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ROYAL SOCIETY OF CHEMISTRY

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Adsorption of a single gold or silver atom on vanadium oxide clusters

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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The bonding properties between the single atom and the support have a close relationship with the stability and reactivity of single-atom catalysts. As a model system, structural and electronic properties of bimetallic oxide clusters $MV_3O_y^q$ (M = Au or Ag, $q = 0, \pm1$, and y = 6-8) are systematically studied using the density functional theory. The single noble metal atom Au or Ag tends to be adsorbed on the periphery of the V oxide clusters. Au prefers V sites for oxygen-poor clusters and O sites for oxygen-rich clusters, while Ag prefers O sites for most cases. According to the natural population analysis, Au may possess positive or negative charges in the bimetallic oxide clusters, while Ag usually possesses positive charges. The bonding between Au and V has relatively high covalent character according to the bond order analysis. This work may provide some clues for understanding the bonding properties of single noble metal atoms on the support in practical single-atom catalysts, and serve as a starting point for further theoretical studies on the reaction mechanisms of related catalytic systems.

1. Introduction

Gold (Au) exhibits unique catalytic properties in various reactions, such as the oxidation of CO at low temperature, when it is deposited as nanoparticles on metal oxide surfaces.[1] Due to the complexity of the surface reaction systems, the reaction mechanisms are still far from clear with debates on the active sites and the role of gold. Some studies suggested that Au with different charge states (cationic,[2] anionic,[3] and zerovalent[4]) or with low coordination numbers[5] plays a crucial role, while some others emphasized the importance of the oxide support or the perimeter sites between the support and the Au atoms.[6] A theoretical research based on *ab initio* molecular dynamics simulations suggested that a single Au atom (i.e., Au_1) was dynamically generated from Au_{20}/CeO_2 as the active centre in the reaction process, indicating that in ordinary heterogeneous catalysis the actual active centre may be hidden by appearances and difficult to be identified.[7]

The *single-atom catalysis* (SAC) proposed recently opens a new way to maximize the use of noble metal atoms (e.g. Au, Ag, and Pt) and has a great potential for achieving high chemical activity and selectivity.[8] Because the surface structures in SAC are well-defined with uniform single-atom dispersion, investigations on SAC have the facility to determine the active centre and understand the catalytic mechanisms, therefore offer some rational strategies for the design of novel catalysts.[9] However, it is still a challenge to study the heterogeneous catalytic processes on a surface for SAC due to high technical requirements, no matter using experimental or theoretical methods. To simplify the problem, a possible way is to use the cluster model, which can be treated under isolated, controlled, and reproducible conditions in experiments and reliably handled by theoretical quantum chemical calculations.[10] Recently, He *et al.* studied reactions on a series of oxide clusters doped with Au_1 by high-resolution mass spectrometry combined with density functional theory (DFT) calculations.[11-15] The Au_1 atom was found to play unique roles in various reactions, including the oxidation of CO on $Au(TiO_2)_{2,3}O_{1,2}^-$,[11] $AuFeO_3^-$,[12] and $AuAl_3O_{4,5}^+$,[13] as well as the activation of H_2 on $AuCeO_2^+$ [14] and multiple C-H bonds on $AuNbO_3^+$.[15] At different stages of the reactions, the Au_1 atom acts as a CO trapper and an effective electron storage to accept or release electrons. These studies provide some detailed insights into the roles of Au in SAC for CO oxidation at a molecular level, and show the applicability and advantage of the cluster models in studying the mechanisms of SAC reactions.

