Virginia Commonwealth University*, [beheras@vcu.edu](mailto:beheras@vcu.edu)

Nicholas King

*Virginia Commonwealth University*

Devleena Samanta

*Virginia Commonwealth University, Stanford University*

Puru Jena

*Virginia Commonwealth University*, [pjena@vcu.edu](mailto:pjena@vcu.edu)

Follow this and additional works at: [http://scholarscompass.vcu.edu/phys\\_pubs](http://scholarscompass.vcu.edu/phys_pubs)

 Part of the [Physics Commons](#)

Behera, S., King, N., Samanta, D., et al. Potential of ZrO clusters as replacement Pd catalyst. *The Journal of Chemical Physics*, 141, 034301 (2014). Copyright © 2014 AIP Publishing LLC.

Downloaded from

[http://scholarscompass.vcu.edu/phys\\_pubs/104](http://scholarscompass.vcu.edu/phys_pubs/104)

This Article is brought to you for free and open access by the Dept. of Physics at VCU Scholars Compass. It has been accepted for inclusion in Physics Publications by an authorized administrator of VCU Scholars Compass. For more information, please contact [libcompass@vcu.edu](mailto:libcompass@vcu.edu).

## Potential of ZrO clusters as replacement Pd catalyst

Swayamprabha Behera,<sup>1</sup> Nicholas King,<sup>1</sup> Devleena Samanta,<sup>2</sup> and Puru Jena<sup>1,a)</sup>

<sup>1</sup>Department of Physics, Virginia Commonwealth University, Richmond, Virginia 23284, USA

<sup>2</sup>Department of Chemistry, Virginia Commonwealth University, Richmond, Virginia 23284, USA and  
 Department of Chemistry, Stanford University, Stanford, California 94305, USA

(Received 26 March 2014; accepted 24 June 2014; published online 15 July 2014)

Atomic clusters with specific size and composition and mimicking the chemistry of elements in the periodic table are commonly known as superatoms. It has been suggested that superatoms could be used to replace elements that are either scarce or expensive. Based on a photoelectron spectroscopy experiment of negatively charged ions, Castleman and co-workers [Proc. Natl. Acad. Sci. U.S.A. **107**, 975 (2010)] have recently shown that atoms of Ni, Pd, and Pt which are well known for their catalytic properties, have the same electronic structure as their counterpart isovalent diatomic species, TiO, ZrO, and WC, respectively. Based on this similarity they have suggested that ZrO, for example, could be a replacement catalyst for Pd. Since catalysts are seldom single isolated atoms, one has to demonstrate that clusters of ZrO also have the same electronic structure as same sized Pd clusters. To examine if this is indeed the case, we have calculated the geometries, electronic structure, electron affinity, ionization potential, and hardness of Pd<sub>n</sub> and (ZrO)<sub>n</sub> clusters ( $n = 1-5$ ). We further studied the reaction of these clusters in neutral and charged forms with H<sub>2</sub>, O<sub>2</sub>, and CO and found it to be qualitatively different in most cases. These results obtained using density functional theory with hybrid B3LYP functional do not support the view that ZrO clusters can replace Pd as a catalyst.  
 © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4887086>]

### I. INTRODUCTION

Of the 90 elements in the periodic table that occur in nature, some are highly abundant like Si while some others are scarce or expensive. Among the latter category are elements such as Ga, As, Se, Cd, In, and Te that are 4-8 orders of magnitude less abundant than Si. Similarly, elements such as Pd and Pt that serve as catalysts, and rare earth elements that form the essential components of magnets, are expensive. Since these elements are critical to technology and society, it will be ideal to find ways in which they can be replaced by earth-abundant elements. This is where atomic clusters may be useful, if they can be designed and synthesized, with suitable size and composition, to mimic the chemistry of scarce or expensive elements. This idea was put forth more than 20 years ago by Khanna and Jena<sup>1</sup> who termed such clusters as “superatoms.” They suggested that superatoms can be regarded as “man-made” elements belonging to the third-dimension of a new three-dimensional periodic table. Just as conventional crystals are formed with atoms as the building blocks, one can imagine that a novel class of cluster assembled materials can be formed with stable superatoms as the building blocks. This possibility was demonstrated first by focusing on Al<sub>13</sub> cluster. With 39 electrons, Al<sub>13</sub> has an electronic configuration of 1S<sup>2</sup> 1P<sup>6</sup> 1D<sup>10</sup> 2S<sup>2</sup> 1F<sup>14</sup> 2P<sup>5</sup> in the jellium model<sup>2</sup> and requires only one electron to satisfy the electronic shell closure rule, just as Cl with an electronic configuration of  $ns^2 np^5$  requires only one electron to fulfill the octet-rule. Intense peak of Al<sub>13</sub><sup>-</sup> anion in the mass spectrum and its inertness towards oxygen observed by Castleman and co-workers<sup>3</sup> pro-

vided evidence for its unusual stability. Thus, it was hypothesized that Al<sub>13</sub> can mimic the chemistry of a Cl atom. Li *et al.*<sup>4</sup> later measured the electron affinity (EA) of Al<sub>13</sub> to be 3.62 eV which is nearly identical with the electron affinity of Cl, namely, 3.61 eV. With a metal cation like K<sup>+</sup>, Khanna and Jena<sup>5</sup> then predicted that Al<sub>13</sub><sup>-</sup> can form the anionic component of a cluster-salt, namely KAl<sub>13</sub>. This prediction<sup>5</sup> was later confirmed by Zheng *et al.*<sup>6</sup> who showed through photoelectron spectroscopy experiment that Al<sub>13</sub> can indeed form a salt-like ionic molecule when interacting with an alkali metal, namely, KAl<sub>13</sub>, just as Cl does, namely, KCl.

In the past decade, considerable research has been carried out to design and synthesize superatoms using a variety of electron counting rules such as the octet rule,<sup>7</sup> the 18-electron rule,<sup>8</sup> and the Wade-Mingos rule,<sup>9</sup> in addition to the jellium rule discussed in the above. A few cluster assembled materials have also been synthesized.<sup>10</sup> Much of these works, however, have concentrated on superatoms mimicking the properties of elements that are neither scarce nor expensive.

Recently, Castleman and co-workers<sup>11</sup> have expanded this concept to more technologically relevant transition metal elements. Carrying out photoelectron spectroscopy experiment of negatively charged ions of group 10 elements, namely, Ni<sup>-</sup>, Pd<sup>-</sup>, and Pt<sup>-</sup> which are well known for their catalytic properties, the above authors showed that the electronic properties of these atoms are very similar to diatomic species, TiO<sup>-</sup>, ZrO<sup>-</sup>, and WC<sup>-</sup>, respectively. To illustrate this result, we note that the electronic configurations of Pd, Zr, and O are [Kr] 4d<sup>10</sup>, [Kr] 5s<sup>2</sup> 4d<sup>2</sup>, and [He] 2s<sup>2</sup> 2p<sup>4</sup>, respectively. Thus, Pd is isoelectronic with ZrO. In a similar vein, Ni and Pt are isoelectronic with TiO and WC, respectively. Note that in an earlier work, Boudart and Levy<sup>12</sup> had reported that the

<sup>a)</sup> Author to whom correspondence should be addressed. Electronic mail: [pjena@vcu.edu](mailto:pjena@vcu.edu)

surface of WC exhibited similar catalytic behavior as that of Pt. Thus, ZrO could be considered as a superatom mimicking the chemistry of Pd.

This is an important result if this analogy could persist in clusters since reduction of extremely active NO by CO is known to take place<sup>13</sup> in the presence of highly dispersed Pd clusters supported on alumina. In a later perspective article, Castleman<sup>14</sup> has reiterated this point. A recent study<sup>15</sup> of the interaction of hydrocarbons such as ethane and propane with Pd<sup>+</sup> cation shows some encouraging results – the reactivity pattern between positively charged Pd atom and ZrO diatomic species is found to be similar.

We note that the properties of bulk ZrO are very different from that of Pd; while the former is a semiconductor, the latter is a metal. However, one knows that at the nano-scale matter does behave differently than from its bulk. Is this the case with ZrO and Pd nano-clusters? Since catalysts are rarely single atoms and are usually supported on a substrate, the fundamental questions that now need to be answered are whether Pd<sub>n</sub> clusters react the same way as (ZrO)<sub>n</sub> clusters do with simple gas molecules such as H<sub>2</sub>, O<sub>2</sub>, and CO? How do the reactions with gas molecules differ when these clusters are supported on different substrates?

