Theoretical Study of H_2O and O_2 Adsorption on Au Small Clusters

Mitsutaka Okumura[a,c,*], Masatake Haruta[b,c], Yasutaka Kitagawa[a] and Kizashi Yamaguchi[a]

[a] Graduate School of Science, Osaka University, 1-1 Machikaneyama, Toyonaka, Osaka, 560-0043, Japan

[b] Department of Applied Chemistry, Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University, 1-1 Minami-osawa, Hachioji 192-0397, Tokyo, Japan

[c] Core Research for Environmental Science and Technology (CREST), Japan Science and Technology Agency, Kawaguchi-shi, Saitama 332-0012, Japan * E-mail:ok@chem.sci.osaka-u.ac.jp

Abstract

Hybrid Density functional calculations have been carried out for Au_{10}, Au_{10}-H_2O, Au_{10}-O_2, and Au_{10}-H_2O-O_2 model clusters. The results show that all the Au_{10} clusters examined have a weak interaction with H_2O and neutral and negatively charged Au_{10} clusters have a weak interaction with O_2. Moreover, it is also found that the negative charge densities of O_2 were greatly increased in the case of the coadsorption of O_2 and H_2O on the surface of the negatively charged Au_{10}. These findings suggest that the presence of H_2O enhances the activation of O_2 on the surface of an Au cluster.

Introduction

In recent years, gold has been attracting industrial and scientific interest for its catalytic activity in such reactions as propylene partial oxidation, odour decomposition, the direct production of H_2O_2 from H_2 and O_2, and CO oxidation at low temperatures, especially when Au is deposited as nanoparticles on selected metal oxides (1-5). Highly dispersed gold catalysts exhibit unique catalytic activity not only at low-temperature, but also in the presence of moisture.

These features make the catalysts advantageous for applications under ambient conditions. In general, however, fundamental work is usually carried out under relatively dry conditions. Therefore, it is important to examine the effect of moisture to understand the unique catalytically activity by gold. The effect of moisture in gold catalysts has been investigated mainly for CO oxidation, since moisture has a remarkable effect. From detailed quantitative analyses, it has been found that moisture enhances the catalytic activities for no less than two orders of magnitude and the effect of moisture depends on the type of metal oxide support present (6,7).

Despite all the investigations on Au catalysts, the reaction mechanism still remains uncertain. It is well known that both the electronic state and the structure of Au clusters are dramatically changed depending on which support is selected. Moreover, even if the support used is the same, the characteristics of the Au clusters deposited could be different depending on the surface condition, such as reduced and oxidized surfaces of the support. In order to simplify the system, the unsupported hemispherical cluster system with hole/electron doping is applied here instead of the complex surface models. For this model, we have carried out the qualitative assessment for oxygen activation and H_2O adsorption on the surface of the Au clusters.

The present theoretical study has been undertaken to shed light in the interaction between O_2 and H_2O and the Au cluster as a first step for understanding the catalytic activity of Au catalysts in the presence of moisture. Hybrid density functional theory (DFT) calculations have been mainly carried out on the charge transfer interaction between Au and oxygen or H_2O in Au model clusters.

Computational procedure

Unrestricted hybrid DFT (UB3LYP) (8) calculations were first carried out for the model clusters. LANL2DZ basis set was used for the Au atom. D95V+pd (with polarization and diffuse functions identical to 6-31+G**) basis sets were adapted for the H and O atoms (9-12). The Au_{10}-O_2, Au_{10}-H_2O and Au_{10}-H_2O-O_2 clusters were optimized with C_1 symmetry using the B3LYP method, where the geometry of the Au_{10} clusters was fixed. In these models, the upside Au atoms in an Au_{10} cluster were chosen as the interaction site for the adsorbates in order to investigate the interaction between the adsorbates

Table 1

Mulliken charge densities of Au_{10}-O_2 Au_{10}-H_2O and Au_{10}^--H_2O-O_2 model clusters.

