The Influence of Silver Cluster Size and Carbon Nanotubes on CO Adsorption: A DFT Study

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Abstract

The adsorption energies of CO on silver clusters and on silver clusters supported on an armchair (5,5) single-walled carbon nanotubes (SWNT) have been investigated by means of the B3LYP hybrid density functional calculation. It was found that the adsorption energies of CO on Ag3 and Ag4 clusters (–11.0 and –16.2 kcal/mol, respectively) are drastically decreased in the presence of the armchair (5,5) SWNT supporting material (–4.8 and –5.8 kcal/mol, respectively). However, the adsorption energies of CO on the silver clusters supported on the carbon nanotubes were found to sharply increase with decreasing the silver cluster size to Ag2 and Ag (–16.5 and –18.9 kcal/mol, respectively). This size-dependent behavior of the adsorption energies of CO can be explained by the counteraction of the charge transfer between a CO molecule and Agn–SWNTs and the Pauli repulsion energy.

Keywords: Silver cluster, CO adsorption, carbon nanotubes.

Introduction

Understanding the properties of metal nanoparticles and nanoaggregation is a great deal of current interest. Particularly, it is clear that the catalytic activity of supported metal nanoparticles depends on the metal–support interaction and metal particle size. From previous works, it has been shown that the silver nanoparticles supported on metal oxides, e.g. TiO_2, SiO_2 and Al_2O_3, perform highly selective catalytic hydrogenation of crotonaldehyde to the desired unsaturated alcohol products as well as the various types of reactions [1-5]. Recently, single-walled carbon nanotubes (SWNT) have been widely used in many fields, such as chemical sensor, optics, catalysts, and nanoelectronic devices. Various metals have been deposited on the sidewall of SWNT for their applications in the selective detection of trace amounts of small molecule gases. The interaction between transition metal atoms and SWNT has been extensively investigated through experimental and theoretical studies. It has been reported that the presence of defects, especially the single vacancy, enhances the interaction between metal and carbon nanotubes [1-2, 6-7].

In this study, we systematically investigate the adsorption of a CO molecule on the Ag_n (where n = 3 and 4) clusters and on the Ag_n (where n = 1 – 4) clusters deposited on a vacant site of the armchair (5,5) SWNT using a density functional theory (DFT) at the B3LYP level of calculation. The objectives of this study are to elucidate the influence of the carbon nanotubes and of the metal cluster size on the CO adsorption. The adsorption of CO on different sites of Ag_3–SWNT is also studied in order to search for the most favorable adsorption site of CO. The results obtained from this study are believed to provide fundamental aspects concerning the hybrid metal-SWNT complexes which are important for finding a highly efficient catalyst.

Computational details

In this work, the armchair (5,5) SWNT was used as a supporter of small silver cluster (Ag–Ag_4) for investigating the adsorption of a CO molecule. A quantum cluster model consisting of 99 carbon atoms with 20 hydrogen atoms capped at the ends of the fragment was used for representing the SWNT structure. The atomic vacancy was formed by removing one carbon atom from one of the hexagon rings. This vacant site was used as a deposit site for the Ag_n (where n = 1 – 4) clusters for exploring the adsorption behavior of CO. All calculations were performed based on the density functional theory (DFT), employing Becke's three-parameter hybrid exchange functional combined with the Lee, Yang, and Parr correlation functional (B3LYP) [8] implemented in a Gaussian 03 program [9]. The 6–31G(d) basis set was used for C, O and H atoms whereas the relativistic effective core pseudopotential of Hay and Wadt functional was used for an Ag atom [10].

The adsorption energies (E_{ads}) were calculated as followed

$$E_{ads} = E_{(CO\text{-}Agn\text{-}SWNT)} - E_{(Agn\text{-}SWNT)} - E_{(CO)} \quad (1)$$

where $E_{(CO\text{-}Agn\text{-}SWNT)}$ is the total energy of the adsorption complex concerning the CO–Ag_n–SWNT cluster, $E_{(Agn\text{-}SWNT)}$ is the total energy of the substrate, (the Ag_n-$C_{99}H_{20}$), $E_{(CO)}$ is the total energy of a corresponding CO molecule.

