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DFT studies of interaction of Ir cluster with O_2, CO and NO

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Abstract

Hybrid DFT calculations have been carried out for IrCO, IrNO, IrO_2, $Ir_{13}CO$, $Ir_{13}NO$, and $Ir_{13}O_2$ clusters in order to investigate the electronic state and the catalytic activity of Ir catalyst. The results of Ir model clusters show that the surface atoms of the Ir_{13} cluster have small negative charges and the clusters have strong interactions with adsorbates.

Keywords: Iridium catalyst; Ir cluster; DFT; Surface adsorption

1. Introduction

Catalytic CO oxidation and NO reduction have lately drawn considerable attention due to the growing applications for air purification, pollution control in automobiles, incinerator exhaust gases, etc. [1,2]. In addition to many different metal oxide catalysts, a wide variety of precious metal catalysts has been studied for these reactions. Although Ir is situated among the same 5f orbital metals as Pt and Au, it has been investigated as a catalyst only for limited reactions, hydrazine decomposition for rocket thrusters, the hydrogenation of unsaturated hydrocarbons and etc. [3,4]. Probably, this is because Ir resources are rare and expensive. Fujitani et al. have discovered that Ir/SiO_2 show marked catalytic activity for NO reduction with H_2 and also have shown the detail analysis of NO reduction on Ir (1 1 1) surface [5]. Lately, it was found that Ir/TiO_2 prepared by deposition-precipitation (DP) method was active at temperatures below room temperature for CO oxidation although Ir/TiO_2 prepared by impregnation (IMP) method was almost inactive for CO oxidation [6]. TEM observations for Ir/TiO_2 prepared by DP showed that Ir was dispersed over the TiO_2 surface as a nanoparticle with a diameter less than 2 nm [7]. On the other hand, the diameters of Ir/TiO_2 by IMP was much larger than that of Ir/TiO_2 prepared by DP. These results suggest that the size of Ir particle and the selection of support would influence the catatlytic activity. However, it is hard to discuss the size effect of Ir cluster and the support effect separately by experiment while the theoretical investigation of the support effect is also hard due to the limit of the computer resources. Therefore, Ir_{13} models, which are the smallest cluster with inner atoms were examind as a first step for understanding the catalytic activities of Ir catalysts by using hybrid DFT calculations.

2. Computational method

Unrestricted hybrid DFT (UB3LYP) [8] calculations were first carried out for small model clusters. LANL2DZ basis set was used for Ir atom and LANL2DZ + pd (with polarization and diffuse functions identical to 6-31 + G^{**}) basis sets were adapted for O_2, CO and NO molecules [9–12]. All the geometries of models systems were fully optimized with C_1 symmetry. The geometry of cubooctahedral Ir_{13} was also optimized. Finally, the Ir_{13}–O_2 Ir_{13}–CO and Ir_{13}–NO clusters were optimized with C_1 symmetry using the B3LYP method, where the geometry of the Ir_{13} clusters were fixed. The Mulliken charges of each atom were calculated by the Mulliken population analysis. The natural orbital analysis was also carried out for Ir_{13} model systems in order to understand the

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electronic state of those systems. All these calculations except for the geometry optimization of clusters were carried out by the Gaussian98 program [13].

3. Results

3.1. Interaction of Ir with O_2, CO and NO

In order to study the interactions of Ir with O_2, CO and NO molecules, the Ir–X ($X = O_2$, CO and NO) models were examined. The optimized structures and the characteristics of the Ir–X models are summarized in Fig. 1 and Table 1, respectively. It was found that the binding energy of Ir–O_2 model is 17.70 kcal/mol and the charge density of O_2 is −0.505. This result suggests that the charge transfer from Ir to O_2 was occurred and an active O_2 species would be presented. In the next, Ir–CO and Ir–NO models were also examined. The obtained binding energies were 25.25 and 41.25 kcal/mol, respectively and the charge densities of CO and NO are −0.380 and −0.205, respectively. Therefore, it was found that these species interact with Ir atom strongly and the charge transfer was also occurred from Ir to the adsorbed molecules.