In the present paper, we have attempted to answer these questions. First, we have calculated the atomic structures of Pd<sub>n</sub> and (ZrO)<sub>n</sub> clusters for  $n = 1-5$  in neutral, cationic, and anionic forms. The electronic structures of these clusters were analyzed by computing their ionization potentials (IPs), electron affinities, binding energies, and hardness. Reactions of H<sub>2</sub>, O<sub>2</sub>, and CO with these clusters both in neutral and charged forms were carried out to determine their binding energies, atomic, and electronic structures. We realize that when clusters are supported on a substrate charge exchange may occur, leaving the supported clusters in positively or negatively charged state. Thus, studies of the reaction of charged clusters may illustrate qualitatively the role of the support. For a quantitative understanding of the catalytic properties of supported clusters, however, explicit interaction of the substrate needs to be taken into account. This is the goal of our future project. The choice of the above gas molecules for exploring the catalytic properties of Pd<sub>n</sub> and isoelectronic (ZrO)<sub>n</sub> clusters is dictated by the importance of chemical reactions such as hydrogenation and dehydrogenation<sup>16,17</sup> and CO-oxidation.<sup>18</sup> For example, an anode material formed by combining Pd with Pt has been found to be resistant to CO poisoning<sup>19,20</sup> in fuel cell applications.

The paper is organized as follows: The computational details used in this study are described in Sec. II. Results are presented in Sec. III which is divided into two parts. First, the structural and electronic properties of Pd<sub>n</sub> and (ZrO)<sub>n</sub> (for  $n = 1-5$ ) are presented. Second, the interactions of the gas molecules (H<sub>2</sub>, O<sub>2</sub>, and CO) with small neutral and charged clusters of Pd<sub>n</sub> and (ZrO)<sub>n</sub> ( $n = 1-3$ ) are discussed. Section IV provides a summary of our conclusions.

## II. COMPUTATIONAL DETAILS

Calculations are performed using density functional theory (DFT) and Becke three parameter Lee–Yang–Parr

(B3LYP) hybrid functional for exchange and correlation (XC) potential.<sup>21,22</sup> Stuttgart pseudo potential (SDD)<sup>23</sup> basis sets for Pd and Zr atoms and triple- $\zeta$  valence plus polarization (TZVP) basis sets for O, C, and H atoms embedded in the Gaussian 03 program<sup>24</sup> are used for all the calculations. This level of theory has been found to accurately predict the ground state, spin multiplicity, and reaction energies of clusters composed of these elements.<sup>25–27</sup> First, the calculated EAs, vertical IPs, hardness ( $\eta$ ), and binding energies ( $E_b$ ) of these clusters are compared to see if Pd<sub>n</sub> clusters mimic the properties of (ZrO)<sub>n</sub> clusters. The interaction of gas molecules with these clusters is studied next by calculating their adsorption energies ( $E_{ads}$ ). Different initial geometries are considered where the gas molecules binding to Pd<sub>n</sub> and (ZrO)<sub>n</sub> (where  $n = 1-3$ ) are taken in both molecular and dissociated form. For each of these clusters, different possible spin multiplicities are considered. Extensive search over isomers and spin multiplicities allowed us to identify the ground state structure and spin of all the neutral, anionic, and cationic clusters. EA is calculated as the energy difference between the ground states of the anion and its corresponding neutral. Vertical IP is calculated as the energy difference between the neutral and positively charged cluster, both at the ground state geometry of the neutral. Hardness ( $\eta$ ) is given by (IP – EA). The binding energies,  $E_b$  of clusters are calculated as

$$E_b(X_n) = [nE(X) - E(X_n)], \quad (1)$$

where  $E(X)$  and  $E(X_n)$  ( $X = \text{Pd, ZrO}$ ) represent the total energies of  $X$  and  $X_n$  species.

The adsorption energy  $E_{ads}$  of a gas molecule is calculated as

$$E_{ads} = -\{E[X_n Y]^q - [E(X_n^q) + E(Y)]\}, \quad (2)$$

where  $Y = \text{H}_2, \text{O}_2, \text{CO}$ .  $q = 0, -1, +1$  represent the neutral, anionic, and cationic clusters of  $X_n$ , respectively. Note that the energies in Eq. (2) correspond to the preferred spin multiplicities of the parent and the products. We used the default optimization algorithm included in Gaussian (i.e., Berny algorithm) to obtain the lowest energy geometry.<sup>28</sup> The SCF convergence threshold for all runs was set at a total energy change of  $1 \times 10^{-6}$  a.u., while geometry optimization convergence criteria were  $0.45 \times 10^{-3}$ ,  $0.3 \times 10^{-3}$ ,  $1.8 \times 10^{-3}$ , and  $1.2 \times 10^{-3}$  a.u. for maximum force, RMS force, maximum displacement, and RMS displacement, respectively. Nature of bonding is determined from natural bond orbitals (NBO) analysis. Optimizations are carried out without any symmetry constraint. These are followed by frequency calculations to confirm that the structures represent genuine minima in the potential energy surface. Results are compared with prior theoretical and experimental results, where available.

## III. RESULTS AND DISCUSSION

### A. Comparison between Pd<sub>n</sub> and (ZrO)<sub>n</sub> clusters ( $n = 1-5$ )

We begin with a discussion of the geometries and electronic structure of bare Pd<sub>n</sub> and (ZrO)<sub>n</sub> ( $n = 2-5$ ) clusters to see whether they both exhibit similar chemistry. To gain this

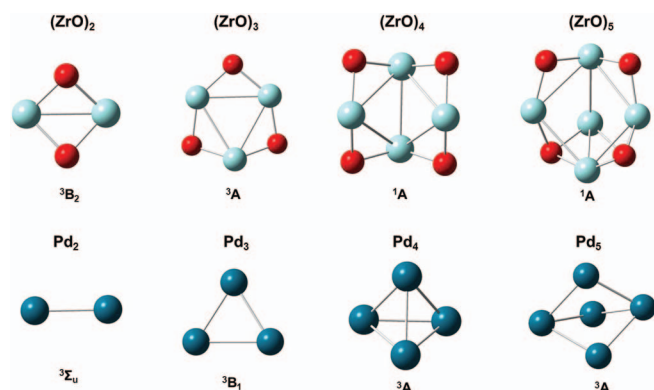


FIG. 1. Ground state geometries with electronic state of neutral  $(\text{ZrO})_n$  and  $\text{Pd}_n$  ( $n = 2-5$ ) clusters.

insight, we have calculated EA, vertical IP, hardness ( $\eta$ ), and binding energy ( $E_b$ ) of these clusters. In Figure 1, we compare their ground state geometries. Corresponding values of EA, IP,  $\eta$ , and  $E_b$  values are given in Table I and compared with available experimental data. The geometries of  $\text{Pd}_n$  clusters become three-dimensional at  $n = 4$  and agree with earlier work.<sup>29-31</sup>  $(\text{ZrO})_n$  clusters, on the other hand, become three-dimensional from  $n = 2$ . In addition, geometries of  $(\text{ZrO})_n$  clusters are marked by both Zr–O and Zr–Zr bonds. We note that the ground state spin multiplicities of all  $\text{Pd}_n$  clusters studied are triplet while this is not case with corresponding  $(\text{ZrO})_n$  clusters.

The EAs of  $\text{Pd}_n$  clusters, with the exception of  $\text{Pd}_3$ , agree with experiment within 0.3 eV. This sets the limit on the accuracy of the DFT/B3LYP level of theory. The ionization potentials of  $\text{Pd}_n$  clusters decrease steadily with cluster size reaching a value of 6.81 eV for  $\text{Pd}_5$ . The hardness also decreases with cluster size reaching a value of 5.09 eV for  $\text{Pd}_5$ . The results for  $(\text{ZrO})_n$  clusters are rather different, both in magnitude as well as in trend. The geometries of  $(\text{ZrO})_n$  clusters show no O–O bonds and each O atom is bound to two Zr atoms. This is because the binding energy of ZrO is 7.4 eV

TABLE II. Adsorption energies ( $E_{\text{ads}}$ ) in eV and electronic states in parentheses of neutral  $\text{Pd}_n$  and  $(\text{ZrO})_n$  ( $n = 1-3$ ) clusters interacting with  $\text{H}_2$ ,  $\text{O}_2$ , and CO.