Results and discussion

In this work, we present our study into three subsections. First, the interaction of a CO molecule with silver trimer and silver tetramer will be discussed. Later, we will show the results concerning the adsorption of CO molecule on the complex of silver metal clusters deposited on the carbon nanotubes. Finally, we will summarize the influence of the metal cluster size on the CO adsorption.

Interaction of CO molecule and metal clusters

The adsorption of CO on Ag_3 and Ag_4 clusters was studied in order to get insights into the interaction between CO and the silver clusters in the absence of the SWNT supporting material. The optimized geometries of Ag_3, Ag_4, CO–Ag_3 and CO–Ag_4 complexes are shown in Fig. 1 and their optimized parameters are listed in Table 1. One can see that the adsorption energy increases from –11.0 to –16.2 kcal/mol with the increase of the silver cluster size from Ag_3 to Ag_4, in good agreement with the shorter Ag–CO distance (212.0 pm) in the CO-Ag_4 complex compared with that in the CO–Ag_3 complex (216.5 pm).

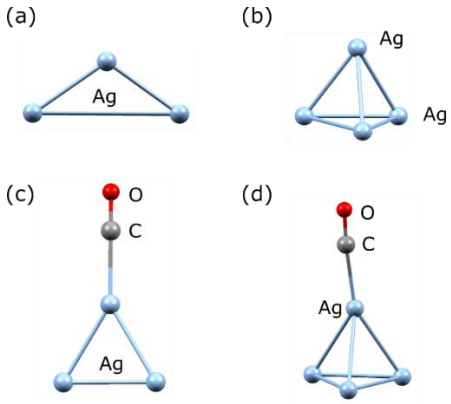

Figure 1. Optimized structures of Ag_3 (a) and Ag_4 (b) clusters and their adsorption complexes: CO•••Ag_3 (c) and CO•••Ag_4 (d).

Table 1. Optimized parameters of adsorption complexes concerning CO molecule deposited on Ag_3 and Ag_4 metal clusters.

	Free Ag_3	Free Ag_4	CO•••Ag_3	CO•••Ag_4
			On-top site (Fig. 1c)	On-top site (Fig. 1d)
r(Ag-Ag), pm	268.0×2, 438.0	287.6×4	270.9×2, 288.8	287.6×4
r(Ag-C), pm	-	-	216.5	212.0
r(C-O), pm	-	-	114.0	114.3
E_{ads}, kcal/mol	-	-	–11.0	–16.2

Adsorption of CO molecule on the Ag_3-$C_{99}H_{20}$ cluster

In this subsection, the effect of the SWNT supporting material on the adsorption energies of CO on Ag_3 was investigated. Different orientations of CO adsorbed on the Ag_3–$C_{99}H_{20}$ cluster were considered. Their optimized geometries are shown in Fig. 2 and their selected parameters are summarized in Table 2.

The results show that the adsorption of CO on the Ag_3–$C_{99}H_{20}$ cluster is exothermic by about 5–7 kcal/mol. Moreover, it was found that the interaction of CO in the on-top position of Ag_3 (Fig. 2b) is weaker than the interaction of CO in other positions (Fig.2c and 2d). The adsorption in mode 2C (Fig. 2c) was found to be the most stable structure, with the adsorption energy of –7.3 kcal/mol. In this structure, CO interacts with an Ag atom residing in close proximity to the SWNT. Therefore, more electron density around this Ag atom can be expected. Strong adsorption of CO on this position was observed although the Ag–C distance of mode 2C is longer than that of mode 2D.