3.2. Characteristics of Ir_{13} cluster

The investigated Ir_{13} cluster was shown in Fig. 1 (d). This Ir_{13} cluster has cubooctahedral shape. For this Ir_{13} clusters, UB3LYP/LANL2DZ calculations were carried out. The calculated energies were listed in Table 2. The ground state of Ir_{13} is quartet. The bond distance between Ir atoms is 2.682 Å while the bond distance in the bulk Ir is 2.715 Å. The calculated ionization potential (IP) value of Ir_{13} was 6.34 eV. This IP value which is only two-thirds that of the Ir atom (9.10 eV) decreases with increasing cluster size due to the broadening of the band structure. This value is larger than the work function of Ir(1 1 1) surface (5.76 eV). Additionally, the HOMO-LUMO gap of is 1.28 eV. The Mulliken charges of Ir_{13} listed in Table 3 show that their surfaces are negatively charged thought these values are much smaller than those of Au_{13} (∼−0.5) [14,15]. Therefore, the electronic states of the surface Ir atoms in Ir_{13} clusters resemble that of a neutral Ir atom rather than the anionic atom.

3.3. Interaction of Ir_{13} cluster with O_2, CO and NO

The Ir_{13}–O_2 model was calculated to study the interaction between the Ir_{13} cluster and the O_2 molecule. The schematic

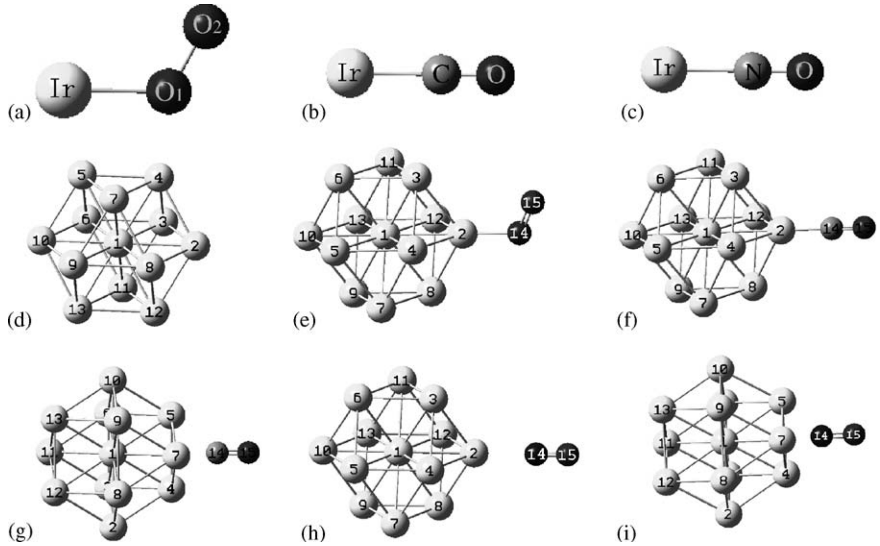

Fig. 1. Calculated structures of model clusters: (a) Ir–O_2, (b) Ir–CO, (c) Ir–NO, (d) cobooctahedral Ir_{13}, (e) Ir_{13}–O_2, (f) a-top type Ir_{13}–CO, (g) hollow type Ir_{13}–CO, (h) a-top type Ir_{13}–NO, and (i) hollow type Ir_{13}–NO.

Table 1
Optimized structures and binding energies of Ir–XO models calculated by UB3LYP/LANL2DZ method

System[b]	Spin state	R(Ir–O) Å	R(X–O) Å	A(Ir–X–O)[c]	Mulliken charges[a]			Binding energy (kcal/mol)
					Ir	X_1	O_2	
IrO_2 (X = O)[b]	Doublet	1.872	1.295	117.75	0.502	−0.478	−0.027	17.70
IrCO (X = C)[b]	Quartet	1.944	1.159	180.0	0.376	−0.070	−0.306	25.25
IrNO (X = N)[b]	Triplet	1.809	1.203	180.0	0.205	−0.147	−0.058	41.25

[a] The charge Mulliken charges resulting form a Mulliken population analysis.
[b] LANL2DZ + pd was used for the basis set of O_2,CO and NO.
[c] Angle in degree.