Cluster	$E_{\text{ads}}$ (eV)		
	$\text{H}_2$	$\text{O}_2$	CO
ZrO	1.28 ( $^1\text{A}$ )	3.76 ( $^1\text{A}$ )	0.50 ( $^1\text{A}$ )
Pd	0.75 ( $^1\text{A}'$ )	0.64 ( $^3\text{A}''$ )	1.79 ( $^1\text{A}$ )
$(\text{ZrO})_2$	2.09 ( $^1\text{A}$ )	9.20 ( $^1\text{A}$ )	1.27 ( $^3\text{A}$ )
$(\text{Pd})_2$	1.64 ( $^1\text{A}'$ )	1.07 ( $^3\text{A}$ )	2.53 ( $^1\text{A}$ )
$(\text{ZrO})_3$	1.78 ( $^3\text{A}$ )	8.77 ( $^1\text{A}$ )	2.00 ( $^3\text{A}$ )
$(\text{Pd})_3$	1.47 ( $^1\text{A}$ )	1.57 ( $^3\text{A}_2$ )	2.51 ( $^1\text{A}'$ )

while that of  $\text{O}_2$  is 5.21 eV. Unlike  $\text{Pd}_n$  clusters, the spin multiplicities of  $(\text{ZrO})_n$  clusters are singlet for  $n = 4, 5$  and triplet for  $n = 2, 3$ . The electron affinities of  $(\text{ZrO})_n$  clusters quantitatively differ from those of  $\text{Pd}_n$  clusters, although the variation with size does not differ significantly. Similar to the  $\text{Pd}_n$  clusters, the hardness of  $(\text{ZrO})_n$  clusters decrease with cluster size, but their magnitudes are significantly smaller. Since electron affinity, ionization potential, and hardness all influence the interaction of clusters with gas molecules, it would appear that these two sets of clusters will not exhibit similar chemical properties as their size grows. This is indeed the case as we will see in subsection B where we discuss the actual reactions with gas molecules.

## B. Interaction of gas molecules ( $\text{H}_2$ , $\text{O}_2$ and CO) with neutral $\text{Pd}_n$ and $(\text{ZrO})_n$ clusters ( $n = 1-3$ )

In this section, we study the reactivity of simple gas molecules such as  $\text{H}_2$ ,  $\text{O}_2$ , and CO with neutral  $\text{Pd}_n$  and  $(\text{ZrO})_n$  ( $n = 1-3$ ) clusters in order to compare the chemical behavior of these systems. The corresponding adsorption energies are given in Table II. The reactivity of these gas molecules with the anionic and cationic  $\text{Pd}_n$  and  $(\text{ZrO})_n$

TABLE I. Electron Affinity (EA), Vertical Ionization Potential (IP), Hardness ( $\eta$ ), and Binding Energy ( $E_b$ ) of  $(\text{ZrO})_n$  and  $\text{Pd}_n$  clusters for  $n = 1-5$ . Available experimental results are given in parentheses.

Cluster	EA (eV)	IP (eV)	$\eta$ (eV)	$E_b$ (eV)
ZrO	1.29 (expt: $1.3 \pm 0.3$ ) <sup>a</sup>	7.49	6.20	
$(\text{ZrO})_2$ $C_{2v}$	1.18	5.70	4.52	3.17
$(\text{ZrO})_3$ $C_1$	1.20	5.52	4.32	7.38
$(\text{ZrO})_4$ $C_1$	1.33	5.64	4.31	12.31
$(\text{ZrO})_5$ $C_1$	1.76	4.96	3.20	15.91
Pd	0.78 (expt: $0.562 \pm 0.005$ , $0.557 \pm 0.008$ ) <sup>b</sup>	8.70 (exp: $8.3365 \pm 0.0001$ , $8.3369 \pm 0.0001$ ) <sup>c,d</sup>	7.92	
$\text{Pd}_2$ $D_{infv}$	1.53 (expt: $1.685 \pm 0.008$ , $1.30 \pm 0.15$ ) <sup>e,f</sup>	7.63 (exp: $7.7 \pm 0.3$ ) <sup>c,d</sup>	6.10	0.90 (expt: $0.74 \pm 0.26$ ) <sup>g</sup>
$\text{Pd}_3$ $C_{2v}$	2.13 (expt: $1.35 \pm 0.10$ , $1.50 \pm 0.10$ ) <sup>d,h</sup>	7.67	5.54	2.45
$\text{Pd}_4$ $C_1$	1.51 (expt: $1.35 \pm 0.10$ ) <sup>d</sup>	6.91	5.40	4.83
$\text{Pd}_5$ $C_1$	1.72 (expt: $1.45 \pm 0.10$ ) <sup>d</sup>	6.81	5.09	6.34

<sup>a</sup>O. C. Thomas, S. J. Xu, T. P. Lipka, and K. H. Bowen, *J. Clust. Sci.* **10**, 525 (1999).

<sup>b</sup>H. Hotop and W. Lineberger, *J. Phys. Chem. Ref. Data* **14**, 731 (1985).

<sup>c</sup>D. R. Lide, *Handbook of Chemistry and Physics*, 74th ed. (CRC, Boca Raton, FL, 1994).

<sup>d</sup>K. A. Gingeric, *Naturwissenschaften* **54**, 43 (1967).

<sup>e</sup>J. Ho, K. Ervin, M. Polak, M. Gilles, and W. Lineberger, *J. Chem. Phys.* **95**, 4845 (1991).

<sup>f</sup>G. Gantefor, M. Gausa, K. Meiwesbroer, and H. Lutz, *J. Chem. Soc.-Faraday Trans.* **86**, 2483 (1990).

<sup>g</sup>D. R. Lide, *Handbook of Chemistry and Physics*, 76th ed. (CRC Press, Boca Raton, FL, 1995).

<sup>h</sup>K. Ervin, J. Ho, and W. Lineberger, *J. Chem. Phys.* **89**, 4514 (1988).



clusters will be discussed in subsequent sections. To assess the accuracy of our computational approach, we have calculated the binding energies (bond lengths) of  $H_2$ ,  $O_2$ , and  $CO$  which are, respectively, 4.77 eV (0.74 Å), 5.21 eV (1.21 Å), and 12.73 eV (1.13 Å). These agree well with corresponding experimental values, namely, 4.48 eV<sup>32</sup> (0.73 Å),<sup>32</sup> 5.12 eV<sup>33</sup> (1.21 Å),<sup>34</sup> and 11.10 eV<sup>35</sup> (1.128 Å).<sup>36</sup>

### 1. Interaction with $H_2$

The calculated ground state geometries of  $H_2$  interacting with neutral  $Pd_n$  and  $(ZrO)_n$  clusters are given in Figure 2. We note that hydrogen binds to Pd in quasi-molecular form with a H–H bond length of 0.86 Å which is slightly larger than the corresponding bond length of 0.74 Å in isolated  $H_2$  molecule. H atoms remain almost neutral with a charge of  $-0.02e$  on each. The binding energy of  $H_2$  to Pd atom is 0.75 eV (see Table II). Our computed structure of  $PdH_2$  and adsorption energy of  $H_2$  agrees well with previous theoretical calculations.<sup>32,37</sup> Other higher energy isomers of  $PdH_2$  are given in Figure SI-1 in the supplementary material.<sup>46</sup> We note that the above adsorption energy is significantly larger than the physisorption energy of  $H_2$ , namely, 0.21 eV/ $H_2$  on Pd(111).<sup>38</sup> The interaction of  $H_2$  with ZrO is qualitatively different. Here, the H–H bond breaks and both the H atoms bind to Zr with each carrying a charge of  $-0.43e$ . The corresponding adsorption energy is 1.28 eV. This result at first may seem surprising since the binding energies of PdH and ZrH are 2.51 eV and 2.37 eV, respectively. The difference originates from the electronic structure of Pd and Zr atom. Pd atom has an outer electronic configuration of  $d^{10}s^0$  while that of Zr is  $d^2s^2$ . Since both  $H_2$  and Pd atom have closed electronic shells, the interaction between them is weak and

