Understanding of the activity difference between nano gold and bulk gold by relativistic effects

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Abstract

It is a challenge to thoroughly understand the astonishing difference in catalytic activity between nano gold and bulk gold for some oxidation reactions. In this work, the Au-O interactions in various surroundings were investigated by DFT calculations and compared with the Ag-O interactions. We have found the three points. First, only Au-O bond can be significantly strengthened by the linear O-Au-O structure. Second, the Au-O bond is always stronger than the Ag-O bond when the bonds are embedded in common surroundings. Third, the Au-O bond becomes weaker than the Ag-O bond when the number of neighboring Au atoms becomes large, because the Au-O interactions are suppressed by the presence of neighboring gold atoms. The origin of

these three points can be attributed to wider spatial extension of d orbitals of gold, induced by strong relativistic effects. The strong relativistic effects make nano gold with smaller coordinate numbers highly active due to the ease in forming strong Au-O bonds, especially for the O-Au-O bond, whereas gold atoms in bulk with larger coordination numbers chemically inert due to the strong suppression by neighboring gold atoms destabilizing the O-Au-O bond.

Keywords: nano gold; Au-O interactions; relativistic effects; DFT calculations

1. Introduction

Gold as the noblest of all the metals [1] has been traditionally regarded as an inactive metal, while nano gold highly dispersed on oxide support displays unique and excellent catalytic activity for low temperature CO oxidation [2], water gas shift reaction [3], epoxidation of propene using H₂ and O₂[4], selective oxidation of alcohol [5], removal of NO_x[6], etc. Nano gold catalysts attract much attention and great efforts have been devoted to uncover the puzzle: why nano gold is highly active while usual bulk gold is chemically inert. Several explanations were proposed in recent years, such as, quantum size effects [7], low coordinated gold atoms [8], high oxidation states of gold[9,10], defects on oxide supports [11], a high density of gold/oxide perimeter interfaces [12,13] etc. These proposals may explain why nano gold is more active, but the reason of such a huge activity difference, unique to gold

beyond other materials, is still unclear.

Gold with extremely high ionization potential and electron affinity is the most electronegative metal. It is well known that relativistic effects play an important role in the properties of gold since the influence of relativistic effects becomes maximum at gold among the elements with $Z < 100$ [14]. For example, relativistic effects affect or induce the color of gold, the marked reduction in covalent-bond lengths involving gold atoms, the stability of oxidation state III in gold, Au-Au bond strength, oxygen insolubility in gold etc.[14,15] In principle, the catalytic activity of gold should be influenced by relativistic effects, while, so far as we know, how relativistic effects really affect the catalytic activity of gold is still ambiguous.

The unique ability of gold to catalyze oxidation reactions at low temperatures is one of the most important phenomena within all the catalytic properties of gold. In this case, the study of the Au-O interactions will help us not only to understand the O₂ activation as well as oxidation reaction mechanism on gold but also to grasp the origin of the activity in nano gold catalysis. Our previous study using density-functional theory (DFT) calculations showed that the linear O-Au-O structure plays a critical role in the oxidation reaction of gold catalysts, since it could strengthen the Au-O π bonding [16,17] In addition, the linear O-Au-O structures are also observed by FTIR matrix investigation [18]. In the present work, DFT calculations are applied to the Au-O interactions in different surroundings, including surfaces and some small cluster models, and the results are compared with those applied to the Ag-O interactions. The difference between the Au-O and Ag-O interactions and its dependence on local

coordination are thoroughly investigated, and are analyzed from the viewpoint of relativistic effects. Finally, the activity difference between nano gold and bulk gold is discussed.