Table 2
Total energies and ionization potential (IP) of Ir models calculated by UB3LYP/LANL2DZ

Model	Spin state	Total energy (h)	IP[a]
Ir$_{13}$	Doublet	−1360.975	
	Quartet	−1360.990	6.34
	Sextet	−1360.982	
Ir	Quartet	–	9.45

[a] IP in eV, the experimental IPs of Ir atom and Ir(1 1 1) surface are 9.10 and 5.76 eV, respectively.

diagram of Ir$_{13}$–O$_2$ model was depicted in Fig. 1 (e). The variations in the Mulliken charges of the Ir1$_3$–O$_2$ model, listed in Table 3, demonstrate a charge transfer from the surface Ir atoms to O$_2$. As shown in Table 4, the binding energy calculated by LANL2DZ + pd was about 19.98 kcal/mol. From the calculations, it was found that O$_2$ molecule could be strongly adsorbed onto the surface of Ir$_{13}$.

The interaction between the Ir$_{13}$ cluster and the CO molecule were examined in the next. The schematic diagrams of a-top and hollow type models were depicted in Fig. 1 (f) and (g), respectively. As shown in the optimized structures of the a-top and hollow type Ir$_{13}$–CO models that were listed in Table 4, the binding energies calculated were about 57.72 and 35.58 kcal/mol, respectively. Therefore, these results also showed that CO molecule could be adsorbed onto the surface of Ir$_{13}$ strongly. The Mulliken charges for both a-top type Iru$_{13}$–CO and hollow type Ir$_{13}$–CO models were listed in Table 3. It was proved that the Mulliken charges of the Ir atoms that interacted with CO molecule directly became positive and total Mulliken charges of CO became negative. This means that the charge transfer interaction is presented. The interaction between the surface Ir atoms in Ir$_{13}$ cluster and CO is composed of the σ-type donation and π^*-type back donation. The π^*-type back donation from Ir$_{13}$ to CO is a dominant factor for this charge transfer interaction because the total Mulliken charges of CO became negative.

The interaction between the Ir$_{13}$ clusters and NO molecule were also examined. The schematic diagrams of these models were also depicted in Fig. 1 (h) and (i). As shown in the optimized structures of the a-top and hollow type Ir$_{13}$–NO models that were listed in Table 4, the binding energies calculated were 69.26 and 46.76 kcal/mol, respectively. Therefore, it was found that the interactions between NO molecule and Ir$_{13}$ cluster were also strong. The Mulliken charges for both a-top type Ir$_{13}$–NO and hollow type Ir$_{13}$–NO models were listed in Table 3. From the calculation results, it was proved that the charge transfer interaction was also presented.

Table 3
Mulliken charges[a] of Ir$_{13}$–O$_2$, Ir$_{13}$–CO and Ir$_{13}$–NO calculated byUB3LYP method

Atom	Ir$_{13}$	Ir$_{13}$–O$_2$	Ir$_{13}$–CO		Ir$_{13}$–NO	
			A-top	Hollow	A-top	Hollow
Ir$_1$	1.380	1.431	1.378	1.129	1.407	1.189
Ir$_2$	−0.118	0.082	0.680	−0.138	0.176	−0.141
Ir$_3$	−0.095	−0.034	−0.082	−0.119	−0.014	−0.115
Ir$_4$	−0.120	−0.058	−0.103	0.366	−0.012	0.313
Ir$_5$	−0.098	−0.108	−0.160	0.342	−0.099	0.306
Ir$_6$	−0.114	−0.114	−0.166	−0.143	−0.119	−0.133
Ir$_7$	−0.130	−0.116	−0.130	0.329	−0.117	0.307
Ir$_8$	−0.118	−0.070	−0.086	−0.150	−0.018	−0.153
Ir$_9$	−0.142	−0.142	−0.186	−0.145	−0.149	−0.136
Ir$_{10}$	−0.120	−0.102	−0.127	−0.125	−0.116	−0.126
Ir$_{11}$	−0.098	−0.098	−0.102	−0.148	−0.077	−0.112
Ir$_{12}$	−0.141	−0.073	−0.095	−0.176	−0.014	−0.142
Ir$_{13}$	−0.089	−0.107	−0.144	−0.116	−0.101	−0.125
X$_{14}$		−0.373	−0.030	−0.264	−0.388	−0.454
O$_{15}$		−0.118	−0.649	−0.642	−0.359	−0.480

[a] The charge Mulliken charges resulting form a Mulliken population analysis.