$H_2$  binds quasi-molecularly. This kind of bonding of  $H_2$  with transition metal atoms has been demonstrated by Kubas.<sup>39,40</sup> The structure of  $ZrOH_2$  where  $H_2$  binds molecularly to the Zr-site is 1.14 eV higher in energy (see Figure SI-2 in the supplementary material<sup>46</sup>). In  $Pd_2H_2$  cluster, the H–H bond breaks and the adsorption energy more than doubles to 1.64 eV. This result agrees well with that of Zeng and Ni<sup>32</sup> and Efremenko *et al.*<sup>37</sup> However, Cui *et al.*<sup>25</sup> reported a ground state structure with a H–Pd–Pd–H dihedral angle of 168.5°. We found this structure to have an imaginary frequency and automatically led to the structure given in Figure 2. The structure of the anionic  $Pd_2H_2$  shown later in Figure 8 is, however, similar to the one reported by Cui *et al.*<sup>25</sup> for neutral  $Pd_2H_2$ . In  $(ZrO)_2H_2$  cluster, the H–H bond also breaks, but both the H-atoms remain bound to only one of the Zr atoms. The geometry of  $(ZrO)_2H_2$  where the H-atoms bound to two different Zr atoms is 0.19 eV higher in energy (as shown in Figure SI-4 in the supplementary material<sup>46</sup>) than the ground state (as shown in Figure 2). The corresponding adsorption energy increases from 1.28 eV in  $(ZrO)H_2$  to 2.09 eV in  $(ZrO)_2H_2$ . In  $Pd_3H_2$ , the  $H_2$  molecule dissociates with one H atom being bridge bonded to two Pd atoms while the other binds on the hollow site formed by three Pd atoms. Zeng and Ni<sup>32</sup> and Cui *et al.*<sup>41</sup> had found that in the ground state of  $Pd_3H_2$  each H-atom prefers to bind to the bridge sites. We find this isomer to be nearly degenerate ( $\sim 0.02$  eV) in energy (see Figure SI-5 in the supplementary material<sup>46</sup>) with the one shown in Figure 2.

In  $(ZrO)_3H_2$ , the H atoms bind to separate Zr atoms. The H-atoms binding to single Zr atom is found to be nearly degenerate ( $\sim 0.06$  eV) in energy, which is shown in Figure SI-6 in the supplementary material.<sup>46</sup> The difference between binding energies of  $H_2$  to  $Pd_3$  and  $(ZrO)_3$  narrows to 0.31 eV, with binding to  $(ZrO)_3$  being stronger than that to  $Pd_3$ . We note that in  $(ZrO)_n$  clusters, the H atom always prefers to bind to Zr and not to O atoms, even though the O–H binding energy is 4.59 eV while that of Zr–H is 2.37 eV. This is because the Zr–O binding energy, as mentioned before, is substantially large, namely, 7.4 eV. Thus, ZrO binding will be disturbed if H atoms were to bind to O.

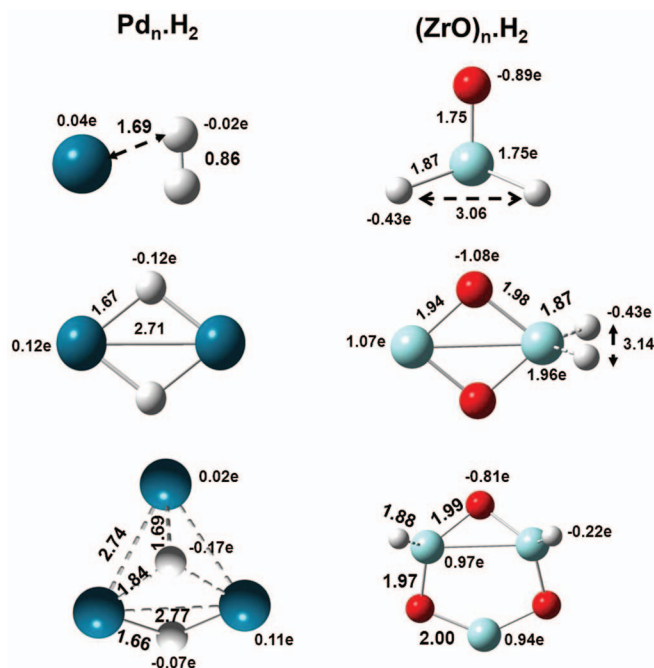


FIG. 2. Ground state geometries of  $H_2$  interacting with neutral  $Pd_n$  and  $(ZrO)_n$  clusters. The bond lengths are given in Å and the NBO charges are given in units of electron charge, e.

### 2. Interaction with $O_2$

The interaction of  $O_2$  with  $Pd_n$  is very different from that with  $(ZrO)_n$  clusters. In Figure 3, we plot these geometries for  $n = 1-3$ . The corresponding adsorption energies of  $O_2$  as well as spin multiplicities are given in Table II. Oxygen binds quasi-molecularly to Pd in *superoxo* form. The O–O bond in  $PdO_2$  is 1.26 Å which is slightly elongated compared to that in isolated  $O_2$  molecule, namely, 1.21 Å. The charge on each of the O atom is  $-0.21e$ . Our computed structure and binding energy of  $PdO_2$  agree well with previous theoretical calculations.<sup>42</sup> The structure of  $PdO_2$  where the O–O bond breaks is found to be 1.33 eV higher in energy (see Figure SI-1 in the supplementary material<sup>46</sup>). The reason O–O bond remains nearly molecular can be seen by comparing the binding energy of PdO and  $O_2$  dimers which are 2.35 eV and 5.21 eV, respectively. However, in  $(ZrO)_2O_2$ ,

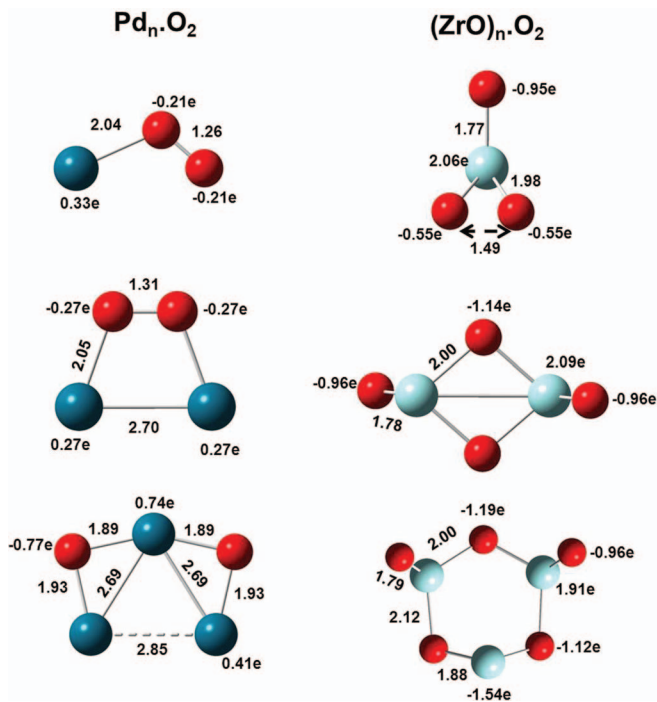


FIG. 3. Ground state geometries of  $O_2$  interacting with neutral  $Pd_n$  and  $(ZrO)_n$  clusters. The bond lengths are given in Å and the NBO charges are given in units of electron charge, e.

oxygen binds in the *peroxo* form with the O–O bond stretched to 1.49 Å with each O atom carrying a charge of  $-0.55e$ . This result is due to the large binding energy of ZrO dimer, as pointed out before. The adsorption energies of  $O_2$  to Pd and ZrO are, respectively, 0.64 eV and 3.76 eV. In addition, while  $PdO_2$  is a spin triplet,  $(ZrO)_2O_2$  is a spin singlet. The difference in the interaction with  $O_2$  persists in larger  $Pd_n$  and  $(ZrO)_n$  clusters. In  $Pd_2O_2$  cluster, oxygen continues to bind in quasi-molecular form where the two O atoms are 1.31 Å apart and the charge on each of the O atom is  $-0.27e$ . The ground state reported by Huber *et al.*<sup>42</sup> has the O-atoms sitting on the Pd–Pd bridge-sites. We find this structure to be 0.57 eV higher in energy (see Figure SI-3 in the supplementary material<sup>46</sup>) than the geometry given in Figure 3.

In the  $(ZrO)_2O_2$  cluster, on the other hand, the  $O_2$  molecule dissociates and the O atoms, with each carrying a charge of  $-0.96e$ , bind to the two Zr atoms. This result is also reflected in their adsorption energies. While  $O_2$  is bound to  $Pd_2$  with 1.07 eV, it is substantially larger in  $(ZrO)_2$ , namely, 9.20 eV. In both  $Pd_3O_2$  and  $(ZrO)_3O_2$  clusters, the  $O_2$  molecule breaks. However, the difference in adsorption energy persists. The binding energy of  $O_2$  to  $Pd_3$  is 1.57 eV while that to  $(ZrO)_3$  is 8.77 eV. The reason why  $O_2$  is bound much more strongly on  $(ZrO)_n$  than  $Pd_n$  is because the binding energy of ZrO, namely, 7.4 eV is much larger than that of PdO, namely, 2.35 eV.