To compare with the CO adsorption on the on-top position of Ag_3 cluster (Fig. 1c), the CO adsorption on the Ag_3-$C_{99}H_{20}$ complex (mode 2B, Fig. 2b) has been studied. The adsorption energy of CO corresponding mode 2B was calculated to be –4.8 kcal/mol, which is lower than the CO adsorption on Ag_3 cluster (–11.0 kcal/mol). This implies that the SWNT destabilizes the adsorption of CO by 6.2 kcal/mol. The presence of SWNT lengthens the Ag–CO distance from 216.5 pm (Fig. 1c) to 245.8 pm (Fig. 2b).

Adsorption of CO molecule on the Ag_4–$C_{99}H_{20}$ cluster

To elucidate the adsorption of CO on three-dimensional metal cluster, the Ag_4 deposited on $C_{99}H_{20}$ cluster (Ag_4–$C_{99}H_{20}$) was employed as a substrate for the CO adsorption. In this work, the CO adsorbed only at the on-top position of Ag_4–$C_{99}H_{20}$ cluster. The optimized structure of the Ag_4–$C_{99}H_{20}$ and adsorption complex, CO–Ag_4–$C_{99}H_{20}$, are shown in Fig. 3. Their selected parameters are documented in Table 3. During the CO interaction, the structure of Ag_4 moiety of adsorption complex of mode 3B (Fig. 3b) slightly differs from that of mode 3A (Fig. 3a). This means that the CO weakly binds to the Ag_4–$C_{99}H_{20}$ complex which is in agreement with our calculated adsorption energy of the CO, –5.8 kcal/mol. However, this adsorption energy is smaller than that of the adsorption of CO on the Ag_4 tetramer (–16.2 kcal/mol, Fig. 1d). The difference is probably due to the effect of carbon nanotubes that can get electrons from silver metal cluster and destabilizes the CO adsorption.

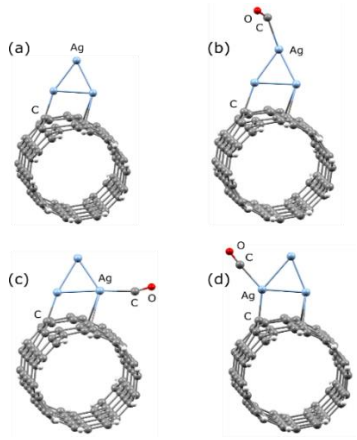

Figure 2. Optimized structures of Ag_3–$C_{99}H_{20}$ cluster (Fig. 2a, mode 2A) and their adsorption complexes: CO•••Ag_3–$C_{99}H_{20}$ (Fig. 2b, mode 2B), CO•••Ag_3–$C_{99}H_{20}$ (Fig. 2c, mode 2C), CO•••Ag_3–$C_{99}H_{20}$ (Fig. 2d, mode 2D).

Table 2. Calculated parameters of adsorption complexes concerning CO molecule deposited on the Ag_3–$C_{99}H_{20}$ cluster.

	Ag_3–$C_{99}H_{20}$ (Fig. 2a)	CO•••Ag_3–$C_{99}H_{20}$		
		mode 2B (Fig. 2b)	mode 2C (Fig. 2c)	mode 2D (Fig. 2d)
r(C-O), pm	-	113.9	113.6	114.0
r(Ag-C), pm	-	245.8	232.6	224.7
∠(Ag-C-O), °	-	137	162	177
r(Ag-Ag), pm	271.9, 278.7, 282.1	284.9, 271.8, 276.0	273.3, 277.8, 280.2	268.3, 284.6, 298.0
r(Ag-C_{tub})[a], pm	217.3, 241.3, 285.6	217.5, 245.4, 291.1	216.8, 262.5, 285.2	217.8, 238.3, 264.4
E_{ads},[b] kcal/mol		–4.8	–7.3	–6.3

[a] Distances between Ag atom and the nearby C atoms of the carbon nanotubes.

[b] Adsorption energy of CO molecule deposited on theAg$_3$–$C_{99}H_{20}$ cluster.

