DFT study of adsorption of CO₂ on palladium cluster doped by transition metal

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Abstract. We report on a theoretical study of CO₂ adsorption on Pd₆-M (M: Ni, Cu, Pt, Rh) cluster using first-principles density functional theory (DFT) calculations. We find that CO₂ molecule is adsorbed with a bidendate configuration on Pd₇ and on most of Pd₆-M clusters. The bidendate adsorption configuration is formed due to the filling of the unoccupied πᵤ* orbital of CO₂ molecule upon its interaction with d-orbitals of the cluster. We find that transition metal doping could modify the adsorption energy, adsorption site and adsorption configuration of CO₂ molecule on Pd₆ cluster. We also predict that the usage of Pd₆-M clusters as CO₂ hydrogenation catalysts might facilitate the formations of HCOO/COOH.

1. Introduction

Global warming is one of the most serious problems that the humanity facing today. The root of this problem is the excessive carbon dioxide (CO₂) emission to the atmosphere. Such excessive emission might be reduced by applying CO₂ utilization. One of the possible schemes for CO₂ utilization is the conversion of CO₂ into methanol (CH₃OH) through hydrogenation process. The hydrogenation of CO₂ into methanol has also become a very important research topic in the alternative energy research field due to potential applications of methanol [1]. Methanol can be used as convenient liquid fuel for an internal combustion engine and direct methanol fuel cell (DMFC) [1]. Moreover, methanol also provides an efficient way to store hydrogen atoms [2, 3].

At large industry, the hydrogenation process of CO₂ into methanol is performed at high pressure using Cu/ZnO/Al₂O₃ catalyst [4]. However, the highest CO₂ conversion methanol rate on this well developed catalyst is still only about 25% [5]. Therefore, the development of new catalysts that have better performance is needed.
As an attempt to overcome this challenge, we try to use palladium cluster (Pd₇) doped by transition metal (Pd₇M; M= Ni, Cu, Pt, Rh) as a candidate for a new \( \text{CO}_2 \) hydrogenation catalyst. The use of Pd cluster as a candidate for \( \text{CO}_2 \) hydrogenation catalyst is motivated by the unique size-effects of metal cluster that usually results in a better catalytic activity as compared to the catalytic activity of flat surface. The \( \text{CO}_2 \) conversion to methanol requires the presence of adsorbed H atoms on the catalyst surface. A good \( \text{CO}_2 \) hydrogenation catalyst must be able to provide these H atoms through the dissociation of the incoming \( \text{H}_2 \) molecule. A previous theoretical study reports that Pd₇ cluster can facilitate the \( \text{H}_2 \) dissociation process as compared to the other Pdₓ clusters [6]. Therefore, we use this Pd₇ cluster as the basic of our cluster model. Transition metals doping are also introduced to modify the cluster-adsorbate interaction.

As an initial study, we perform theoretical investigation of \( \text{CO}_2 \) adsorption on Pd₆M clusters using density functional theory (DFT) calculations. This adsorption is the initial step of the \( \text{CO}_2 \) hydrogenation process to form methanol. The knowledge of this \( \text{CO}_2 \) adsorption state will provide some insights on how the subsequent hydrogenation step might proceed.

2. Computational Details
All calculations are carried out using the Gaussian 09 program [7]. We use the B3LYP exchange-correlation functional and mixed basis sets to perform geometry optimization, following ref [8]. The 6-31++G** basis sets are used for light atoms (H, C and O) and the double valence orbital (LANL2DZ) basis sets with an effective core potential are used for Pd, Cu, Ni, Pt and Rh atoms.

We use the natural bond orbital (NBO) population scheme for molecular orbital analysis and atomic charge calculations [9]. PdₓM clusters are spin-polarized systems, but spin contamination is considered to be sufficiently small and does not affect the bond distances because all the calculated \( <S^2> \) values vary by less than 10% of the corresponding ideal values[10]. To obtain the difference in electron population of a molecule before and after adsorption (\( \Delta q_{\text{CO}_2} \)), we subtract the total population of valence electrons on each atom of interest.

To obtain the most stable configuration of \( \text{CO}_2 \) adsorption on PdₓM clusters, we initially put \( \text{CO}_2 \) molecule on various possible adsorption sites on the clusters and perform geometry optimization without any geometry constraint. We then choose the most stable adsorption configurations (with the lowest total energy) from each clusters and disregard the other adsorption states. The adsorption energy of a molecule on PdₓM cluster is defined as:

\[
E_{\text{ad}} = E_{\text{tot}} - (E_{\text{Pd}_x\text{M}} + E_{\text{CO}_2} + \Delta ZPE),
\]

where \( E_{\text{tot}} \) corresponds to the total energy of combined system, \( E_{\text{Pd}_x\text{M}} \) corresponds to the total energy of PdₓM cluster, \( E_{\text{CO}_2} \) corresponds to the total energy of \( \text{CO}_2 \)molecule and \( \Delta ZPE \) is the difference in the zero-point energy correction for the total system and the isolated systems. The corresponding spin configurations for the calculation of \( E_{\text{tot}} \), \( E_{\text{Pd}_x\text{M}} \) and \( E_{\text{CO}_2} \) are set in their respective spin groundstate configurations. In this formulation, negative adsorption energy refers to stable adsorption and vice versa.
3. Results and Discussions