### 3. Interaction with CO

The equilibrium geometries of  $Pd_n$  and  $(ZrO)_n$  clusters interacting with CO are given in Figure 4. The corresponding

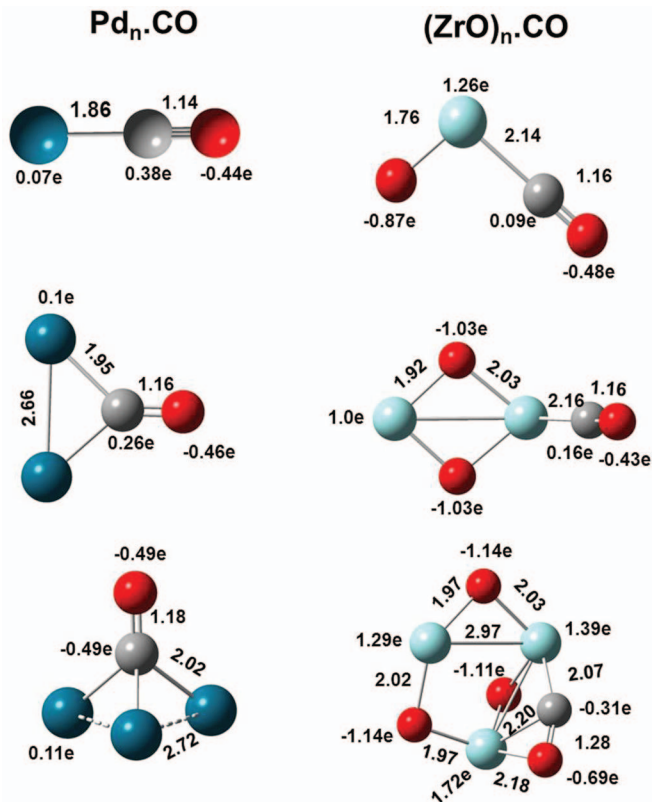


FIG. 4. Ground state geometries of CO interacting with neutral  $Pd_n$  and  $(ZrO)_n$  clusters. The bond lengths are given in Å and the NBO charges are given in units of electron charge, e.

adsorption energies are given in Table II. In the case of Pd and ZrO, the CO binds molecularly with the C atom attached to the metal atom. Unlike the case with  $H_2$  or  $O_2$ , the adsorption energy of CO to Pd is higher than that to ZrO. In  $Pd_2CO$ , the CO binds molecularly with C atom attached to both the Pd atoms. The geometry where the C–O bond breaks is energetically unfavorable (see the supplementary material<sup>46</sup>). Our computed structures and binding energies of PdCO and  $Pd_2CO$  agree well with previous theoretical calculations.<sup>43,44</sup> In  $(ZrO)_2CO$ , however, the CO binds to one of the Zr atoms. The adsorption energies of CO to Pd and  $Pd_2$  are about 1.29 eV and 1.26 eV larger than that to ZrO and  $(ZrO)_2$ , respectively. In  $Pd_3CO$ , only C atom of CO binds to all the Pd atoms, while both the C and O atoms of CO bind to two different Zr atoms in  $(ZrO)_3$  cluster. This makes the C–O bond to stretch significantly, thereby increasing the adsorption energy of CO to  $(ZrO)_3$ . The structure where CO binds molecularly to single Zr-site is found to be 0.68 eV higher in energy (see Figure SI-6 in the supplementary material<sup>46</sup>). The adsorption energy of CO to  $Pd_3$  is also 0.51 eV higher than that to  $(ZrO)_3$ . The reason why CO remains molecular in all the  $Pd_n$  and  $(ZrO)_n$  clusters is because of the very large binding energy of CO mentioned earlier, namely, 12.73 eV. The binding energies of CO to  $Pd_n$  clusters are larger than those to  $(ZrO)_n$  clusters because C binds to more Pd atoms than Zr atoms. In a similar vein, the reason for C in CO preferring to bind to Zr instead of O is not to disrupt the very significant ZrO bonding.

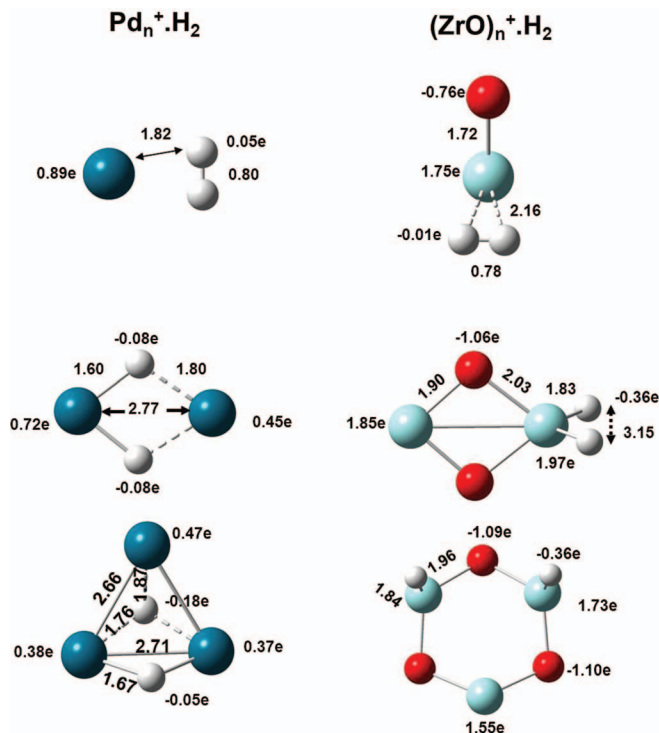


FIG. 5. Ground state geometries of  $\text{H}_2$  interacting with cationic  $\text{Pd}_n^+$  and  $(\text{ZrO})_n^+$  clusters. The bond lengths are given in Å and the NBO charges are given in units of electron charge, e.

### C. Interaction of gas molecules ( $\text{H}_2$ , $\text{O}_2$ , and CO) with cationic $\text{Pd}_n$ and $(\text{ZrO})_n$ clusters ( $n = 1-3$ )

We now present the results of  $\text{Pd}_n^+$  and  $(\text{ZrO})_n^+$  clusters interacting with  $\text{H}_2$ ,  $\text{O}_2$ , and CO.

#### 1. Interaction with $\text{H}_2$

The equilibrium geometries of  $\text{Pd}_n^+$  and  $(\text{ZrO})_n^+$  clusters interacting with  $\text{H}_2$  are plotted in Figure 5. The corresponding adsorption energies are given in Table III. Hydrogen atoms bind quasi-molecularly with both  $\text{Pd}^+$  and  $\text{ZrO}^+$  clusters with adsorption energies that are rather similar. Note that these results are consistent with the polarization model described by Niu *et al.*<sup>45</sup> where the electric field produced by the metal cations polarizes the  $\text{H}_2$  molecule and no charge transfer takes place between H and the parent atoms. The bonding patterns of  $\text{H}_2$  to the both the cationic clusters of  $\text{Pd}_n$

TABLE III. Adsorption energies ( $E_{\text{ads}}$ ) in eV and electronic states in parentheses of  $\text{Pd}_n^+$  and  $(\text{ZrO})_n^+$  ( $n = 1-3$ ) clusters interacting with  $\text{H}_2$ ,  $\text{O}_2$ , and CO.