2. Methods

DFT calculations are performed by using Vienna Ab Initio Simulation Package(VASP)[19]. The exchange-correlation energy and potential are described by the generalized gradient approximation in the form of PBE [20]. Testing calculations with fully relativistic effects including the spin-orbit coupling (SOC) are preformed and it is found that the SOC effects strengthen the Au-O bond by about 0.15 eV and the Au-Au bond by about 0.05 eV compared to the results with scalar relativistic effects. Since SOC effects are insufficient to overthrow the conclusions, DFT calculations in the scalar relativistic level are adopted in this work. Plane waves with a cutoff of 400 eV are used for projector augmented wave (PAW) potentials.[21·22] The criteria for the convergence in the structural relaxation are the residual force less than 0.02 eV Å⁻¹. The optimized lattice constants for bulk Au, Ag, Rh and Pd are 4.1709, 4.1667, 3.8424 and 3.9584 Å, which are in reasonable agreement with the experimental values of 4.08, 4.09, 3.80 and 3.89 Å, respectively [23]. All Au, Ag, Rh and Pd surfaces are modeled by a five-layer slab with a vacuum thickness of 15 Å, where the adsorbed species are placed on one side. The top three layers are relaxed, while the two bottommost layers are fixed at their bulk positions. A 3x3 supercell is used for the (111) and (100) surfaces with the Monkhorst-Pack (MP) 4x4x1 k-point mesh. A 2x2 supercell is used for the (321) surface with the MP 3x3x1 k-point mesh.

A (15 Å x 16 Å x 17 Å) unit cell for isolated gas-phase molecules or atoms is carried out and the Brillouin zone is sampled with one k-point. The binding energy (BE) is defined as $BE = [E(\text{system}+\text{O}) - E(\text{system}) - N(\text{O}) * E(\text{O})] / N(\text{O})$, where $E(\text{system}+\text{O})$ and $E(\text{system})$ are the total energies of systems with and without the oxygen, respectively. $E(\text{O})$ is the energy of an isolated O atom and $N(\text{O})$ is the number of oxygen atoms. The reaction barrier is calculated by force reversed method. [24] Spin polarization is considered during all the calculations.

3. Results and discussion

As shown in Figures 1a, 1b, 1e and 1f, the calculated BE of an O-Au-O trimer (-3.46 eV) is much larger than that of a Au-O dimer (-3.02 eV), while the BE of an O-Ag-O trimer (-2.61 eV) is weaker than that of a Ag-O dimer (-2.71 eV). This indicates that the Au-O bond is strongly enhanced in a linear O-Au-O structure, since π bond plays a key role in the Au-O bond [16]. It should be noted that the calculated binding energy of Au-O with -3.02 eV, which is significantly stronger than Huber and Herzberg's experimental value with -2.33 eV [25], but is in good agreement with Hecq's experimental value with -3.0 eV [26]. It is well known that silver has a valence electronic configuration [d10s1] similar to that of gold, and thus silver should display similar π bond enhancement in a linear O-Ag-O structure. However, such enhancement is ambiguous for silver. Note that the BE of O-Cu-O (-3.67 eV) is likewise weaker than that of Cu-O (-3.80 eV). Therefore, the significant π -bond enhancement by a linear structure is only observed for gold within coinage metals.

Next, the BEs of Au-O and Ag-O dimers are compared with those of oxygen

adsorption on the top of (111) surfaces, as shown in Figures 1(a), 1(c), 1(e) and 1(g). The BE of a Au-O dimer (-3.02 eV in Figure 1a) is larger than that of a Ag-O dimer (-2.71 eV in Figure 1e), while the BE of the oxygen adsorption on a Au(111) surface (-2.06 eV in Figure 1c) is weaker than that on a Ag(111) surface (-2.35 eV in Figure 1g). Compared to the Au-O bond in a dimer, the Au-O bond is dramatically weakened on a Au(111) surface. The weakening of the Au-O bond compared to that of Ag-O bond is observed also on the flat (100) surfaces, as the BE on the top of Au(100), -2.09 eV, weaker than that on Ag(100), -2.33 eV. Interestingly, the BE of oxygen adsorption on a stepped Au(321) surface, -2.46 eV, is stronger than that on the corresponding Ag(321) surface, -2.33 eV. This implies that the smaller coordination number of gold atoms on the stepped Au(321) surface compared to those on Au(111) and Au(100) surfaces should induce the stronger Au-O bond, namely, higher reactivity. The property of less coordinated gold atoms with higher activity is consistent with that found in CO adsorption on gold [27]. Furthermore, this implies the possibility that neighboring gold atoms may hinder the reactivity of gold on (111) and (100) surfaces.