Atom	Au_{10}	Au_{10}^-	Au_{10}^+	Au_{10}-O_2	Au_{10}^--O_2	Atom	Au_{10}-H_2O	Au_{10}^--H_2O	Au_{10}^+-H_2O	Atom	Au_{10}^--H_2O-O_2
Au1	1.134	1.046	1.224	1.096	1.031	Au1	1.069	1.090	1.120	Au1	0.961
Au2	-0.148	-0.304	-0.085	-0.143	-0.206	Au2	-0.176	-0.283	-0.090	Au2	-0.202
Au3	-0.145	-0.229	0.020	-0.153	-0.285	Au3	-0.167	-0.211	0.008	Au3	-0.253
Au4	-0.080	-0.150	-0.020	-0.097	-0.167	Au4	-0.126	-0.184	-0.0730	Au4	0.073
Au5	-0.080	-0.153	-0.013	0.000	-0.018	Au5	0.190	-0.160	0.108	Au5	-0.024
Au6	-0.146	-0.240	0.002	-0.163	-0.279	Au6	-0.182	-0.292	-0.064	Au6	-0.287
Au7	-0.152	-0.297	-0.077	-0.163	-0.265	Au7	-0.189	-0.267	-0.101	Au7	-0.295
Au8	-0.080	-0.152	-0.014	-0.087	-0.158	Au8	-0.136	-0.174	-0.073	Au8	-0.212
Au9	-0.150	-0.270	-0.032	-0.153	-0.225	Au9	-0.168	-0.306	-0.052	Au9	-0.239
Au10	-0.153	-0.251	-0.006	-0.160	-0.282	Au10	-0.176	-0.232	-0.009	Au10	-0.276
O11				0.004	-0.071	O11	-0.700	-0.679	-0.673	O11	-0.685
O12				0.017	-0.075	H12	0.391	0.319	0.412	H12	0.364
						H13	0.372	0.378	0.406	H13	0.470
										O14	-0.174
										O15	-0.269

and the hemispherical Au_{10} cluster itself. The geometry of the hemispherical Au_{10} cluster was extracted from the geometry of spherical Au_{13} cluster optimized by the B3LYP method. The charge density of each atom was calculated using a Mulliken population analysis. All these calculations were carried out using the Gaussian98 program (13).

Results

1 The characteristics of the Au_{10} model clusters

The hemispherical gold cluster shown in Figure 1(a) was investigated as it was well known that the hemispherical Au clusters were deposited on the support surface in the highly active Au catalysts. The structure of the Au_{10} cluster was extracted from a cubooctahedral Au_{13} cluster. For this Au_{13} cluster, the distance between the core-outer atoms was only optimized using B3LYP/LANL2DZ in the cuboocatahedral shape. Both an electron and a hole doping were investigated for this Au_{10} cluster. In these calculations, the geometries used for the Au_{10}^- and Au_{10}^+ clusters are fixed to be the same as that of the neutral Au_{10}. In Table 1, the Mulliken charge densities of the neutral, anionic and cationic Au_{10} clusters are summarized. In our previous work, it was found that the surface Au atoms

