

Density functional study on the structural, frontier orbital, electronic, and magnetic properties of the transitional metal clusters $\text{Pd}_5(\text{CO})_n$ ($n = 1$ to 6)

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Abstract. The generalized gradient approximation based on density functional theory is used to analyze the structural, electronic, and magnetic properties of the transition metal clusters $\text{Pd}_5(\text{CO})_n$ ($n=1$ to 6). For Pd_5CO , the most stable isomer is the singlet state structure with C atom adsorbed on the hollow site in the form of CO molecule, as same as the conclusion reported by Zanti *et al* (Eur. J. Inorg. Chem. 2009, 3904). In the most stable isomers of $\text{Pd}_5(\text{CO})_2$ and $\text{Pd}_5(\text{CO})_3$, the first CO molecule is adsorbed on the hollow site, while the second and the third CO molecules are adsorbed on the bridge sites, whereas, for the most stable $\text{Pd}_5(\text{CO})_n$ ($n=4,5,6$), all CO molecules are adsorbed on the bridge sites. It is known from the adsorption energy that $\text{Pd}_5(\text{CO})_2$ should be the most possible adsorption product. The energy gap indicates that $\text{Pd}_5(\text{CO})_n$ ($n=1$ to 6) have the enhanced dynamical stability compared to Pd_5 , and $\text{Pd}_5(\text{CO})_3$ should be most dynamically stable of all. The chemisorptions of CO molecules onto the Pd_5 cluster are non-dissociative and the strength of C-O bond becomes weaker while more CO molecules are adsorbed. Along with the increase of the CO molecules in $\text{Pd}_5(\text{CO})_n$ ($n=1$ to 6), the ability for detaching electrons is weakened and that for obtaining electrons is improved. The magnetic moment of Pd_5 is $2\mu_B$, however, $\text{Pd}_5(\text{CO})_n$ ($n=1$ to 6) have no magnetic moment.

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Key words: Pd_5 , Pd_5CO , $\text{Pd}_5(\text{CO})_n$, density functional theory, geometric structure, electronic properties

1 Introduction

Because of the closed-shell configuration and unusual magnetic property of the Pd atom, Palladium clusters have become a kind of very important catalytic materials, which have

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been widely researched. Experimentally, Judai *et al.*[1] have reported that the small Pd_n ($n < 31$) clusters not only could tune a catalytic process by changing the cluster size, but also could catalyze chemical reactions at low temperature. Theoretically, Ni *et al.*[2] have explored that H_2 was either physically adsorbed to the Pd atom in some cases, or chemically dissociated to be H atoms in other cases. Endou *et al.*[3] have found that when NO is adsorbed on Pd_2 , there exists charge transfer between NO and Pd_2 , leading to the increase of the strength of the N-O bond. Qiu *et al.*[4] have reported the high stabilities and narrowing of the HOMO-LUMO energy gaps for the Pd_nS ($n = 3, 5, 7$) clusters. Dufaur *et al.*[5] have discovered that the strength of the N-O bond is dramatically weakened when the molecule is adsorbed on the small Pd_n clusters due essentially to an electrostatic repulsion between N and O.

As is known, the adsorption mechanism of CO molecules on the transitional metal clusters surface has become a hot research topic. For example, Tian *et al.*[6] have found that the CO molecule are adsorbed on the atop site of the Pd_n clusters for $n = 2, 4, 7, 8$ and on the bridge site for $n = 3, 5, 6$. Zanti *et al.*[7] have explored the most stable structure of Pd_5 is a trigonal bipyramid with the D_{3h} symmetry, moreover, the Pd_5CO isomer with C atom adsorbed on the hollow site in the CO molecule form is the most stable, as same as the conclusion gotten by us, but the detailed analysis about the electronic structure have not been paid attention to. Ge *et al.*[8] have shown that the Pd_5CO cluster with O atom adsorbed on the atop site in the CO molecule form should be the most stable. Kalita *et al.*[9] have reported that the C atom of CO adsorbed on the top site in the lowest energy structure of Pd_5CO , which did not accord with our results. Therefore, in order to explicitly know the adsorption position and adsorption manner of CO in the most stable Pd_5CO structure, this article intends to study the geometric structure and electronic properties of Pd_5CO in detail. Furthermore, there have been no research reported for $\text{Pd}_5(\text{CO})_n$ ($n = 2$ to 6) clusters until now, so this article will continue to study the geometric, electronic, and magnetic properties of $\text{Pd}_5(\text{CO})_n$ ($n = 2$ to 6) molecules.

This paper chose the Pd_5 cluster for research for two main reasons. On one hand, the Pd_5 cluster was found very active [10]. Generally, the reaction is more likely occurred between the most active molecules. For example, the Mn_n ($n=3,6,8$) clusters have strong activity, and their corresponding CO complexes possess high adsorption ability [6]. Moreover, the most stable $\text{La}_2@\text{C}_{72}$ was formed by doping the most active C_{72} isomer with two La atoms [11]. On the other hand, the most stable structure of Pd_5 is a trigonal bipyramid with the high symmetry [1-10], therefore, the isomers for the Pd_5CO clusters will be relatively less. This paper mainly focuses on the following three specific issues:

- (1) What is the most stable structure of Pd_5 ?
- (2) What are the most stable structures of $\text{Pd}_5(\text{CO})_n$ ($n=1$ to 6)?
- (3) What are the electronic properties and magnetic properties of the most stable structures of $\text{Pd}_5(\text{CO})_n$ ($n = 1$ to 6)?