

## Reaction Intermediates of CO Oxidation on Gas Phase Pd<sub>4</sub> Clusters: A Density Functional Study

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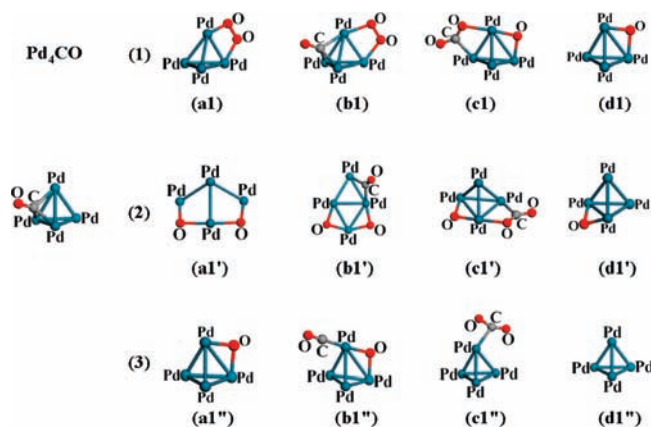
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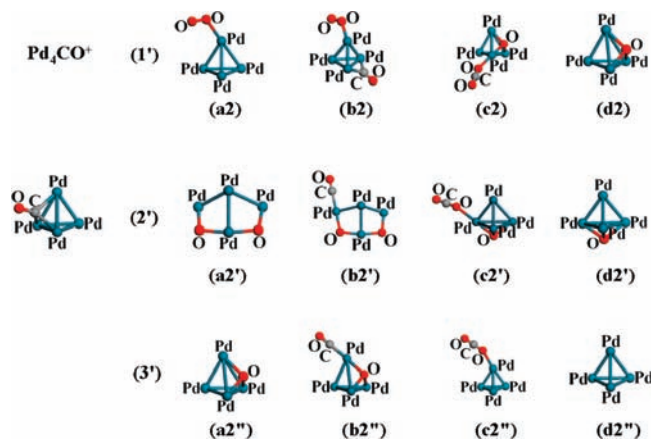
Removal of poisonous carbon monoxide gas emitted mainly in automobile exhaust is a major challenge in catalysis research and has been a subject of many investigations. Precious metals, namely palladium, platinum, and rhodium are efficient catalysts for oxidation of CO with O<sub>2</sub>.<sup>1,2</sup> Thus understanding the adsorption mechanism, dissociation of oxygen, and oxidation of CO at molecular level is of great importance in designing suitable catalysts. Engel and Ertl<sup>3</sup> proposed that oxidation occurs via a Langmuir–Hinshelwood mechanism, in which CO molecules adsorb on the surface and react with chemisorbed oxygen. Experimental studies have also shown that complete dissociation of adsorbed O<sub>2</sub> is needed for oxidation of CO on a Pd surface.<sup>3</sup> Adsorption sites of single CO molecule on a supported Pd<sub>4</sub> cluster have been studied by Hubar and Moseler<sup>4</sup> using density functional theory. Charges of small palladium clusters play significant roles in controlling their catalytic activity.<sup>5–7</sup> In a recent paper, we have reported the various adsorption sites of the CO molecule on neutral and charged Pd<sub>n</sub> (n = 1–7) clusters.<sup>8</sup>

In this communication, for the first time, we have presented a systematic study on the structure and energetics of various reaction intermediates involved in CO oxidation by neutral and charged Pd<sub>4</sub> clusters using density functional theory (DFT). We performed scalar relativistic DFT calculations as implemented in the DMol<sup>3</sup> package<sup>9</sup> using the DNP basis set and BLYP functional. The reliability of this basis set and functional can be judged from the binding energy values of O<sub>2</sub> (–5.72 eV) and CO<sub>2</sub> (–5.76 eV) that are in agreement with the experimental values:<sup>10</sup> –5.12, –5.50 eV, respectively. In our calculations, self-consistent field procedures are performed with a convergence criterion of 2 × 10<sup>–5</sup> a.u. on the total energy and 10<sup>–6</sup> a.u. on the electron density.