in Au_{13} were negatively charged homogeneously and the core Au atom in Au_{13} was positively charged (14). In this neutral Au_{10} cluster, the negative charge densities on the surface Au atoms have a slightly heterogeneous distribution while the core Au atom in Au_{10} is positively charged. It is well known that the highest coordinated atoms have a positive charge in the cluster systems. Moreover, these results suggest that the morphology of the Au cluster affects the surface charge density distribution that would be related to the catalytic activity of Au catalysts. As shown in Table 1, it was also found that the surface charge densities are drastically changed by the electron/hole doping. In Figure 1 (b) and (c), the difference-charge density between electron/hole doped Au_{10} system and the neutral Au_{10} system, superimposed on the atomic configuration is depicted. Charge depletion and charge accumulation are shown in blue and red, respectively. From these figures, it was found that the charge variations were occurring on the whole surface of the Au_{10} cluster. Additionally, the detailed analyses of DFT-derived orbitals of the model systems show that the shape of the deferential charge density maps depicted in Figure 1 (b) and (c) are closely related to the LUMO and HOMO of the neutral Au_{10} system, respectively. This is because the electron/hole doping into the Au_{10} cluster was directly related to the frontier orbitals of the Au_{10} cluster.
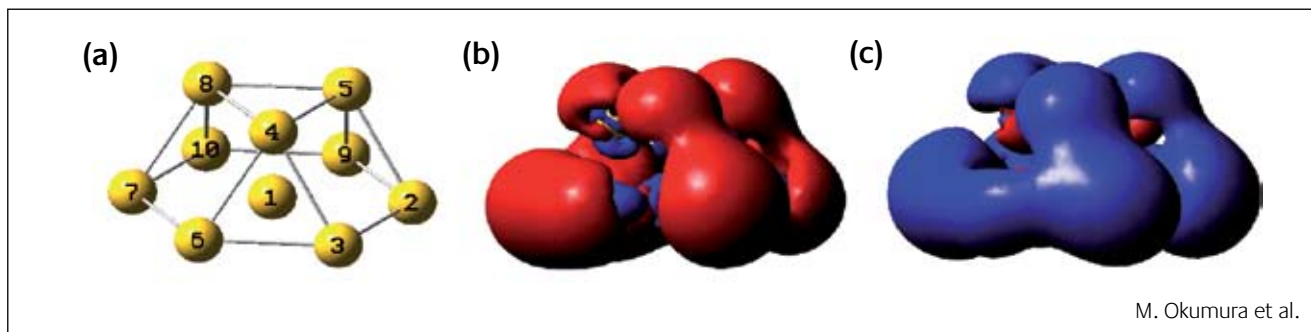
Figure 1

(a) A schematic diagram of calculated structure of Au_{10}, (b) differential charge density between electron doped and neutral Au_{10} clusters, (c) differential charge density between hole doped and neutral Au_{10} clusters.

2   Interaction between Au and O_2 or H_2O

In order to study the interaction between the Au_{10} model cluster and the O_2 molecule, Au_{10}-O_2 models were examined. The calculation results show that Au_{10} and Au_{10}^- clusters, but not Au_{10}^+, have an interaction with O_2. The binding energies of the Au_{10}-O_2 and Au_{10}^--O_2 model systems are 0.33 and 1.95 kcal/mol, respectively. The optimized structures of these models are depicted in Figure 2. Distances between Au and O in both systems are 3.17 and 2.54 Å. The variations in the charge densities of the anionic Au_{10}-O_2 model, listed in Table 1, demonstrate charge transfer from the surface Au atoms to O_2 while the charge densities of O_2 in the neutral Au_{10}-O_2 model show negligibly small charge transfer. In Figure 3, the charge density maps of both the Au_{10}-O_2 and Au_{10}^--O_2 model systems and the spin density map of the Au_{10}^--O_2 model system are depicted. From Table 1 and Figure 3, it can be seen that relatively large charge and spin densities exist between O_2 and Au_{10}^- and on O_2 in Au_{10}^--O_2 although faint charge densities only exist between O_2 and Au_{10} in Au_{10}-O_2. These results indicate that the anionic Au cluster is favourable for the activation of O_2 on the surface of the Au cluster. Wallace and Whetten showed that only even numbers of Au anion clusters interact with O_2 (15). The tendency of their experimental results is similar to our calculation results because the binding energy with O_2 is much larger for the Au_{10}^- cluster than for the neutral Au_{10} cluster. This tendency is closely related to the characteristics of O_2 as an electron acceptor. In previous first-principles calculations, Yoon et al. (16) and Franceschetti et al. (17) suggested that the binding energy with O_2 is larger for negatively charged clusters than for neutral clusters. These results show the same tendencies as ours while their absolute values for the binding energies (0.46~1.30 eV) are much larger than ours. These discrepancies might be due to the different morphology of the Au clusters examined and the geometrical relaxation constraint on the geometrical optimization of our model systems.