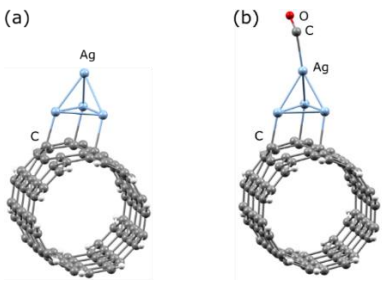

Figure 3. Optimized structures of Ag_4–$C_{99}H_{20}$ cluster and their adsorption complexes: Ag_4–$C_{99}H_{20}$ complex (Fig. 3a, mode 3A), CO•••Ag_4–$C_{99}H_{20}$ (Fig. 3b, mode 3B).

Table 3. Calculated parameters of adsorption complexes concerning CO molecule deposited on the Ag_4–$C_{99}H_{20}$ cluster.

	Ag_4–$C_{99}H_{20}$ (Fig. 3a)	CO•••Ag_4–$C_{99}H_{20}$ mode 3B (Fig. 3b)
r(C-O), pm	-	113.7
r(Ag-C), pm	-	245.4
∠(Ag-C-O), °	-	146
r(Ag-Ag), pm	275.1, 286.7, 294.6, 286.2, 291.0, 294.9	274.8, 288.5, 298.0, 284.8, 288.5, 291.6
r(Ag-C_{tub})[a], pm	242.6, 229.4, 216.2	247.1, 230.7, 216.5
E_{ads},[b] kcal/mol	-	–5.8

[a] Adsorption energy of CO molecule deposited on theAg_3–$C_{99}H_{20}$ cluster.

The influence of metal cluster size on the adsorption of CO molecule

In this subsection, the comparison of energetic and structural properties of CO adsorption on the Ag_n–$C_{99}H_{20}$ cluster (n = 1 – 4) has been discussed. All parameters of their adsorption complexes with the position of CO at the on-top site are collected in Table 4 and their optimized structures are shown in Fig. 4. From our calculated adsorption energies, the interaction of CO decreases sharply with increasing the Ag cluster size from 1 to 4 atoms. The corresponding adsorption energies of CO are –18.9, –16.5, –4.8 and –5.8 kcal/mol for the Ag–$C_{99}H_{20}$, Ag_2–$C_{99}H_{20}$, Ag_3–$C_{99}H_{20}$ and Ag_4–$C_{99}H_{20}$ complexes, respectively. This result is in agreement with the Ag–CO distance observed from the adsorption complexes. The Ag–CO distances of these complexes lengthen from 208.9 pm (CO•••Ag–$C_{99}H_{20}$) to 245.0 pm (CO•••Ag_4–$C_{99}H_{20}$) while the C–O bonds shorten slightly from 114.2 (CO•••Ag–$C_{99}H_{20}$) to 113.7 pm (CO•••Ag_4–$C_{99}H_{20}$). This result can be explained by the transfer of electron between CO and Ag_n–SWNT, counteracted by the Pauli repulsion. One can see from the results, the strong metal-metal interaction within the Ag_3 and Ag_4 metal clusters produces the weak interaction of CO molecule. Consequently, the longer Ag–CO distances are observed for the Ag_3–$C_{99}H_{20}$ and Ag_4–$C_{99}H_{20}$ complexes as well as the reduction of the adsorption energy of CO. Moreover, the effect of SWNT size ($C_{79}H_{20}$ and $C_{99}H_{20}$) on the CO adsorption was investigated. The properties of their adsorption complexes, CO•••Ag–$C_{79}H_{20}$ and CO•••Ag–$C_{99}H_{20}$, are summarized in Table 4 . We found that the structural property of both complexes is similar as well as the adsorption energies of CO, -18.0 kcal/mol (CO•••Ag–$C_{79}H_{20}$) and -18.9 kcal/mol (CO•••Ag–$C_{99}H_{20}$). Therefore, the influence of SWNT size on the adsorption of CO is small for this system.