The Au doped metal oxide clusters mentioned above were studied case by case, and a systematic study is desired to find some general rules. As the first step to understand the catalytic mechanisms, the adsorption behaviour of a single noble atom on surfaces has a close relationship with the stability and reactivity of the single-atom catalysts and thus is very important for rational and precise design of active sites in SACs at the atomic level.[9,16] Therefore, in this work, we performed a systematic theoretical investigation on the adsorption behaviour of Au_1 on selected vanadium (V) oxide clusters, considering that V oxides are widely used as heterogeneous catalysts[17] and a strong synergistic effect between Au and vanadia was found in some catalytic reactions.[18]

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The studied V oxide clusters were selected according to the Δ value which clarifies the oxygen-richness or poorness of an oxide cluster. The $\Delta \equiv 2y - nx + q$ for $M_xO_y^q$, where q is the charge number and n counts the highest oxidation state of element M ($n = 5$ for M = V).[19] We studied neutral, cationic, and anionic V_3O_y clusters with $\Delta = -3$ (V_3O_6), -2 ($V_3O_6^+$ and $V_3O_7^-$), -1 (V_3O_7), 0 ($V_3O_7^+$ and $V_3O_8^-$), and +1 (V_3O_8), respectively. The adsorption of Ag_1 on these clusters was also studied for comparison.