Next, Au_{10}-H_2O models were examined to study the interaction between the Au_{10} clusters and H_2O molecule. The binding energies of the Au_{10}-H_2O, Au_{10}^--H_2O and Au_{10}^+-H_2O model systems are 5.28, 6.56 and 12.46 kcal/mol, respectively. Therefore, the tendency of H_2O adsorption on Au_{10} model clusters is different from that of O_2 adsorption because all Au_{10}-H_2O models examined have an interaction with H_2O and

the binding energy of Au_{10}^+-H_2O is largest among them. The optimized structures of these models are depicted in Figure 2 (c), (d) and (e). These results indicate that the mode of H_2O adsorption in the Au_{10}^--H_2O model system is completely different from those in the Au_{10}-H_2O and Au_{10}^+-O_2 model systems. The water molecule on the negatively charged Au_{10} is aligned with the protons directed toward the negatively charged Au cluster surface. We could attribute the resulting alignment of the adsorbed water in Au_{10}^--H_2O model to the electrostatic attraction from the negatively charged Au_{10} surface.

Wallace et al. also reported that the interaction between an anionic Au cluster and CO is stronger than that between anionic Au clusters and O_2 (17). This tendency is similar to our calculation results for the interaction between an Au cluster and H_2O. The common characteristic of both H_2O and CO is their ability to donate electrons to Au clusters. Therefore, it was found that the interactions between Au clusters and adsorbates have a close affinity with both the electronic state of the Au cluster and the characteristics of the adsorbates as acceptors or donors to the Au cluster. The variations in the charge densities of the Au_{10}-H_2O, Au_{10}^--O_2 and Au_{10}^+-H_2O models listed in Table 1, indicate charge transfer from an H_2O molecule to the surface Au atoms while Mulliken analysis is a relatively coarse method. These results imply that the presence of an H_2O molecule promotes an increase of the surface negative charge densities in the Au_{10} cluster because this charge transfer from H_2O to the Au cluster occurred in all the Au_{10}-H_2O clusters. Moreover, it is known that Au clusters catalyse several interactions with the inert support, such as active carbon, and gold nanoparticles themselves are catalysts in the liquid phase. This may also be related to the presence of H_2O. Therefore, we conclude that the presence of H_2O molecules plays an important role in the modification of the electronic state of Au clusters.