Cluster	$E_{\text{ads}}$ (eV)		
	$\text{H}_2$	$\text{O}_2$	CO
$\text{ZrO}^+$	1.02 ( $^2A$ )	2.93 ( $^2A$ )	1.75 ( $^2A''$ )
$\text{Pd}^+$	0.85 ( $^2A'$ )	0.72 ( $^2A''$ )	1.76 ( $^2\Sigma$ )
$(\text{ZrO})_2^+$	1.53 ( $^2A$ )	5.98 ( $^2A$ )	1.32 ( $^2A$ )
$(\text{Pd})_2^+$	0.94 ( $^2A_1$ )	0.99 ( $^2A_2$ )	1.81 ( $^2A$ )
$(\text{ZrO})_3^+$	1.60 ( $^2A$ )	8.19 ( $^2A$ )	2.31 ( $^2A$ )
$(\text{Pd})_3^+$	1.84 ( $^2A$ )	1.19 ( $^2A$ )	2.70 ( $^2A$ )

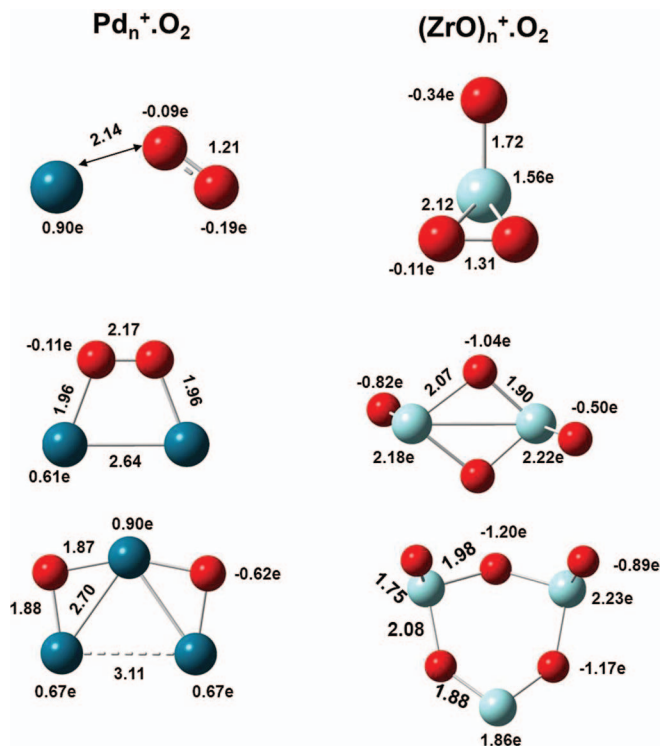


FIG. 6. Ground state geometries of  $\text{O}_2$  interacting with cationic  $\text{Pd}_n^+$  and  $(\text{ZrO})_n^+$  clusters. The bond lengths are given in Å and the NBO charges are given in units of electron charge, e.

and  $(\text{ZrO})_n$  for  $n = 2, 3$  are very similar. Except for  $(\text{ZrO})_3^+$ , the adsorption energies of  $\text{H}_2$  to  $(\text{ZrO})_n^+$  are higher than that to  $\text{Pd}_n^+$ .

#### 2. Interaction with $\text{O}_2$

In Figure 6, we plot the equilibrium geometries of  $\text{Pd}_n^+$  and  $(\text{ZrO})_n^+$  clusters interacting with  $\text{O}_2$ . In both  $\text{Pd}^+$  and  $\text{ZrO}^+$  clusters,  $\text{O}_2$  binds molecularly, although the O–O bond in  $(\text{ZrO})_n^+\text{O}_2$  is stretched more than that in  $\text{Pd}_n^+\text{O}_2$ . In addition,  $\text{O}_2$  binds in *superoxo* form to  $\text{Pd}^+$  while it binds in *peroxo* form to  $\text{ZrO}^+$ , as seen in the case of corresponding neutral counterparts.

The adsorption energies of  $\text{O}_2$  to  $(\text{ZrO})^+$  and  $\text{Pd}^+$  are significantly different;  $\text{ZrO}^+$  binding being about four times larger than that of  $\text{Pd}^+$ . The bonding pattern of  $\text{O}_2$  to  $\text{Pd}_2^+$  and  $(\text{ZrO})_2^+$  are also different. In  $\text{Pd}_2^+\text{O}_2$ , there is significant interaction between the two O atoms, whereas in  $(\text{ZrO})_2^+\text{O}_2$  both the O-atoms binding to each Zr-site are in the *trans* form. The binding energies between  $\text{O}_2$  and  $(\text{ZrO})_2^+$  is six times larger than that between  $\text{O}_2$  and  $\text{Pd}_2^+$ . The O atoms in  $\text{Pd}_3^+\text{O}_2$  and  $(\text{ZrO})_3^+\text{O}_2$  are bound dissociatively. However, they are bridge bonded in  $\text{Pd}_3^+\text{O}_2$  and radially bonded in  $(\text{ZrO})_3^+\text{O}_2$ . The binding energy of  $\text{O}_2$  to  $(\text{ZrO})_3^+$  is about eight times larger than that to  $\text{Pd}_3^+$ .

#### 3. Interaction with CO

In Figure 7, we plot the equilibrium geometries of  $\text{Pd}_n^+$  and  $(\text{ZrO})_n^+$  clusters interacting with CO. The adsorption



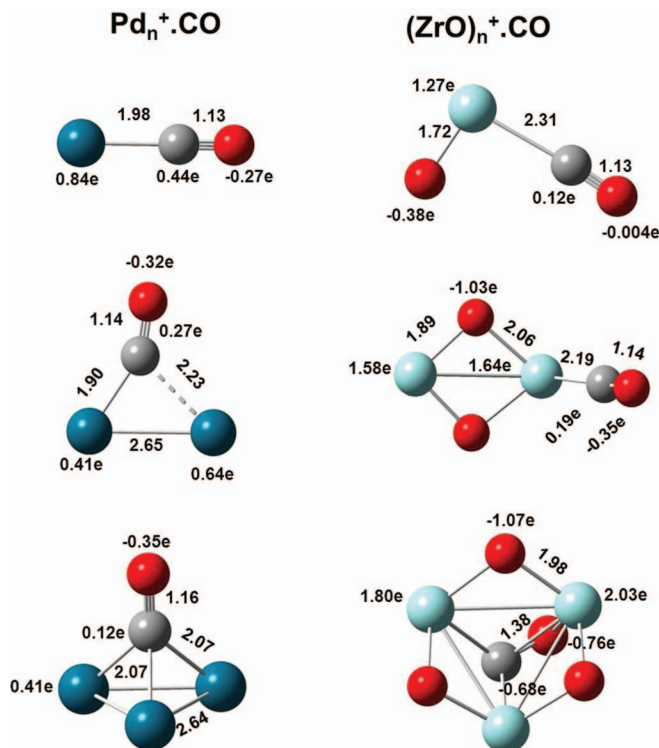


FIG. 7. Ground state geometries of CO interacting with cationic  $\text{Pd}_n^+$  and  $(\text{ZrO})_n^+$  clusters. The bond lengths are given in Å and the NBO charges are given in units of electron charge, e.

energies of the gas molecules are given in Table III. In all clusters, CO binds molecularly with the C-atom attached to the metal atom, except for  $(\text{ZrO})_3^+$  where both C and O bind to two different Zr atoms (similar to its neutral counterpart). Here, the C–O bond is stretched by  $\sim 0.3$  Å. The adsorption energies of CO to  $\text{Pd}_n^+$  and  $(\text{ZrO})_n^+$  are similar for  $n = 1$ , but are different for  $n = 2, 3$ . The spin multiplicities of all these clusters, however, are the same.

#### D. Interaction of gas molecules ( $\text{H}_2$ , $\text{O}_2$ , and CO) with anionic $\text{Pd}_n^-$ and $(\text{ZrO})_n^-$ clusters ( $n = 1-3$ )

In this section, we present the results of  $\text{Pd}_n^-$  and  $(\text{ZrO})_n^-$  clusters interacting with  $\text{H}_2$ ,  $\text{O}_2$ , and CO.

##### 1. Interaction with $\text{H}_2$

The equilibrium geometries of  $\text{Pd}_n^-$  interacting with  $\text{H}_2$  are given in Figure 8. Hydrogen molecule binds dissociatively to both  $\text{Pd}^-$  and  $\text{ZrO}^-$ . We recall that  $\text{H}_2$  binds in quasi-molecular form to neutral Pd as well as to  $\text{Pd}^+$  cation. In the case of  $\text{Pd}^-$ , the extra electron can be donated to the anti-bonding orbital of the  $\text{H}_2$  molecule, breaking the H–H bond. The adsorption energies of the gas molecules are given in Table IV. In  $\text{Pd}_2^-$  and  $(\text{ZrO})_2^-$ , H-atoms again bind dissociatively, but they are radially bonded to both the Pd atoms while they bind to a single Zr atom. In  $\text{Pd}_3^-$  and  $(\text{ZrO})_3^-$ , hydrogen atoms also bind dissociatively. In  $(\text{ZrO})_3^-$ , both hydrogen atoms bind radially to the two Zr atoms. However, in  $\text{Pd}_3^-$  one H atom is bridge bonded while the other is radially