Table 4
Characteristics of Ir$_{13}$–O$_2$, Ir$_{13}$–CO and Ir$_{13}$–NO calculated by UB3LYP method

Molde	Adsorption site	R(Ir–X) Å	R(X–O) Å	A(Ir–X–O)[a]	Binding energy (kcal/mol)
Ir$_{13}$–O$_2$	–	1.939	1.312	112.94	19.98
Ir$_{13}$–CO	A-top	1.845	1.168	180.0	57.72
	Hollow	1.467[b]	1.205	180.0	35.58
Ir$_{13}$–NO	A-top	1.793	1.183	180.0	69.26
	Hollow[b]	1.388[b]	1.241	180.0	46.76

[a] Angle in degree.

[b] Distance from X atom to Ir cluster surface in Å.

Table 5
Vibrational frequencies calculated by UB3LYP method

Molecule	Adsorption site	Calculation (cm^{-1})	Experiment (cm^{-1})
CO	Isolated	2190	2143
	A-top	2021	2060[a]
	Hollow	1721	–
NO	Isolated	1963	1876
	A-top	1839	1811[a]
	Hollow	1430	1443[a]

[a] Experiments were carried out on Ir(1 1 1) surface.

4. Discussion

The calculation results showed that the surface Ir atoms of Ir_{13} cluster have small negative charges (~ -0.1). These results suggest that the charge polarization in Ir cluster is relatively small. This feature is different from that of Au_{13} cluster because the negative charge density of Au_{13} clusters surface is much larger than that of Ir_{13} cluster. Therefore, the decrease of the cluster size mainly influences the increase of both the band gap and the ionization energy of the cluster.

It was also found that Ir_{13} cluster have strong interactions with CO and NO molecules. For a-top and hollow Ir_{13}–CO and Ir_{13}–NO models, the vibrational frequency analyses were also examined. The obtained results were listed in Table 5. The frequencies of hollow site adsorption Ir_{13}–NO and Ir_{13}–CO models are smaller than those of a-top site adsorption models and the negative charge densities of the reactants for hollow site models are larger than those of a-top models. It is well known that the interaction between the metal surface and adsorbents is composed of the σ type donation and π^* type back donation. The schematic diagrams of orbital configurations for both a-top and hollow site type interactions are depicted in Fig. 2. The π^* type back donation of the hollow site adsorption models is more dominant than that of the a-top site adsorption models as the orbital overlap between d orbital of Ir_{13} and π^* orbital of adsorbents become large. As the NO decomposition over Ir(1 1 1) surface is occurred at the hollow site of the Ir(1 1 1) surface, the obtained results are in good agreement with the experimental results of the bulk Ir surface. Natural orbitals (NOs) and its occupation numbers of both a-top and hollow type Ir_{13}-NO models are only depicted in Fig. 3 as similar natural orbital configurations were obtained in both Ir_{13}–NO and Ir_{13}–CO models. These NOs show typical σ type donation and π^* type back donation. Therefore, the adsorption characteristic of the Ir cluster is similar to that of the bulk Ir metal surface. Moreover, the tendency of calculated frequencies also have resemblance to the experimental results of Ir(1 1 1) surface. Consequently, these calculation results indicated that the high dispersion of Ir particles would increase the active surface area of Ir nanoparticle monotonously as the characteristics of Ir cluster itself would be less sensitive for the size of the cluster.