First, a large number of geometries have been optimized for adsorption of various oxygen species (O<sub>2</sub>, 2O, and O), CO, and CO<sub>2</sub> at different adsorption sites of Pd<sub>4</sub><sup>0, ±</sup> clusters by varying their spin multiplicities. The lowest energy neutral and charged Pd<sub>4</sub>–O<sub>2</sub>, Pd<sub>4</sub>–2O, and Pd<sub>4</sub>–O structures are chosen to study the possible complexes corresponding to the coadsorption of O<sub>2</sub>+CO, 2O+CO, O+CO, and O+CO<sub>2</sub>. Frequency calculations have been performed for all the structures, and none of them is found to exhibit any imaginary frequency. Absence of an imaginary frequency verifies the structures to be stable. The zero-point vibrational energy corrections have been included in all



**Figure 1.** Lowest energy structures of Pd<sub>4</sub>CO (first column) and the reaction intermediates of: (a1) Pd<sub>4</sub>O<sub>2</sub>, (b1) Pd<sub>4</sub>O<sub>2</sub>CO, (c1) Pd<sub>4</sub>OCO<sub>2</sub>, (d1) Pd<sub>4</sub>O involved in reaction (1) Pd<sub>4</sub> + O<sub>2</sub> + CO → Pd<sub>4</sub>O + CO<sub>2</sub>; (a1′) Pd<sub>4</sub>2O, (b1′) Pd<sub>4</sub>2OCO, (c1′) Pd<sub>4</sub>OCO<sub>2</sub>, (d1′) Pd<sub>4</sub>O involved in reaction (2) Pd<sub>4</sub> + 2O + CO → Pd<sub>4</sub>O + CO<sub>2</sub> and (a1″) Pd<sub>4</sub>O, (b1″) Pd<sub>4</sub>OCO, (c1″) Pd<sub>4</sub>CO<sub>2</sub>, (d1″) Pd<sub>4</sub> involved in reaction (3) Pd<sub>4</sub> + O + CO → Pd<sub>4</sub> + CO<sub>2</sub>.



**Figure 2.** Lowest energy structures of Pd<sub>4</sub>CO<sup>+</sup> (first column) and the reaction intermediates of: (a2) Pd<sub>4</sub>O<sub>2</sub><sup>+</sup>, (b2) Pd<sub>4</sub>O<sub>2</sub>CO<sup>+</sup>, (c2) Pd<sub>4</sub>OCO<sub>2</sub><sup>+</sup>, (d2) Pd<sub>4</sub>O<sup>+</sup> involved in reaction (1′) Pd<sub>4</sub><sup>+</sup>+O<sub>2</sub> + CO → Pd<sub>4</sub>O<sup>+</sup> + CO<sub>2</sub>; (a2′) Pd<sub>4</sub>2O<sup>+</sup>, (b2′) Pd<sub>4</sub>2OCO<sup>+</sup>, (c2′) Pd<sub>4</sub>OCO<sub>2</sub><sup>+</sup>, (d2′) Pd<sub>4</sub>O<sup>+</sup> involved in reaction (2′) Pd<sub>4</sub><sup>+</sup> + 2O + CO → Pd<sub>4</sub>O<sup>+</sup> + CO<sub>2</sub> and (a2″) Pd<sub>4</sub>O<sup>+</sup>, (b2″) Pd<sub>4</sub>OCO<sup>+</sup>, (c2″) Pd<sub>4</sub>CO<sub>2</sub><sup>+</sup>, (d2″) Pd<sub>4</sub><sup>+</sup> involved in reaction (3′) Pd<sub>4</sub><sup>+</sup> + O + CO → Pd<sub>4</sub><sup>+</sup> + CO<sub>2</sub>.

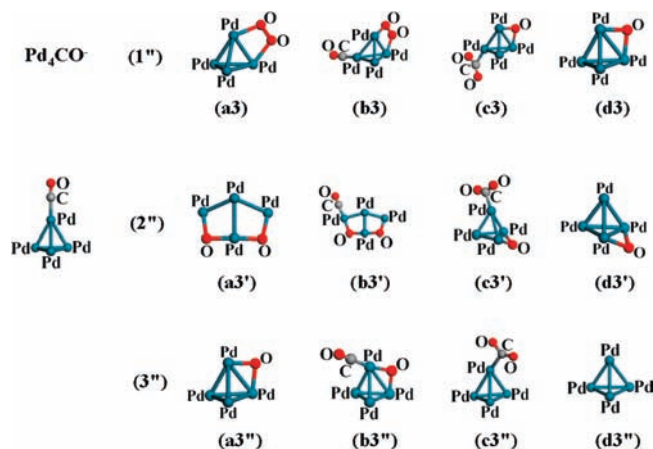
calculations. The zero-point energy (ZPE) corrected binding energy (BE) of adsorbate A with a Pd<sub>4</sub><sup>0, ±</sup> cluster is defined as