3.1. Pd\textsubscript{6}M clusters

The structure of Pd\textsubscript{7} cluster is shown in Fig. 1a. To get the most stable geometry of Pd\textsubscript{6}M cluster, one of Pd atoms of Pd\textsubscript{7} cluster is substituted by an M atom and geometry optimization is performed for all of possible spin multiplicities configurations. This procedure is repeated for each of Pd atoms which are labeled as 1-7 in Fig. 1a and the calculated total energies of these Pd\textsubscript{6}M clusters are then compared to get Pd\textsubscript{6}M configuration with the lowest total energy.

The most stable geometry of Pd\textsubscript{6}M clusters are shown in Figs. 1b-e. Cu, Ni and Rh atoms prefer to substitute atom Pd at site no 3 while Pt atom prefers to substitute atom Pd at site no 2. Strong geometry reconstruction is only found on Pd\textsubscript{6}Rh cluster while the other clusters only have relatively weak geometry reconstruction.

3.2. CO\textsubscript{2} adsorption

The optimized geometries and important ground state parameters of CO\textsubscript{2} adsorption on Pd\textsubscript{6}M clusters are presented on Fig. 2 and Table 1. CO\textsubscript{2} molecule is adsorbed with a bidendate configuration on Pd\textsubscript{7} and most of Pd\textsubscript{6}M clusters, except on Pd\textsubscript{6}Pt cluster where CO\textsubscript{2} molecule is only physically adsorbed in its linear conformation.

The formation of bidendate adsorption configuration is originated from the interaction of \textit{d}-orbitals of the cluster and lowest unoccupied molecular orbitals (LUMOs: \(\pi^*\)) of CO\textsubscript{2} molecule. Upon this interaction, some charge are donated from the cluster to the unoccupied \(\pi^*\) orbital of CO\textsubscript{2} molecule. The occupancy of this \(\pi^*\) orbital enhances the repulsion between C and O atoms of CO\textsubscript{2} molecule. To reduce this repulsion, the C-O bonds of CO\textsubscript{2} molecule are elongated and the linearity of O-C-O angle is broken upon adsorption and hence the bidendate adsorption configuration is formed. The data in Table 1 clearly demonstrate that the C-O bonds of the chemically adsorbed CO\textsubscript{2} molecule are elongated as compared to the C-O bonds of a free CO\textsubscript{2} molecule (\(\sim 1.169\ \text{Å}\)).
The amount of final extra charges which are donated to the adsorbed CO$_2$ molecule (\(\Delta q_{\text{CO}_2}\)) are shown in Table 1. The data shows that the more extra charges reside in the adsorbed CO$_2$ molecule the stronger the CO$_2$ adsorption energy. It is also clear from the data that the \(\Delta q_{\text{CO}_2}\) in Pd$_6$Pt is very small and positive, indicating a weak Pd$_6$Pt-CO$_2$S interaction. The physisorbed CO$_2$ molecule maintains its linear conformation since no extra charges are donated to the \(\pi_u^*\) orbital of the molecule.

Notice that geometry reconstruction is also occurred on the clusters when they interact with CO$_2$ molecule. This process allows the clusters to rearrange their \(d\)-orbitals configuration so that these orbitals could easily interact with the \(\pi_u^*\) orbital of CO$_2$ molecule to facilitate the formation of bidendate adsorption configuration. This geometry reconstruction is quite noticeable from Fig. 2. The change in Pd-X distance before and after CO$_2$ adsorption also demonstrates this geometry reconstruction (see Table 1, the definition of X is explained in the Table caption).

Figure 2 also shows that the adsorbed CO$_2$ molecule binds to the Pd-Pd atoms (sites no 1 and 2 of Fig. 1a) of Pd$_7$ and Pd$_6$Rh clusters while it binds to the Pd-M atoms (sites no 2 and 3) of Pd$_6$Cu and Pd$_6$Ni clusters. Moreover, the CO$_2$ adsorption energies on Pd$_6$Cu and Pd$_6$Ni clusters are stronger than that on Pd$_7$ and Pd$_6$Rh clusters. These results demonstrate that transition metal doping could modify the adsorption energy, adsorption site and adsorption configuration of CO$_2$ molecule on Pd$_7$ cluster.