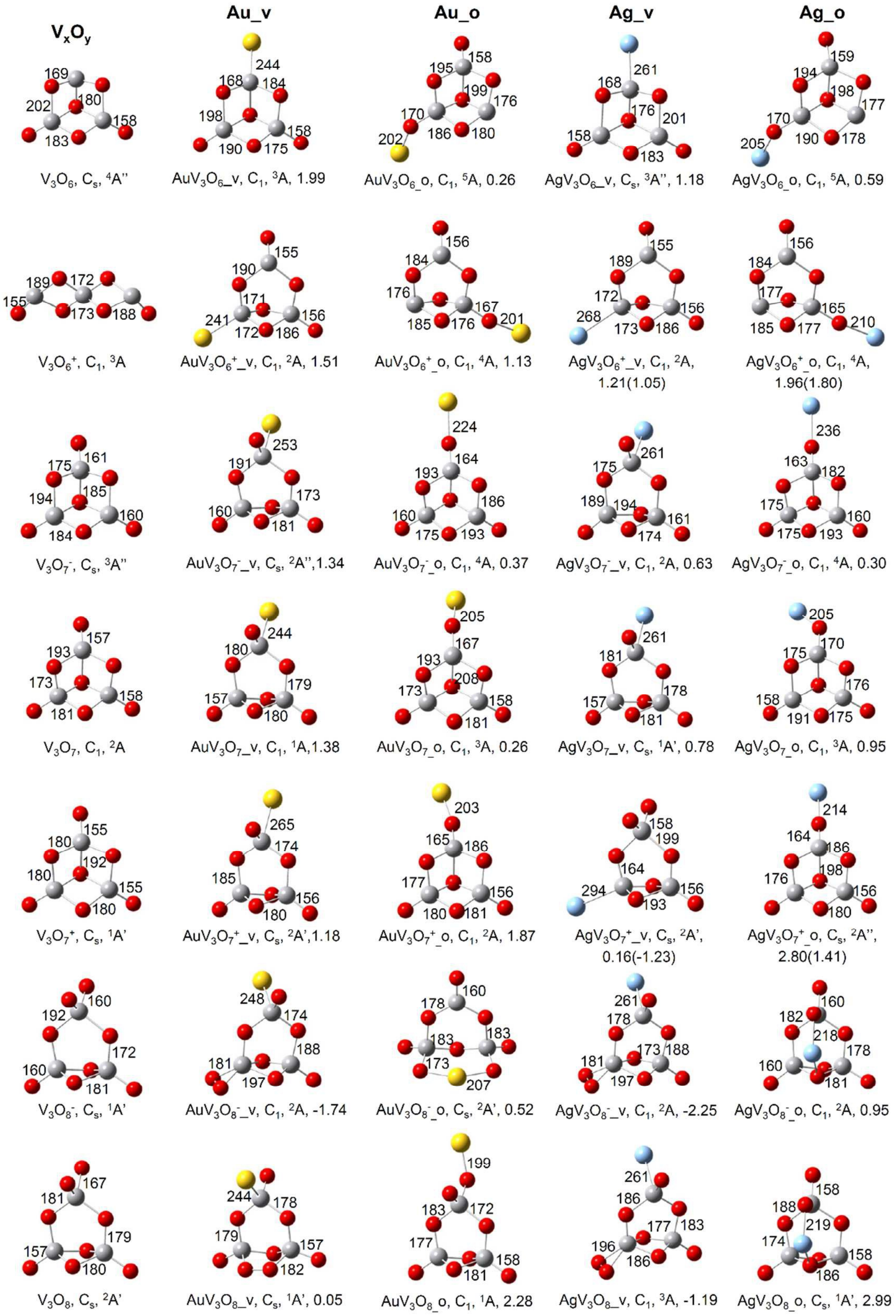

Figure 1. Geometries of V_3O_y and MV_3O_y clusters optimized by using the B3LYP functional (M = Au, Ag). Labels _v and _o indicate the adsorption sites of V and O, respectively. Symmetry, electronic state, and binding energy (E_b) between neutral Au or Ag and V oxide clusters are listed. The binding energy between Ag^+ and V_3O_6 or V_3O_7 are listed in brackets. Lengths are in pm and energies are in eV.

2. Computational methods

DFT calculations were performed using the Gaussian 09 program[20] with the hybrid B3LYP functional.[21-23] This functional has been demonstrated by several research groups to produce reasonably good results for homonuclear V oxide clusters,[24-31] as well as some V-M (M = Si, P, Al, Ag, Ce) heteronuclear oxide clusters,[32-39] compared with various experimental results. Global optimization was carried out for all studied clusters by a home-made Fortran code[40] based on genetic algorithm and DFT calculations. For Au (Ag)-V bimetallic oxide clusters, structures with the Au (Ag) on a number of adsorption sites of the low-lying structures of homonuclear V oxide clusters were also tested. These initial structures were optimized with small basis sets (LANL2DZ for all atoms)[41-43] and coarse convergence criteria in both self-consistent field and optimization steps to save the computational costs. Then low-lying isomers were reoptimized under standard convergence criteria with larger basis sets (def2-TZVP),[44] in which all-electron basis sets with triple-zeta valence and polarization were used for V and O, while for Au and Ag the corresponding effective core potentials[45] were used for inner shell electrons to take into account the scalar relativistic effects. Vibrational frequency calculations at the same theoretical level were performed to ensure that all stable structures have no imaginary frequency, and all the calculated energies reported here are with zero-point vibrational energy (ZPE) correction.

3. Results and discussion

3.1 Geometric structures

As a starting point, homonuclear V oxide clusters $V_3O_y^q$ (q = 0, ±1 and y = 6-8) were fully optimized and the most stable structures are shown in Figure 1. Three typical structures are found, namely, cap (V_3O_6 and $V_3O_7^{-/0/+}$), chain ($V_3O_6^+$), and ring ($V_3O_8^{-/0}$), which are generally consistent with previous works.[24-26,46-52] The exceptions are that the ring structures were suggested as the ground states for V_3O_6,[48-49] $V_3O_6^+$,[48] $V_3O_7^-$,[46] and V_3O_7 [53] in some previous works, while they were found to be low-lying isomers or not stable in our calculations and some other works ($V_3O_6^+$,[24-25,46-47] $V_3O_7^-$,[47] and V_3O_7 [47-49]). For example, we found that the ring structure of $V_3O_6^+$ is higher in energy than the most stable chain structure by 0.11 eV. It should be pointed out that due to the limited accuracy of DFT calculations, the most stable structures we obtained here are not definitely the exact ground states of the clusters. The main purpose of this work is to find some general principles of the interaction between Au/Ag and V oxide clusters. Further studies are required to confirm the ground state structures of V and Au (Ag)-V oxide clusters by combining high-level quantum chemical calculations and experiments such as infrared (multiple-photon) photodissociation (IRPD/IRMPD),[24-27,54] collision-induced dissociation (CID),[28-30] and photoelectron spectroscopy (PES).[31,55-56]