$$BE = (E_{total} - E_{Pd_4^{\pm}} - E_A) + (E_{total}^{ZPE} - E_{Pd_4^{\pm}}^{ZPE} - E_A^{ZPE})$$

where  $E_{total}$  is the total energy of the  $Pd_4^{0,\pm}$  cluster with adsorbed A on it,  $E_{Pd_4^{\pm}}$  is the energy of the  $Pd_4^{0,\pm}$  cluster, and  $E_A$  is the energy of the free A molecule. A more negative BE corresponds to stronger adsorption.

The lowest energy geometries of molecular adsorption (MA), dissociative adsorption (DA), and atomic adsorption (AA) of oxygen on neutral, cationic, and anionic  $Pd_4$  clusters are shown in Figure 1 (a1), (a1'), (a1''); Figure 2 (a2), (a2'), (a2''); and Figure 3 (a3), (a3'), (a3''), respectively. Molecular adsorption (MA) of  $O_2$  takes place preferably in the bridge position of neutral and anionic  $Pd_4$  with triplet and quartet states, respectively. For cationic  $Pd_4$ , adsorption of  $O_2$  takes place in the atop position ( $\angle Pd-O-O = 126.7^\circ$ ) of  $Pd_4$  with a doublet state. Dissociative adsorption of  $O_2$  with the oxygen atoms occupying bridge sites of palladium clusters appears to be energetically most favorable in neutral (singlet state), cationic (doublet state), and anionic (doublet state)  $Pd_4$  clusters. All the lowest energy DA complexes are highly distorted from the gas phase tetrahedral  $Pd_4$  clusters.<sup>11</sup> For neutral, cationic, and anionic  $Pd_4O_2$  complexes, the lowest energy DA structures lie 0.81, 0.83, and 1.13 eV lower in energy than the corresponding most stable MA structures, respectively. Calculated values of binding energies in MA complexes follow the trend:  $Pd_4^- (-2.27 \text{ eV}) > Pd_4 (-1.14 \text{ eV}) > Pd_4^+ (-0.82 \text{ eV})$ . A similar trend is also observed in the case of DA complexes with maximum BE for the  $Pd_4^-$  cluster ( $-3.39 \text{ eV}$ ) followed by  $Pd_4^+$  ( $-1.98 \text{ eV}$ ) and  $Pd_4$  ( $-1.63 \text{ eV}$ ) clusters. Our calculated BE for neutral complexes are higher than the results of Huber et al.<sup>12</sup> We have observed that the O–O bond distances of the adsorbed  $O_2$  molecule in neutral (1.35 Å in MA and 3.86 Å in DA), cationic (1.25 Å in MA and 3.80 Å in DA), and anionic (1.40 Å in MA and 3.90 Å in DA) complexes are larger than that in the free molecule (1.21 Å), being maximum for the dissociative adsorption of oxygen on anionic  $Pd_4$  cluster. Mulliken charge analysis shows that electron charge transfer from palladium to adsorbed  $O_2$  (both in MA and DA) takes place in the order  $Pd_4^- > Pd_4 > Pd_4^+$ . This trend is similar to that of the O–O bond distance, which is due to the fact that metal→oxygen back-donation increases the population of  $\pi^*$  orbital leading to the weakening and lengthening of O–O bonds. Our computed O–O bond length values in neutral complexes are in excellent agreement with those of Huber et al.<sup>12</sup> Adsorption of atomic oxygen takes place in the bridge sites of neutral (singlet state) and anionic  $Pd_4$  (doublet state) clusters, while hollow site adsorption is preferred by O in the cationic  $Pd_4-O$  complex (doublet state). The adsorption site and the Pd–O bond length (1.94 Å) of the neutral  $Pd_4-O$  complex are in agreement with those of Rösch and co-workers.<sup>13</sup> Binding energies of O with neutral, cationic, and anionic  $Pd_4$  clusters are found to be  $-0.66$ ,  $-0.67$ , and  $-1.19 \text{ eV}$ , respectively.