To uncover the reason why the Au-O bond becomes weaker than the Ag-O bond on the flat (111) and (100) surfaces, we investigate the BE of Au-O and Ag-O in different M_x -O (M =Au or Ag, x =1-6) cluster models as shown in Figure 2a-2i. In these models, all the atoms are fixed on the coordinated axis and the M-M bonds are fixed at 2.95 Å. Only the bond length of M-O is optimized. The option of 2.95 Å for the M-M bond length is based on the calculated Au-Au bond length (2.949 Å) and

Ag-Ag bond length (2.946 Å) in the bulk crystals. It is found that the structure of $M_3\text{-O}$ with mutually perpendicular M-M and M-O bonds (Figure 2f) is an important mark to judge the relative stability of O in $\text{Au}_x\text{-O}$ and $\text{Ag}_x\text{-O}$. As long as the $M_3\text{-O}$ structure is locally contained (Figures 2f, 2h-2i), the BE of Ag-O is stronger than that of Au-O. Otherwise, the BE of Au-O is stronger than Ag-O. Clearly, the $M_3\text{-O}$ structure is an effective mark to understand why Au-O bonds are weaker than Ag-O bonds on (111) and (100) surfaces.

To deeply understand the reason why the BE in $\text{Au}_3\text{-O}$ is weaker than that in $\text{Ag}_3\text{-O}$, we calculate the BEs of Au-O in $\text{AuAg}_2\text{-O}$, $\text{Au}_2\text{Ag-O}$ and $\text{Au}_3\text{-O}$ as well as those of Ag-O in $\text{AgAu}_2\text{-O}$, $\text{Ag}_2\text{Au-O}$ and $\text{Ag}_3\text{-O}$ models as shown in Figure 2(m)-2(r). Note that the six models have the same $M_3\text{-O}$ structure shown in Figure 2(f). Comparing the BEs of Au-O bond with those of Ag-O bond in pairs of AuAg_2O and $\text{Ag}_3\text{-O}$, $\text{Au}_2\text{Ag-O}$ and $\text{Ag}_2\text{Au-O}$, and $\text{Au}_3\text{-O}$ and $\text{AgAu}_2\text{-O}$, the Au-O bond shows large BE than Ag-O one. Therefore, the effect to suppress the Au-O (or Ag-O) bond by the neighboring Au atoms is stronger than that by the neighboring Ag atoms. In this way, the reason why the Au-O bond in $\text{Au}_3\text{-O}$ is weaker than the Ag-O bond in $\text{Ag}_3\text{-O}$ can be explained as the stronger suppression by the neighboring Au atoms, in spite of the intrinsically stronger Au-O bond.

To further prove the stronger suppression by neighboring Au atoms, we build additional two slab models as shown in Figures 1d and 1h, where an oxygen atom is adsorbed on a substituted Au atom on Ag(111) and on a substituted Ag atom on Au(111), respectively. The Au-O bond on the Ag(111) surface (Figure 1d) is stronger

than that on the Au(111) surface (Figure 1c), and the Ag-O bond on the Ag(111) surface (Figure 1g) is stronger than that on the Au(111) surface (Figure 1h). In this way, the following two points are confirmed. First, the suppression by neighboring Au atoms is much stronger than that by neighboring Ag atoms. Second, the Au-O bond is intrinsically stronger than the Ag-O bond, as observed in the comparison between the Au-O and Ag-O bonds embedded in the same environment as the Ag(111) surface (Figures 1d and 1g) and the Au(111) surface (Figures 1c and 1h), similarly to the cluster modes investigated in Figure 3.