3   Coadsorption of O_2 and H_2O on the surface of an Au_{10} cluster

From the calculations, it was found that all Au_{10} model systems examined have an interaction with H_2O. The results obtained for H_2O adsorption onto the Au_{10} model systems are qualitatively in good agreement with the experimental results as it is known that the gold surfaces are
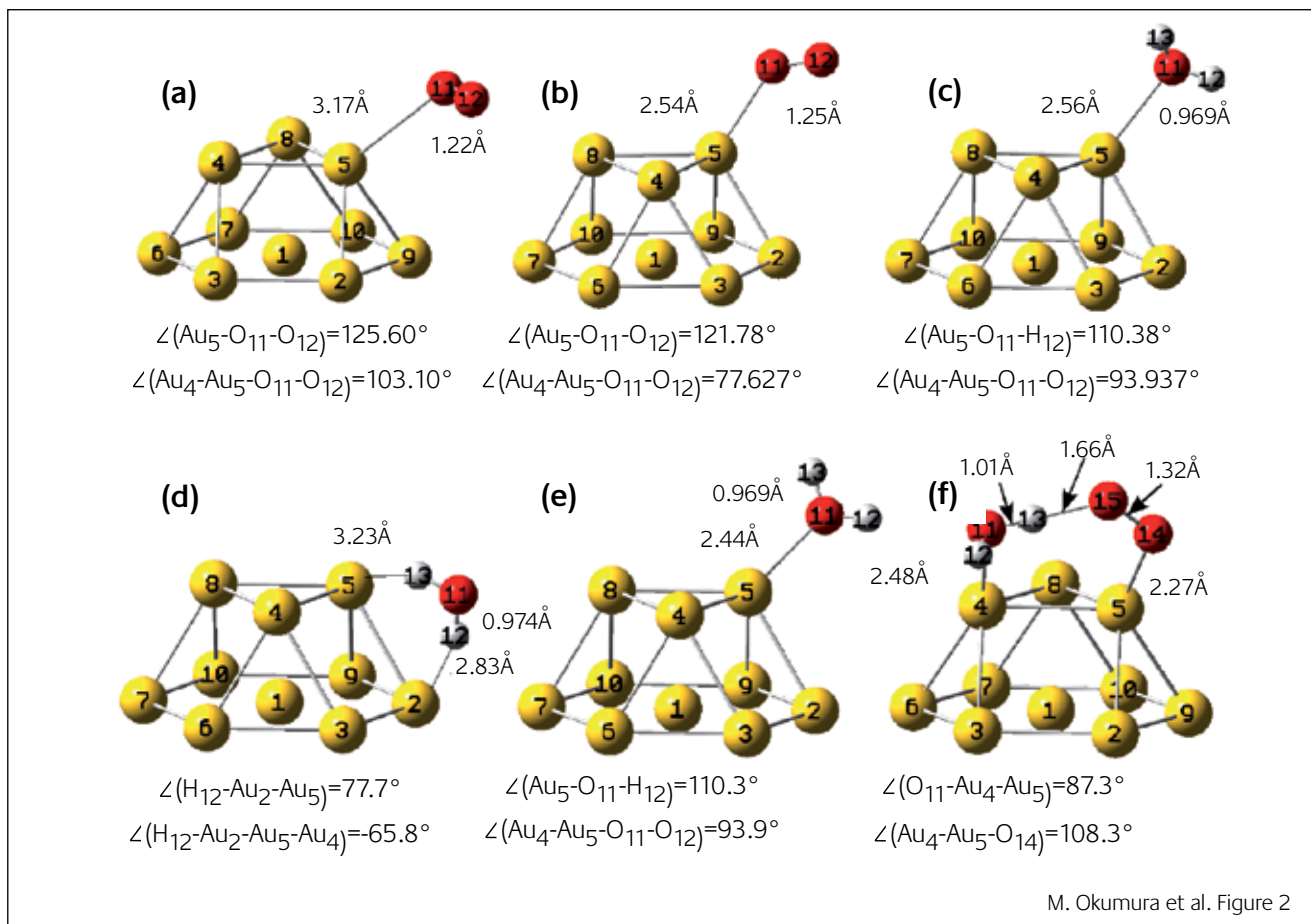
Figure 2

Calculated structures of model clusters: (a)neutral Au_{10}-O_2, (b) electron doped Au_{10}-O_2, (c) neutral Au_{10}-H_2O, (d) electron doped Au_{10}-H_2O, (e) hole doped Au_{10}-H_2O, and (f) electron doped Au_{10}-H_2O-O_2 .
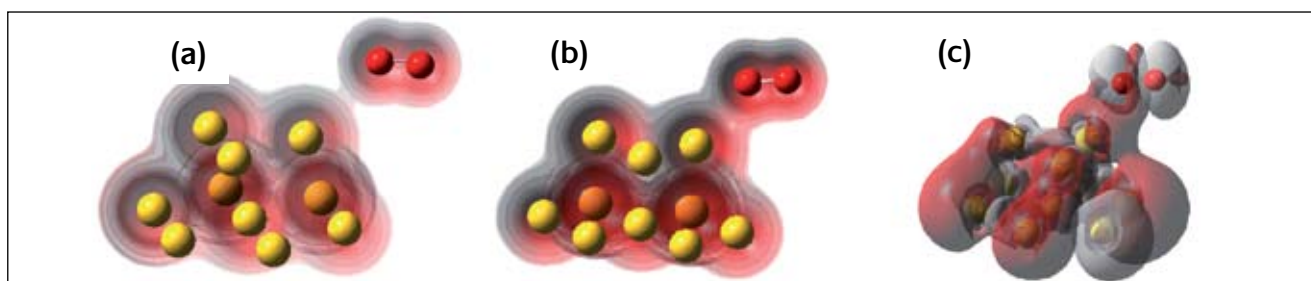

Figure 3

Schematic diagrams of charge density distributions in (a) Au_{10}-O_2 model and (b) Au_{10}^--O_2 model and of spin density distribution in (c) Au_{10}^--O_2 model.