When the dopant atom Au or Ag is introduced, it is found that the structures in which Au/Ag intrudes into the V oxide clusters (i.e., Au/Ag occupies the positions of V or O in the original V oxide clusters) are unstable or highly energized. Instead, the Au/Ag atom is usually adsorbed on the periphery of the V oxide clusters, and both the V and O atoms are possible adsorption sites. Figure 1 shows the most stable structure for each type of adsorption site, denoted as $MV_3O_y^{-/0/+}$_s (M = Au or Ag, and _s = _v or _o for the adsorption site V or O). In a few oxygen-rich clusters ($AuV_3O_8^-$_o and $AgV_3O_8^{0/-}$_o), Au/Ag is bound to two O atoms. Geometric structures do not change much during adsorption, except those for $V_3O_6^+$ (the chain structure of $V_3O_6^+$ to ring structures of $MV_3O_6^+$) and some _v structures of oxygen-rich clusters (such as $AgV_3O_8^{0/-}$_v) for which the atoms need rearrangement to form a V site for Au/Ag adsorption.

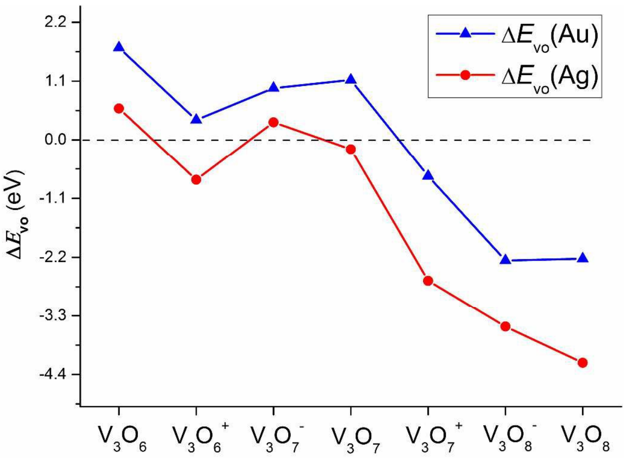

Figure 2. Energy difference between the two adsorption sites. $\Delta E_{vo}(M) = E(MV_3O_y\_o) - E(MV_3O_y\_v)$, where E is the total energy and M = Au or Ag.

3.2 Binding energies

The binding energies (E_b) of neutral Au or Ag atom on $V_3O_y^q$ clusters are listed in Figure 1, which is calculated by

$$E_b = E(M) + E(V_3O_y^q) - E(MV_3O_y^q) \qquad (1)$$

where M = Au or Ag, q = 0, ±1, y = 6-8, and E is the total electronic energy with ZPE. There are three clusters, $AuV_3O_8^-$_v, $AgV_3O_8^-$_v, and AgV_3O_8_v, which have negative values of E_b, indicating that the dissociations of them into Au/Ag and $V_3O_8^q$ are exothermic (i.e., they are thermodynamically unstable). So for these oxygen-rich clusters, the adsorption of Au/Ag on V sites is only kinetically stable (i.e., the adsorption structure is a local minimum on the energy surface, and the above dissociations have barriers and thus cannot happen spontaneously at low temperature). Note that for $AgV_3O_6^+$ and $AgV_3O_7^+$, since the calculated ionic potential of Ag (7.93 eV) is less than those of V_3O_6 and V_3O_7 (8.09 and 9.32 eV, respectively), the dissociation channels into Ag^+ and neutral V oxides are more exothermic than into Ag and cationic V oxides. Taking these channels into account, $AgV_3O_7^+$_v is also thermodynamically unstable by dissociation into Ag^+ and V_3O_7 (corresponding to the E_b

of −1.23 eV in the bracket of Fig. 1).