Now, we know that the Au-O bond is intrinsically stronger than the Ag-O bond, and that the more significant weakening of Au-O than Ag-O on flat surfaces is caused by the stronger suppression by neighboring Au atoms. Therein, the BE of the oxygen adsorption on the top of Au(321) is stronger than that on the corresponding Ag(321) surface, because the surface coordinate number is relatively small. Next, we concentrate on the question why neighboring Au atoms show stronger suppression than Ag. Figure 3a and 3b show the schematic diagram of Au-O (or Ag-O) π -bonding and σ -bonding influenced by the d orbitals of neighboring Au (or Ag) atoms. We can see that the π -bonding contribution of Au-O (or Ag-O) is strongly influenced by the neighboring Au (or Ag) atoms, while the σ -bonding of Au-O (or Ag-O) is less influenced. Therefore, we can predict that the suppression by neighboring Au atoms mainly works on the π -bonding.

Figure 3(a) also shows that the strength of the influence strongly depends on the width or extent of d orbitals of the neighboring atoms. The influence should be

stronger if the d orbitals of the neighboring atoms spatially spread wider. Since the suppression by the neighboring Au atoms is much stronger than that by the neighboring Ag atoms, the width of d orbitals of Au atoms is considered to be much wider than that of Ag atoms. More importantly, the behavior of significant π bond enhancement by the linear O-Au-O structure compared to the O-Ag-O structure can be easily understood if the d orbitals of a Au atom spatially spread much wider than those of a Ag atom.

Here we investigate the width of d orbitals of Au atoms. It is well known that gold exhibits maximum impact of relativistic effects for the elements with $Z < 100$, which makes gold a very unique metal [14]. Because of the higher nuclear charge number of gold ($Z=79$), the velocity of $1s$ electron of a gold atom reaches near 58 % of light velocity. According to the relativistic effects (Einstein's Theory of Special Relativity), the mass of $1s$ electron ($m \approx 1.23m_0$) with high velocity will be much heavier than the rest mass (m_0), and the radius of a $1s$ orbital will contract by about 19 %. Based on the orbital orthogonality and mixing in of the higher continuum orbitals [28, 29], all the other s orbitals will contract accordingly. In addition, all the d and f orbitals will extend due to the enhancement of the shielding effect from the s electrons, as shown in Figure 3c. [30, 14]. Because the relativistic effects on gold are much stronger than on silver, the d orbitals of gold spatially spread much wider than those of silver. The calculated radius of $5d$ orbitals of gold is larger than $4d$ orbitals of silver by 16 % [31], which is in good agreements with the experimental results that the radius of Au^+ is larger than that of Ag^+ by 19 %. [32] .

As is well known, the wider spatial extension of d orbitals of gold could induce wider d band width of gold and stronger Au-Au bond, compared to that of silver. [33,15] Moreover, as mentioned above, the wide spatial extension of d orbitals of gold induces two phenomena. The first is the enhancement of the π -bonding of Au-O. As shown in Figure 3a, the overlap between d orbitals and p orbitals in Au-O π bonding is remarkably larger than that in Ag-O π bonding, while the orbital overlap in σ -bonding shown in Figure 3(b) is not so influenced by the spatially extension of d orbitals. As a result, the π -bonding contribution of Au-O is considerably enhanced. Thus the BE of the O-Au-O trimer is stronger by 0.44 eV than that of the Au-O dimer (Figures 1a and 1b) since the linear O-Au-O trimer can further enhance the overlap of the π -bond [16]. In contrast, the BE of the O-Ag-O trimer is weaker than that of the Ag-O dimer (Figures 1e and 1f). It is predicted that the enhancement of π -bond occurs not only in the Au-O system, but also in various systems as Au-C [34], Au-S, Au-Au etc.

The second is the dramatic weakening of the Au-O π -bonding by the neighboring Au atoms. As shown in Figure 3a, the overlap between the d orbitals of neighboring Au atoms is larger than that of Ag atoms. The increase of Au-Au orbital overlap weakens the Au-O π -bonding, since the orbital symmetries of Au-Au and Au-O have a mismatch. Therefore, a gold atom with a smaller number of gold neighbors shows stronger Au-O bond. For example, the BE of the oxygen adsorption on the stepped Au(321) surface (-2.46 eV) is larger than those on the flat Au(111) and Au(100) surfaces (-2.06 eV and -2.09 eV). It is also predicted that the suppression by

neighboring Au atoms should work not only on the π -bond of Au-O but also on various π -bonds of Ag-O (Figure 3), Au-CO [35], Rh-CO etc.