hydrophilic. Next, the coadsorption of O_2 and H_2O on an Au_{10} surface was also investigated. From these calculations, we found the coadsorption of O_2 and H_2O on an Au_{10}^- surface is as shown in Figure 2 (f). The binding energy for the Au_{10}^--O_2-H_2O model system was found to be 10.2 kcal/mol. In Table 1, the charge densities in the Au_{10}^--O_2-H_2O model system are summarized. By comparing the result of Au_{10}^--O_2-H_2O with those of Au_{10}^--O_2 and $Au_{10}^-$$H_2O$, it was found that the negative charge densities on O_2 in Au_{10}^--O_2-H_2O were greatly increased. As the H-O distance between H_2O and O_2 in Au_{10}^--O_2-H_2O is 1.66 Å, this negative charge increase on O_2 might be associated with the hydrogen bonding between O_2 and H_2O. Therefore, it suggests that the hydrogen bond between O_2 and H_2O in the Au_{10}^--O_2-H_2O model system

also plays an important role in the activation of O_2 on the Au_{10} cluster surface.

Discussion

The results from our calculations indicate that neutral and anionic Au_{10} clusters have a weak interaction with O_2 and all the Au_{10} clusters examined have a relatively strong interaction with H_2O. In both O_2 and H_2O adsorption on the Au_{10} surface, charge transfer plays an important role in the formation of the Au_{10}-O_2 and Au_{10}-H_2O complexes. The direction of the charge transfer in all the Au_{10}-H_2O models examined is preferable to the generation of anionic Au clusters. From

this result, it could be presumed that the anionic Au cluster that is suitable for the activation of O_2 on its surface might be produced by charge donation from adsorbed H_2O molecules adsorbed onto the surface of the Au cluster. An excess of water molecules, however, might act as a poison for O_2 adsorption onto the Au cluster surface. It is known that CO oxidation catalytic activities of Au/SiO_2 and Au/Al_2O_3 are greatly increased with an increase of moisture while with Au/TiO_2 the activity is a maximum at a certain moisture concentration (6). Moreover, TEM observation showed that the shape of Au clusters deposited on SiO_2 is relatively spherical, suggesting that the interaction between the Au cluster and the support is weak and the electronic state of the Au clusters is close to neutral, while those on TiO_2 are hemispherical (3). Therefore, we could presume that the moisture effect of Au catalysts was totally dependent on the moisture concentration in the reactant gas, the morphology of the Au cluster deposited and the selection of supports. Consequently, our calculation results indicate that the anionic Au cluster is activated by H_2O adsorption, and this is in good agreement with the experimental results for CO oxidation over Au catalysts using a reaction gas containing a small amount of H_2O.

We also find that the coadsorption of O_2 and H_2O indicates the formation of a surface adsorbed complex and hydrogen bond between O_2 and H_2O in the Au_{10}^--H_2O-O_2 model system. This result also suggests that the activation of O_2 is promoted by the presence of moisture. Therefore, we conclude here that negatively charged Au atoms on the surface of the cluster, H_2O adsorption onto the surface of the cluster and formation of a hydrogen bond between adsorbed O_2 and H_2O molecules of a surface adsorbed complex all play an important role in activation of O_2 and thereby promote its catalytic activity.

Concluding remarks

The present theoretical calculations have provided the following interpretation on the charge transfer interaction in the active sites of an Au catalyst.

1 The morphology of the Au cluster, such as spherical and hemispherical shapes, affects the surface charge density distribution that is related to the catalytic activity of Au catalysts and the surface charge densities are drastically changed by the electron/hole doping.

2 The presence of H_2O molecules plays an important role in the modification of the electronic state of Au clusters.

3 The hydrogen bonding between O_2 and H_2O in the Au_{10}^--O_2-H_2O model system also promotes the activation of O_2 on the Au_{10} cluster surface.

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About the authors

Mitsutaka Okumura, Yasutaka Kitagawa and **Professor Kizashi Yamaguchi** are staff in the Quantum Chemistry Laboratory in the Department of Chemistry Graduate School for Science at Osaka University, Japan.

Professor Masatake Haruta is at Tokyo Metropolitan University and is very well known for his pioneering work on gold catalysis.

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