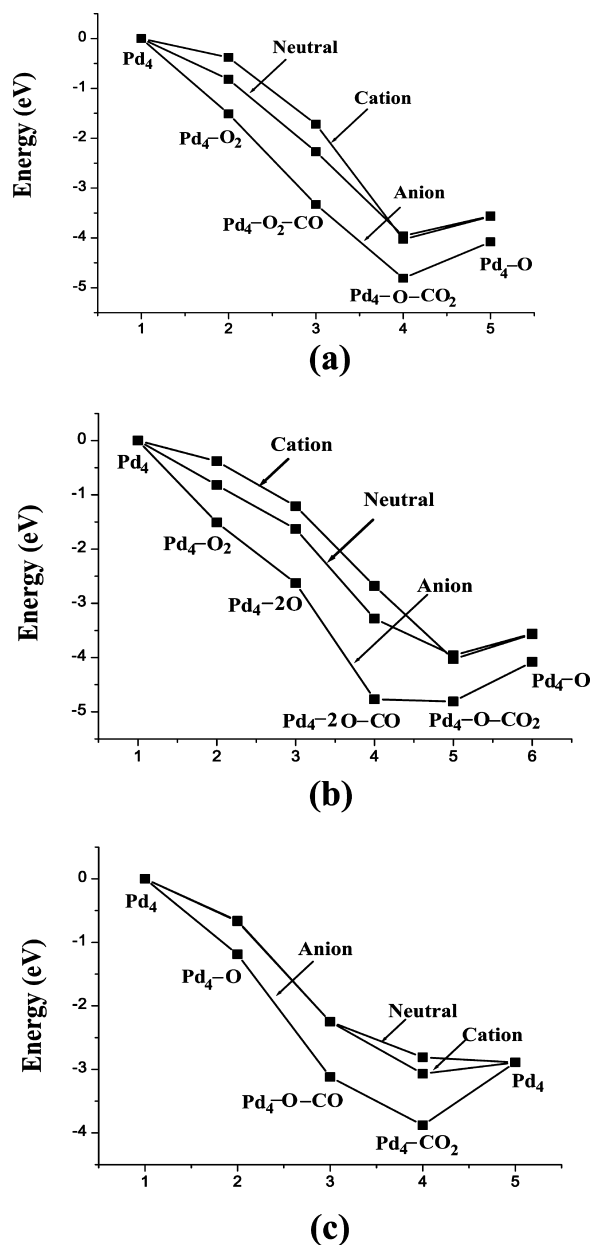
Lowest energy structures of neutral, cationic, and anionic  $Pd_4CO$  complexes are shown in the first columns of Figures 1, 2, and 3, respectively. It has been observed that the CO molecule is adsorbed in the 3-fold position of  $Pd_4^{0,+}$  and slightly tilted at the on-top ( $\angle Pd-C-O=179.6^\circ$ ) adsorption site in  $Pd_4^-$  cluster. The BE of CO in these complexes are in the order of  $Pd_4^- (-1.95$



**Figure 3.** Lowest energy structures of  $Pd_4CO^-$  (first column) and the reaction intermediates of: (a3)  $Pd_4O_2^-$ , (b3)  $Pd_4O_2CO^-$ , (c3)  $Pd_4OCO_2^-$ , (d3)  $Pd_4O^-$  involved in reaction (1'')  $Pd_4^- + O_2 + CO \rightarrow Pd_4O^- + CO_2$ ; (a3')  $Pd_4O_2^-$ , (b3')  $Pd_4O_2CO^-$ , (c3')  $Pd_4OCO_2^-$ , (d3')  $Pd_4O^-$  involved in reaction (2'')  $Pd_4^- + 2O + CO \rightarrow Pd_4O^- + CO_2$  and (a3'')  $Pd_4O^-$ , (b3'')  $Pd_4OCO^-$ , (c3'')  $Pd_4CO_2^-$ , (d3'')  $Pd_4^-$  involved in reaction (3'')  $Pd_4^- + O + CO \rightarrow Pd_4^- + CO_2$ .