These two effects due to the wide spatial extension of d orbitals of gold should induce remarkable dependence of the gold property on its local coordination. On one hand, a large number of low-coordinated gold atoms make nano particles or clusters highly active, since it could form a strong Au-X π -bond with an adsorbate (X). More importantly, the Au-X π -bond can be further strengthened via some collinear or co-planar structures. Specifically, the Au-O bond can be strengthened by linear O-Au-O structures. Thus gold atoms at the perimeter sites of Au-particle/oxide interfaces are highly active for O₂ activation since the linear O-Au-O structure could be formed with the oxygen in an oxide support and the oxygen in an adsorbed O₂ molecule [16, 13, 36]. It should be noted that the formation of strong linear O-Au-O structures is the primary cause of high catalytic oxidation activity of nano gold catalysts. It should be noted that the energies of d electrons increase with the spatial extension of d orbitals, and one may obtain the similar conclusions based on the energy effects of d orbitals. In this work, only the spatial effects are discussed, since the energy effects and spatial effects are always accompanied with each other and spatial effects are more visual than energy effects.

The phenomena of Au-X bond strengthened by linear structure is not only limited in Au-O bonds. As we can see, the basic unit of a AuCl crystal is a linear [Cl-Au-Cl] structure, and a AuCl₃ molecule has a co-planar structure, where the linear or co-planar structure could strengthen the Au-Cl π -bond, leading to the stability of

these structures. On the other hand, gold atoms in large bulk gold are inert, because the Au-X bond is significantly weakened by neighboring gold atoms. Therefore, the adsorption of usual atomic or molecular species are very weak on bulk gold surfaces [37,37]. As a result, the low catalytic oxidation activity of bulk gold may be assigned to the difficulty in forming strong Au-O bonds especially for linear O-Au-O structures. In this way, the remarkable difference in catalytic activity between bulk gold and nano gold may be generated.

Since gold exhibits maximum impact of the relativistic effects, intrinsically active gold atoms become inert in bulk due to the strong suppression by neighboring gold atoms. Based on this, some inspirations could be drawn for gold catalysis. The activity of gold should be partly kept by embedding Ag or some other metals with weak relativistic effects, as seen in Figure 1(d). This implies that gold alloy particles may display better catalytic activity than pure gold particles. To prove this, we calculated O and S adsorption on a Au(111) surface with two silver atoms which substituted gold atoms as shown in Figure 4(a) and 4(b). The linear O-Au-O structure is adopted since it is more stable than other configurations.[16] Compared to O and S adsorption on a Au(111) surface without Ag substitution, the adsorption is strengthened by 0.20 eV and 0.21 eV, respectively.

The O₂ direct dissociation on a Au(100) surface is also calculated, and the reaction barrier is decreased by 10 % with only one silver atom substituted, as shown in Figure 4c. In these systems, the silver atoms do not directly contact with oxygen or sulfur atoms. Therefore, the weak suppression by neighboring Ag should be the

reason of higher activity of the Au-Ag systems in Figure 4(a), 4(b) and 4(c). Higher activity of Au-Ag alloy catalysts was really observed in some experiments. [38,39] These results also indicate the destabilization of Au-O and O-Au-O structures by the neighboring gold atoms in bulk gold system.

The strong suppression by neighboring gold atoms should be effective not only on gold, but also on other active centers, which can be used to prevent the poisoning of active centers by some strong adsorbates. This is important in catalyst design, because many metals are too reactive that they are easily poisoned by some adsorbates. There is a possibility that gold can be used as excellent additives for catalysts to control the reactivity. For example, because of strong adsorption of CO on Rh or Pd metals, their surfaces are saturated by CO and exhibit less activity for CO oxidation at low O_2/CO ratio (for example, $O_2/CO \leq 1$) [40].