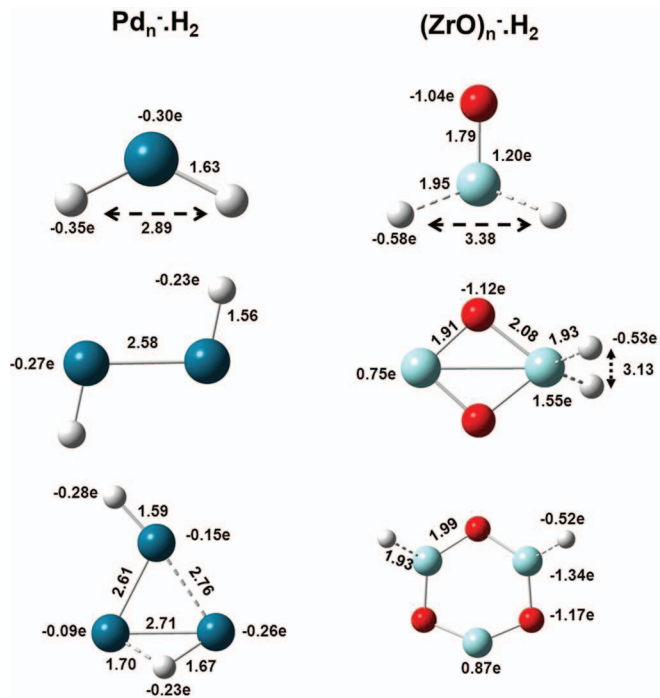


FIG. 8. Ground state geometries of  $\text{H}_2$  interacting with anionic  $\text{Pd}_n^-$  and  $(\text{ZrO})_n^-$  clusters. The bond lengths are given in Å and the NBO charges are given in units of electron charge, e.

bonded. In all these clusters, the adsorption energies of  $\text{H}_2$  to  $(\text{ZrO})_n^-$  are larger than that to  $\text{Pd}_n^-$  clusters. Note that the adsorption of  $\text{H}_2$  to  $\text{Pd}_3^-$  is the lowest as compared to its neutral and cationic counterparts.

##### 2. Interaction with $\text{O}_2$

The equilibrium geometries and binding energies of  $\text{O}_2$  to  $\text{Pd}_n^-$  and  $(\text{ZrO})_n^-$  clusters are given in Figure 9 and Table IV, respectively.

While  $\text{O}_2$  binds in *superoxo* form to  $\text{Pd}^-$ , it binds dissociatively to  $\text{ZrO}^-$ . The NBO charge on the O atoms in the *superoxo* form is  $-0.32e$  while it is  $-1.13e$  in the dissociated form.

The binding energy of  $\text{O}_2$  to  $\text{Pd}^-$  is a factor of four smaller than that to  $\text{ZrO}^-$ . In  $\text{Pd}_2^-$  and  $(\text{ZrO})_2^-$ , the O atoms bind dissociatively, but they are bridge bonded to Pd and radially bonded to Zr. The binding energy of  $\text{O}_2$  to  $(\text{ZrO})_2^-$

TABLE IV. Adsorption energies ( $E_{\text{ads}}$ ) in eV and electronic states in parentheses of  $\text{Pd}_n^-$  and  $(\text{ZrO})_n^-$  ( $n = 1-3$ ) clusters interacting with  $\text{H}_2$ ,  $\text{O}_2$ , and CO.

Cluster	$E_{\text{ads}}$ (eV)		
	$\text{H}_2$	$\text{O}_2$	CO
$\text{ZrO}^-$	1.46 ( $^2A$ )	5.82 ( $^2A$ )	0.84 ( $^4A'''$ )
$\text{Pd}^-$	0.57 ( $^2A'$ )	1.28 ( $^2A'$ )	1.61 ( $^2A'$ )
$(\text{ZrO})_2^-$	2.08 ( $^2A$ )	9.71 ( $^2A$ )	1.29 ( $^2A$ )
$(\text{Pd})_2^-$	1.19 ( $^2A$ )	1.54 ( $^4A_g$ )	2.40 ( $^2A'$ )
$(\text{ZrO})_3^-$	2.22 ( $^4A$ )	9.59 ( $^2A$ )	2.18 ( $^2A$ )
$(\text{Pd})_3^-$	0.69 ( $^2A$ )	2.01 ( $^4A$ )	1.70 ( $^2A$ )



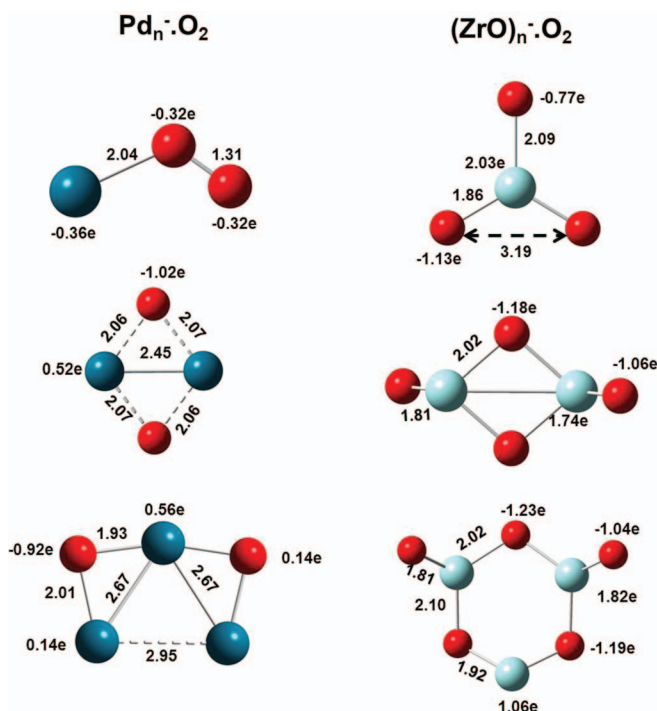


FIG. 9. Ground state geometries of  $\text{O}_2$  interacting with anionic  $\text{Pd}_n^-$  and  $(\text{ZrO})_n^-$  clusters. The bond lengths are given in Å and the NBO charges are given in units of electron charge,  $e$ .

is more than six times as large as it is to  $\text{Pd}_2^-$ . In  $\text{Pd}_3^-$  and  $(\text{ZrO})_3^-$ , O atoms again bind dissociatively, but they are bridge bonded in  $\text{Pd}_3^-$  while they are radially bonded in  $(\text{ZrO})_3^-$ , just as seen in the previous case.

### 3. Interaction with CO

Geometries and binding energies of CO interacting with  $\text{Pd}_n^-$  and  $(\text{ZrO})_n^-$  clusters are given in Figure 10 and

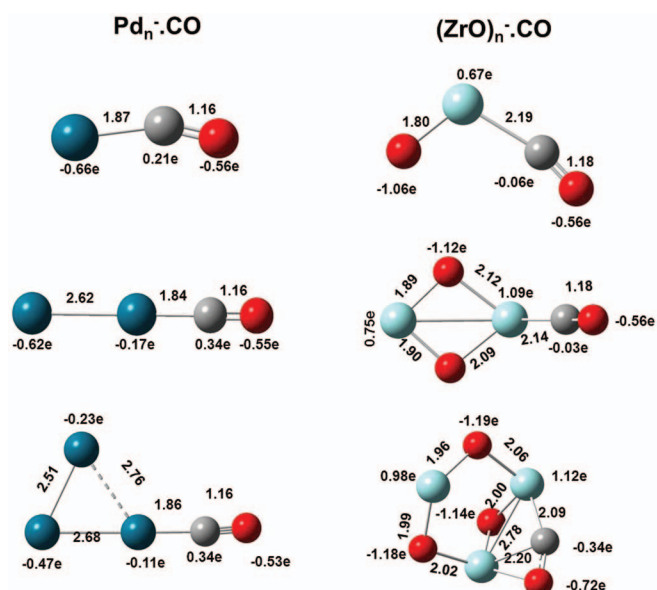


FIG. 10. Ground state geometries of CO interacting with anionic  $\text{Pd}_n^-$  and  $(\text{ZrO})_n^-$  clusters. The bond lengths are given in Å and the NBO charges are given in units of electron charge,  $e$ .

Table IV, respectively. In all cases, CO binds molecularly. With the exception of  $(\text{ZrO})_3^-$  the C atom is attached to a single metal atom in all clusters. In  $(\text{ZrO})_3^-$  the C atom binds to two Zr atoms. The binding energies of CO to  $\text{Pd}_n^-$  are about a factor of two larger than that to  $(\text{ZrO})_n^-$  for  $n = 1, 2$ . However, its binding energy to  $\text{Pd}_3^-$  is smaller than that to  $(\text{ZrO})_3^-$ .