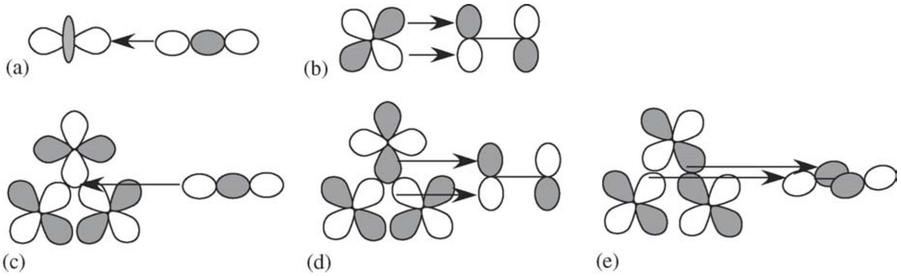

Fig. 2. Schematic diagram of (a) a-top site σ type interaction, (b) a-top site π type interaction, (c) hollow site σ type interaction, (d) hollow site π type interaction and (e) hollow site π type interaction.

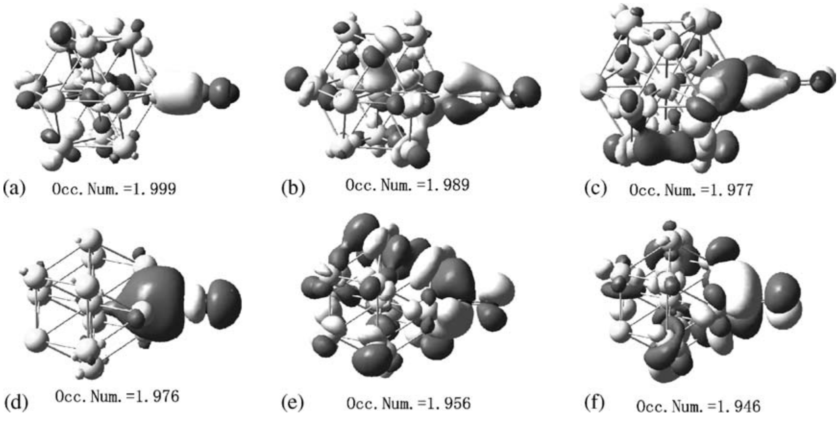

Fig. 3. Natural orbitals and its occupation numbers of (a) a-top type $Ir_{13}NO$ σ type interaction, (b) a-top type $Ir_{13}NO$ π type interaction, (c) a-top type $Ir_{13}NO$ π type interaction, (d) hollow type $Ir_{13}NO$ σ type interaction, (e) hollow type $Ir_{13}NO$ π type interaction and (f) hollow type $Ir_{13}NO$ π type interaction.

From our previous works, it has found that the charge transfer between deposited Au nanoclusters and metal oxide supports were important to modify the electronic state of the deposited Au nanocluster. In this case, the direct hetero-junction between metallic gold and the metal oxide support was obtained, because the oxidic gold is not stable. On the other hand, iridium oxide layer would be generated in the interfacial region between Ir cluster and the metal oxide support as IrO_2 is stable. It is known that IrO_2 is a conductor and its average work function is 4.23 eV. In order to examine the charge transfer between IrO_2 and TiO_2, the local barrier height (LBH) of Ir/TiO_2 model catalyst was measured by using STM [16]. From STM observations, it appeared that the LBH of IrO_2 particles was almost the same as that of the TiO_2 substrate. This result suggests that a charge transfer between $IrO_2$and TiO_2 is small. However, a certain amount of the charge transfer between Ir cluster and the metal oxide support would be occurred depending on the variation of deposited size of Ir particle, the selection of support, the used pretreatment condition, and the catalytic reaction conditions. Therefore, the further investigation must be needed in order to elucidate this complex support effect of Ir catalysts, precisely.

5. Conclusions

The present theoretical calculations have provided the following interpretation on the interaction of Ir cluster with adsorbates:

(1) Ir_{13} showed strong charge transfer interactions with CO and NO. Mulliken charge of the surface Ir atoms, which directly interacts with these reactants in Ir_{13} clusters becomes positive. This positive charge of the surface Ir atom is due to the back donation by the adsorption of CO and NO onto the Ir cluster surface.

(2) The characteristics of Ir cluster itself would be less sensitive for the size of the cluster and similar to those of bulk Ir surface. These features are completely different from the results of Au clusters.

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