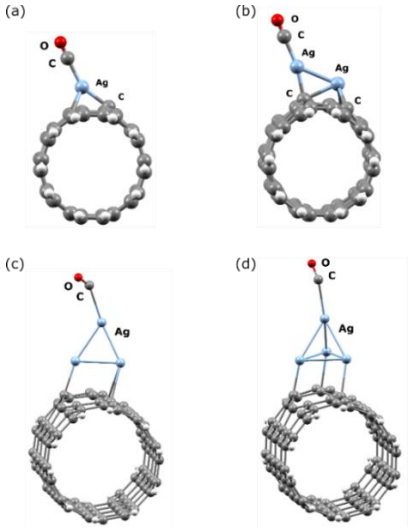

Figure 4. Optimized structure of adsorption complexes concerning CO deposited on Ag_n–$C_{99}H_{20}$ cluster: CO•••Ag–$C_{99}H_{20}$ (a), CO•••Ag_2–$C_{99}H_{20}$ (b), CO•••Ag_3–$C_{99}H_{20}$ (c), CO•••Ag_4–$C_{99}H_{20}$ (d).

Table 4. Calculated parameters of adsorption complexes concerning the CO molecule adsorbed on the Ag_n-$C_{99}H_{20}$ cluster

	$CO^{\bullet\bullet\bullet}Ag_n$-$C_{99}H_{20}$			
	n = 1[b]	n = 2	n = 3	n = 4
r(C-O), pm	114.2 (114.0)	113.8	113.9	113.7
r(Ag-C), pm	208.9 (210.9)	210.4	245.8	245.0
r(Ag-C_{tub})[a], pm	211.9, 226.1, 228.6 (217.3, 239.0, 239.2)	212.2, 208.2, 209.2, 229.6	217.5, 245.4, 291.1	216.5, 230.7, 247.1
E_{ads}, kcal/mol	–18.9 (–18.0)	-16.5	-4.8	-5.8

[a] Distances between Ag atom and the nearby C atoms of the carbon nanotubes.

[b] Parameters in parentheses are corresponding to the $CO^{\bullet\bullet\bullet}Ag$–$C_{79}H_{20}$ adsorption complex.

Conclussion

In this work, the adsorption energies of CO on silver clusters and on silver clusters supported on an armchair (5,5) single-walled carbon nanotubes (SWNT) have been investigated by means of the B3LYP hybrid density functional calculation. From our results, the presence of carbon nanotubes destabilizes the interaction between CO molecule and the supporter of silver cluster (Ag_1–Ag_4). The calculated adsorption energies of CO molecule on the Ag_3 cluster and Ag_3–$C_{99}H_{20}$ complex are –11.0 and –4.8 kcal/mol, respectively. For the Ag_4 cluster and Ag_4–$C_{99}H_{20}$ complex, the interactions of CO are stronger with the adsorption energies of –16.2 and –5.8 kcal/mol, respectively. The transfer of electrons from silver metal clusters to carbon nanotubes affects as a result of the weak interaction of CO on those metal clusters. Moreover, it was found that the adsorption energies of CO on the silver clusters supported on the carbon nanotubes sharply decrease with increasing the silver cluster size, Ag–$C_{99}H_{20}$ (–18.9 kcal/mol), Ag_2–$C_{99}H_{20}$ (–16.5 kcal/mol), Ag_3–$C_{99}H_{20}$ (–4.8 kcal/mol) and Ag_4–$C_{99}H_{20}$ (–5.8 kcal/mol). These results are in agreement with the lengthening of the distance between CO and Ag_n–SWNT complexes. One can see from the results, the strong metal-metal interaction within the Ag_3 and Ag_4 metal clusters can cause the weak interaction of CO molecule. Consequently, the longer Ag–CO distances are observed form their adsorption complexes. The information from our study can be useful for further study concerning the oxidation reaction on the small metal clusters deposited on carbon nanotubes.

Acknowledgments

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