![Figure 2](image)

**Table 1.** Important ground state parameters for CO$_2$ adsorption on Pd$_7$ and Pd$_6$M clusters. X corresponds to the transition metal atom of the cluster that O1 atom binds to.

| Cluster | Before adsorption | | | After adsorption | | | | |
|---|---|---|---|---|---|---|---|---|
| | Pd-X (Å) | Pd-C (Å) | X-O1 (Å) | C-O1 (Å) | C-O2 (Å) | O1-C-O2 (°) | \(E_{\text{ad}}\) (eV) | \(\Delta q_{\text{CO}_2}\) (e) | Ads Site |
| Pd$_7$ | 2.592 | 2.827 | 2.012 | 2.248 | 1.232 | 1.218 | 143.61 | -0.23 | -0.12 | Pd-Pd |
| Pd$_6$Cu | 2.579 | 2.713 | 1.998 | 2.082 | 1.237 | 1.218 | 143.10 | -0.47 | -0.39 | Pd-Cu |
| Pd$_6$Ni | 2.466 | 2.774 | 1.995 | 2.034 | 1.245 | 1.216 | 141.08 | -0.43 | -0.38 | Pd-Ni |
| Pd$_6$Pt | 2.599 | 2.616 | 3.354 | 4.311 | 1.166 | 1.174 | 179.09 | -0.01 | 0.04 | - |
| Pd$_6$Rh | 2.750 | 2.760 | 2.021 | 2.276 | 1.229 | 1.217 | 144.56 | -0.25 | -0.34 | Pd-Pd |
3.3. Discussion

Result from previous subsection shows that CO\textsubscript{2} molecule can be adsorbed with a bidendate configuration on Pd clusters. This adsorption configuration is different with the one on flat metal surfaces such as Cu-based surfaces where CO\textsubscript{2} molecule is only physically adsorbed on the surface with a linear conformation [11-13]. Such physisorption state makes the formation of formate (HCOO) or carboxyl (COOH) from the reaction with an adsorbed H atom becomes very difficult. And indeed, this reaction is one of the most important rate-limiting steps in the methanol synthesis process.

The formation of HCOO/COOH from the reaction of CO\textsubscript{2} molecule and an H atom requires the bending of the O-C-O angle of CO\textsubscript{2} molecule. This bending step is quite difficult to occur on flat metal surfaces since the $\pi^*$ orbital of the physisorbed linear CO\textsubscript{2} molecule is practically empty. Therefore, the usage of Pd\textsubscript{7} and Pd\textsubscript{6}M clusters as catalyst might facilitate this HCOO/COOH formation since CO\textsubscript{2} molecule can be chemically adsorbed on the clusters with a bidendate configuration.

We can also speculate that the formation rate of COOH might be faster on Pd\textsubscript{6}Cu and Pd\textsubscript{6}Ni clusters as compared to the other Pd\textsubscript{6}M clusters. This is because COOH formation does not require significant geometry transformation from the bidendate configuration of the adsorbed CO\textsubscript{2} molecule. Therefore, system that has stronger CO\textsubscript{2} chemisorption strength might have better COOH formation rate due to the lower probability of CO\textsubscript{2} desorption. However, we cannot say the same thing for HCOO formation case since this formation requires significant geometry transformation from the bidendate adsorption configuration. Detail mechanisms of HCOO/COOH formations and other important rate-limiting reactions for the methanol synthesis on Pd\textsubscript{7} and Pd\textsubscript{6}M clusters will be discussed in our future publication [14].

4. Summary

We report on a theoretical study of the adsorption of CO\textsubscript{2} molecule on Pd\textsubscript{6}M clusters using DFT calculations. We find that CO\textsubscript{2} molecule is adsorbed with a bidendate configuration on Pd\textsubscript{7} and on most of Pd\textsubscript{6}M clusters. The bidendate adsorption configuration is formed due to the filling of the unoccupied $\pi^*$ orbital of CO\textsubscript{2} molecule upon its interaction with the $d$-orbitals of the cluster. We find that the adsorbed CO\textsubscript{2} molecule binds to the Pd-Pd sites of Pd\textsubscript{7} and Pd\textsubscript{6}Rh clusters while it binds to the Pd-M sites of Pd\textsubscript{6}Cu and Pd\textsubscript{6}Ni clusters. Moreover, the CO\textsubscript{2} adsorption energies on Pd\textsubscript{6}Cu and Pd\textsubscript{6}Ni clusters are stronger than that on Pd\textsubscript{7} and Pd\textsubscript{6}Rh clusters. All of these results show that transition metal doping could modify the adsorption energy, adsorption site and adsorption configuration of CO\textsubscript{2} molecule on Pd\textsubscript{7} cluster. We also speculate that the usage of Pd\textsubscript{6}M clusters might facilitate the formations of HCOO/COOH.

Acknowledgements

This work is funded by Ministry of Research and Technology of Indonesia (RISTEK) through "Insentif Ristek Sinas- 2015" grant. All calculations were performed using High Performance Computer facility in Insitut Teknologi Bandung.
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