eV)  $> Pd_4^+ (-1.37 \text{ eV}) > Pd_4 (-1.32 \text{ eV})$ . Figure 1(c1''), Figure 2(c2''), and Figure 3(c3'') show the lowest energy structures of  $Pd_4-CO_2^{0,\pm}$  complexes. It is seen from the figures that the  $CO_2$  molecule binds to neutral and anionic  $Pd_4$  clusters through the C atom, while  $CO_2$  adsorption in the cationic  $Pd_4$  cluster takes place through one of its O atoms. Mulliken charge analysis shows that in neutral and anionic  $Pd_4-CO_2$  complexes, the C atom of  $CO_2$  withdraws charge from the palladium atom to which it is connected. On the other hand, charge transfer occurs from the O to the Pd atom of  $Pd_4^+$ , which participates in Pd–O bonding. This charge transfer is accompanied by a flow of electron inside the  $CO_2$  molecule in the direction of  $O \rightarrow C \rightarrow O \rightarrow Pd$ . The BE of the adsorbates with neutral and anionic  $Pd_4$  clusters follows the order  $CO > O_2 > O > CO_2$ . This observation agrees well with the previous experimental study<sup>5</sup> on reactivity order of palladium cluster anions. A small positive value of BE for  $CO_2$  with neutral  $Pd_4$  cluster signifies the repulsive nature of the adsorption process. This is in agreement with the observation that surface reactions of nickel group metals with  $CO_2$  at room temperature result in no adsorption or dissociation of  $CO_2$ .<sup>14</sup>

We have chosen the lowest energy adsorption complexes of oxidized  $Pd_4$  clusters to further investigate the coadsorption of  $O_2+CO$ ,  $2O+CO$ ,  $O+CO$ , and  $O+CO_2$  on gas-phase  $Pd_4^{0,\pm}$  clusters. The lowest energy structures of the coadsorption complexes of neutral, cationic, and anionic  $Pd_4$  clusters are shown in Figure 1 (b1, c1, b1', c1', b1'', c1''); Figure 2 (b2, c2, b2', c2', b2'', c2''), and Figure 3 (b3, c3, b3', c3', b3'', c3''), respectively. It is observed that, among the lowest energy  $Pd_4-O-CO_2$  coadsorption complexes, the  $CO_2$  molecule binds through one of its O atoms and the C atom in cationic and anionic  $Pd_4O$ , respectively. The charge transfer processes in these two complexes are similar to those of  $Pd_4-CO_2^{\pm}$  complexes. In the case of the neutral  $Pd_4-O-CO_2$  complex, binding of the  $CO_2$  molecule with  $Pd_4O$  takes place through the C and one O atom. In this complex, both the C and O atoms withdraw charge from the Pd atoms to which they are coordinated.



**Figure 4.** Energetic profiles of complete reaction cycles for CO oxidation on Pd<sub>4</sub><sup>0, ±</sup> clusters: (a) molecular O<sub>2</sub>, (b) dissociated O<sub>2</sub>, and (c) a single atomic O reacting with CO.

With the available data, we have constructed and compared three different reaction pathways: Pd<sub>4</sub>+O<sub>2</sub>+CO → Pd<sub>4</sub>O+CO<sub>2</sub>, Pd<sub>4</sub>+2O+CO → Pd<sub>4</sub>O+CO<sub>2</sub>, and Pd<sub>4</sub>+O+CO → Pd<sub>4</sub>+CO<sub>2</sub>, which combine CO with molecular, dissociated, and atomic forms of oxygen on neutral, cationic, and anionic Pd<sub>4</sub> clusters

to produce CO<sub>2</sub>. Figure 4 shows the calculated energy profiles of these reactions. It is seen from the figure that there is a deep energy sink on the potential energy surface of the CO oxidation process on the anionic Pd<sub>4</sub> cluster due to its strong binding energies with CO and CO<sub>2</sub>. This indicates worse reaction energetics for the CO oxidation process by the Pd<sub>4</sub><sup>-</sup> cluster hindering the formation and desorption of CO<sub>2</sub> in comparison with those of neutral and cationic Pd<sub>4</sub> clusters. Further, among the three reaction channels (Figure 4a, b, and c), the reaction energy profile for dissociated oxygen is found to be more exothermic in nature and it exhibits a shallower sink than those for molecular and atomic oxygens. Therefore, dissociated oxygen may be considered as a superior oxidant for CO oxidation on gas-phase tetra palladium clusters.

In summary, by investigating the possible reaction paths for CO oxidation over Pd<sub>4</sub> clusters, we have found that Pd<sub>4</sub><sup>0</sup> and Pd<sub>4</sub><sup>+</sup> clusters are more suitable catalysts compared to Pd<sub>4</sub><sup>-</sup>. In addition, the dissociated form of the oxygen molecule is found to be a better oxidant than its molecular and atomic forms. These arguments could be utilized in studying clusters with larger size, clusters of other metals, and supported metal clusters. Experiments using neutral and cationic palladium clusters as catalysts for oxidation of CO would be instructive.

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