## IV. CONCLUSION

Using density functional theory, we have calculated the equilibrium geometries, electronic structure, and binding affinity of neutral, cationic, and anionic  $\text{Pd}_n$  and  $(\text{ZrO})_n$  ( $n = 1-5$ ) clusters interacting with  $\text{H}_2$ ,  $\text{O}_2$ , and CO molecules. Our objective was to examine to what extent the chemistry of Pd clusters mimics that of their isoelectronic ZrO clusters. The electronic structure was probed by calculating the ionization potential as well as electron affinity while the reaction of the gas molecules was studied by examining the nature of their adsorption and corresponding adsorption energies. In general, neither the electronic structure nor the interaction of gas molecules were found to be similar with few exceptions dealing with the interaction of hydrogen. In particular, we found the interaction of  $\text{Pd}_n$  with  $\text{O}_2$  to be qualitatively different from that between  $(\text{ZrO})_n$  and  $\text{O}_2$ . Thus, our calculations do not support the ansatz put forward by Castleman<sup>11,14,15</sup> and co-workers that ZrO can replace Pd in its function as a catalyst.

## ACKNOWLEDGMENTS

Research was supported by the (U.S.) Department of Energy (DOE), Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award # DE-FG02-96ER45579. We also acknowledge resources of the National Energy Research Scientific Computing Center, which is supported by the Office of Science of the (U.S.) Department of Energy under Contract No. DE-AC02-05CH11231.

- <sup>1</sup>S. Khanna and P. Jena, *Phys. Rev. B* **51**, 13705 (1995).
- <sup>2</sup>W. Knight, K. Clemenger, W. De Heer, W. Saunders, M. Chou, and M. Cohen, *Phys. Rev. Lett.* **52**, 2141 (1984).
- <sup>3</sup>R. Leuchtner, A. Harms, and A. Castleman, *J. Chem. Phys.* **94**, 1093 (1991).
- <sup>4</sup>X. Li, H. B. Wu, X. B. Wang, and L. S. Wang, *Phys. Rev. Lett.* **81**, 1909 (1998).
- <sup>5</sup>S. Khanna and P. Jena, *Chem. Phys. Lett.* **219**, 479 (1994).
- <sup>6</sup>W. J. Zheng, O. C. Thomas, T. P. Lippa, S. J. Xu, and K. H. Bowen, *J. Chem. Phys.* **124**, 144304 (2006).
- <sup>7</sup>G. L. Gutsev and A. I. Boldyrev, *Chem. Phys.* **56**, 277 (1981).
- <sup>8</sup>P. Pyykko and N. Runeberg, *Angew. Chem.-Int. Ed.* **41**, 2174 (2002).
- <sup>9</sup>X. Li, A. Grubisic, S. T. Stokes, J. Cordes, G. F. Gantefoer, K. H. Bowen, B. Kiran, M. Willis, P. Jena, R. Burgert, and H. Schnoekel, *Science* **315**, 356 (2007).
- <sup>10</sup>D. A. Knight, R. Zidan, R. Lascola, R. Mohtadi, C. Ling, P. Sivasubramanian, J. A. Kaduk, S.-J. Hwang, D. Samanta, and P. Jena, *J. Phys. Chem. C* **117**, 19905 (2013).
- <sup>11</sup>S. J. Peppernick, K. D. D. Gunaratne, and A. W. Castleman, *Proc. Natl. Acad. Sci. U.S.A.* **107**, 975 (2010).
- <sup>12</sup>R. Levy and M. Boudart, *Science* **181**, 547 (1973).
- <sup>13</sup>M. Valden, J. Aaltonen, E. Kuusisto, M. Pessa, and C. Barnes, *Surf. Sci.* **307**, 193 (1994).
- <sup>14</sup>A. W. Castleman, *J. Phys. Chem. Lett.* **2**, 1062 (2011).

- <sup>15</sup>E. C. Tyo, A. W. Castleman, A. C. Reber, and S. N. Khanna, *J. Phys. Chem. C* **115**, 16797 (2011).
- <sup>16</sup>M. Che and C. Bennett, *Adv. Catal.* **36**, 55 (1989).
- <sup>17</sup>S. Rather, R. Zacharia, S. W. Hwang, M. Naik, and K. S. Nahm, *Chem. Phys. Lett.* **438**, 78 (2007).
- <sup>18</sup>G. Ertl, *Adv. Catal.* **213**, 37 (1990).
- <sup>19</sup>L. Carrette, K. A. Friedrich, and U. Stimming, *ChemPhysChem* **1**, 162 (2000).
- <sup>20</sup>W. J. Zhou, W. Z. Li, S. Q. Song, Z. H. Zhou, L. H. Jiang, G. Q. Sun, Q. Xin, K. Poulianitis, S. Kontou, and P. Tsiakaras, *J. Power Sources* **131**, 217 (2004).
- <sup>21</sup>A. Becke, *J. Chem. Phys.* **98**, 5648 (1993).
- <sup>22</sup>C. Lee, W. Yang, and R. Parr, *Phys. Rev. B* **37**, 785 (1988).
- <sup>23</sup>M. Dolg, H. Stoll, H. Preuss, and R. Pitzer, *J. Phys. Chem.* **97**, 5852 (1993).
- <sup>24</sup>M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, Gaussian 03, Revision C.02, Gaussian, Inc., Wallingford, CT, 2004.
- <sup>25</sup>Q. Cui, D. G. Musaev, and K. Morokuma, *J. Chem. Phys.* **108**, 8418 (1998).
- <sup>26</sup>J. Moc, D. G. Musaev, and K. Morokuma, *J. Phys. Chem. A* **104**, 11606 (2000).
- <sup>27</sup>G. E. Johnson, R. Mitric, E. C. Tyo, V. Bonacic-Koutecky, and A. W. Castleman, *J. Am. Chem. Soc.* **130**, 13912 (2008).
- <sup>28</sup>M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, Gaussian 03, Revision B.01, Gaussian, Inc., Pittsburgh, PA, 2003.
- <sup>29</sup>B. Kalita and R. C. Deka, *J. Chem. Phys.* **127**, 244306 (2007).
- <sup>30</sup>J. Rogan, G. Garcia, J. A. Valdivia, W. Orellana, A. H. Romero, R. Ramirez, and M. Kiwi, *Phys. Rev. B* **72**, 115421 (2005).
- <sup>31</sup>I. Efremenko and M. Sheintuch, *J. Mol. Catal. A* **160**, 445 (2000).
- <sup>32</sup>M. Ni and Z. Zeng, *J. Mol. Struct.: THEOCHEM* **910**, 14 (2009).
- <sup>33</sup>M. W. Chase, *NIST-JANAF Thermochemical Tables* (American Chemical Society, New York, 1998).
- <sup>34</sup>C. Chieh, *Bond Lengths and Energies* (University of Waterloo, 2007).
- <sup>35</sup>B. deB Darwent, *Bond Dissociation Energies in Simple Molecules (NSRDS-NBS)* (U.S. National Bureau of Standards, Washington, DC, 1970).
- <sup>36</sup>K. P. Huber, and G. Herzberg, *Molecular Spectra and Molecular Structure, Constants of Diatomic Molecules* (Van Nostrand, New York, 1979), Vol. IV, p. 154.
- <sup>37</sup>I. Efremenko, E. D. German, and M. Sheintuch, *J. Phys. Chem. A* **104**, 8089 (2000).
- <sup>38</sup>W. Dong and J. Hafner, *Phys. Rev. B* **56**, 15396 (1997).
- <sup>39</sup>G. J. Kubas, *J. Organomet. Chem.* **635**, 37 (2001).
- <sup>40</sup>G. J. Kubas, *J. Organomet. Chem.* **694**, 2648 (2009).
- <sup>41</sup>Q. Cui, D. G. Musaev, and K. Morokuma, *J. Phys. Chem. A* **102**, 6373 (1998).
- <sup>42</sup>B. Huber, H. Hakkinen, U. Landman, and M. Moseler, *Comput. Mater. Sci.* **35**, 371 (2006).
- <sup>43</sup>G. Zanti and D. Peeters, *Eur. J. Inorg. Chem.* **2009**, 3904 (2009).
- <sup>44</sup>N. E. Schultz, B. F. Gherman, C. J. Cramer, and D. G. Truhlar, *J. Phys. Chem. B* **110**, 24030 (2006).
- <sup>45</sup>J. Niu, B. Rao, and P. Jena, *Phys. Rev. Lett.* **68**, 2277 (1992).
- <sup>46</sup>See supplementary material at <http://dx.doi.org/10.1063/1.4887086> for the isomers of H<sub>2</sub>, O<sub>2</sub>, and CO adsorbed on neutral Pd<sub>n</sub> and (ZrO)<sub>n</sub> (n = 1-3). The energy difference ΔE (in eV) of the isomers with respect to its ground state is given.