According to our calculations, the adsorption of CO is quite strong on Rh and Pd surfaces. The adsorption energy is -1.89 eV on the top of a Rh(111) surface and -1.36 eV on Pd(111) surface. In Figure 4d, each Rh atom is surrounded by gold atoms on the (111) surface by substitution. The calculated adsorption energy of CO on the Rh atom on this surface is decreased to -1.68 eV. On the similar Pd(111) surface with Au substitution, the adsorption energy is reduced to -1.16 eV. This suggests that the CO adsorption on Rh-Au or Pd-Au alloys should be weaker than on Rh or Pd catalysts. Thus, Rh-Au or Pd-Au alloys may display higher catalytic activity for CO oxidation at low O_2/CO ratio. Experimentally, it has been shown that Rh-Au catalysts and Pd-Au catalysts display higher catalytic activity than corresponding pure Rh and Pd

catalysts at low O₂/CO ratio (O₂/CO=0.5) [41, 42].

Although the reaction mechanisms may be different from the usual gold catalysis, more and more evidences prove that the addition of gold can improve the catalytic or chemical activity of some transition metals. Besides the enhancement of the activity of Ag, Rh and Pd for CO oxidation [41, 43], the presence of gold promotes Cu reactivity with HCl [44], enhances the intrinsic catalytic activity of Pd for organic synthesis reactions [45] or synthesis of hydrogen peroxide [46], and improves the activity of Pt for selective aerobic oxidation of polyols [47] etc. The role of gold in these catalysts may be related to the spatial wide extension of *d* orbital induced by the strong relativistic effects.

4. Conclusions

In this work, the Au-O interactions in different surroundings are compared with the Ag-O interactions by DFT calculations. It is found that only Au-O bonds can be significantly strengthened by the linear O-Au-O structures. The Au-O bond is always stronger than the Ag-O bond when the Au-O or Ag-O bonds are embedded in common surroundings. The suppression by the neighboring gold atoms on the Au-O or Ag-O bond is stronger than that by the neighboring silver atoms. The reason of all these phenomena can be assigned to the spatial extent of *d* orbitals of gold wider than that of silver, due to the stronger relativistic effects of gold. The wider spatial extension of *d* orbitals of gold leads to two influences. First, gold atoms in clusters or particles with smaller coordination numbers are active due to the ease in forming

strong Au-O bonds, especially for the O-Au-O bond. Second, gold atoms in bulk with larger coordination numbers are chemically inert, because the strong suppression by neighboring gold atoms destabilizes the O-Au-O structures. The present work helps us to understand the mechanism of the activity of gold catalysts for oxidation reactions, and provides us a possible guide in the catalyst design.

Acknowledgments

The authors greatly thank Prof. Y. Iizuka for fruitful discussions. This study was supported by Grant-in-Aid for Specially Promoted Research Grant No. 19001005 from the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT). A part of this study was supported by the Management Expenses Grants for National Universities Corporations from MEXT, and by Japan Science and Technology Agency (JST), Core Research for Evolutional Science and Technology (CREST).

Figure 1. The structures of a Au-O dimer (a), an O-Au-O trimer (b), O on the Au(111) surface (c), O on a Au substituted Ag(111) surface (d), a Ag-O dimer (e), an O-Ag-O trimer (f), O on the Ag(111) surface (g) and O on a Ag substituted Au(111) surface (h)

Figure 2. The schematic structures of M_x -O models (M =Au or Ag, x =1~6) and the binding energies (unit: eV) of O in M_x -O are shown

Figure 3. The schematic diagram of Au-O (or Ag-O) π -bonding (a) and σ -bonding (b) influenced by the d orbitals of neighboring Au (or Ag), and the contraction of s orbitals and extension of d orbitals of gold due to the relativistic effects (c). The circles by solid and dot lines represent the orbitals with and without the relativistic effects, respectively

Figure 4. The top views of a linear O-Au-O structure on a Au(111) surface with two surface gold atoms substituted by silver atoms (a), a linear S-Au-S structure on a Au(111) surface with two surface gold atoms substituted by silver atoms (b), the transition structure of O₂ dissociation on a Au(100) surface with one subsurface gold atom substituted by silver atom (c), and a CO adsorption structure on a Rh(111) surface with each surface rhodium atom surrounded by gold atoms on the (111) surface via substitution (d)

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Graphical abstract