For clear comparison of the two adsorption sites for a certain $MV_3O_y^q$ cluster (M = Au, Ag), Figure 2 plots the energy difference of the two sites (ΔE_{vo}), which was calculated by $\Delta E_{vo}(M) = E(MV_3O_y\_o) - E(MV_3O_y\_v)$ (E is the total energy), or alternatively, $\Delta E_{vo}(M) = E_b(M \text{ on } V) - E_b(M \text{ on } O)$. As the Δ (i.e., the oxidation degree of a cluster) increases, ΔE_{vo} decreases generally for both Au and Ag, which is quite apparent that the O site becomes favourable when the clusters have more O atoms. Positive values of ΔE_{vo} indicate that V site is preferred for most oxygen-poor clusters (Δ = −3, −2, and −1 clusters, i.e., V_3O_6, $V_3O_6^+$, $V_3O_7^-$, and V_3O_7), except the cases of Ag on $V_3O_6^+$ and V_3O_7, while the O site is preferred for oxygen-rich clusters (Δ = 0 and +1, i.e., $V_3O_7^+$, $V_3O_8^-$, and V_3O_8) with negative ΔE_{vo}. There are four vanadium oxide clusters taking V and three taking O as the favourite adsorption sites for Au, while the corresponding numbers for Ag are two and five, respectively. Ag prefers O site to V site even for the oxygen-poor clusters $V_3O_6^+$ and V_3O_7, and the curve of $\Delta E_{vo}(Au)$ is always above that of $\Delta E_{vo}(Ag)$, which supports that Au prefers V site more than Ag does. This trend is also supported by the fact that for each V oxide cluster, $E_b(Au) > E_b(Ag)$ for V sites while $E_b(Au) < E_b(Ag)$ for O sites (except $V_3O_7^-\__O$) from the data of E_b in Figure 1.

3.3 Comparison with diatomic molecules

Studies on the properties of diatomic molecules MO, MV (M = Au, Ag), and VO are helpful to understand the adsorption behaviour of Au_1/Ag_1 on V oxide clusters. The dissociation energy into thermodynamically most stable products (D_0) and the bond length of these diatomic molecules are listed in Table 1. The D_0 values of AuV (or AuO) are generally larger than those of AgV (or AgO), except that $D_0(AuO^-)$ is close to $D_0(AgO^-)$, which is consistent with shorter AuV and AuO bond lengths with respect to those of AgV and AgO, respectively. The values of D_0(MV) is comparable to those of D_0(MO), within 1 eV for all charge states, and $D_0(MV^+) > D_0(MO^+)$ while $D_0(MV^-) < D_0(MO^-)$, which implies that V and O are two competition sites for Au/Ag adsorption. For neutral molecules, $D_0(AuV) > D_0(AuO)$ while $D_0(AgV) < D_0(AgO)$, which supports that Au is superior to Ag for bonding with V. Since the D_0 of the diatomic molecule VO is much larger (by more than 3.7 eV) than those of AuV, AuO, AgV and AgO regardless of charge states, it is quite apparent that the Au/Ag prefers to be adsorbed on the periphery of V_3O_y clusters to avoid breaking the strong V-O bonds.

When the Au atom is adsorbed on the V site of $V_3O_y^{-/0/+}$, the [Au-V] moiety has quite large positive charges ($q_{[Au-V]}$ is about 0.59-1.44 |e|) and the bond length of [Au-V] is about 2.4-2.6 Å (Table 2), which is close to that of the diatomic cation AuV^+. So it is expected that the bonding of [Au-V] in the bimetallic oxide clusters may have some similarities to that of AuV^+. The E_b([Au-V]) values in $AuV_3O_6\_v$ (1.99 eV) and $AuV_3O_6^+\_v$ (1.51 eV, or 1.62 eV if the ring structure of $V_3O_6^+$ is used) are close to those of $D_0(AuV^+$, 1.87 eV). Similarly, since the value of $q_{[Au\text{-}O]}$ is close to zero or negative (about −0.66 to 0.17 |e|), [Au-O] moiety may be similar to diatomic AuO or AuO^-. The E_b([Au-O]) values for $AuV_3O_7^+\_o$ (1.87 eV) and $AuV_3O_8\_o$ (2.28 eV) are close to those of D_0(AuO or AuO^-, ca. 2.0 eV). Analogously, in $AgV_3O_y^{-/0/+}$ clusters, [Ag-V] moiety is similar to AgV^+, and [Ag-O] is to AgO or AgO^-. Note that $D_0^+(AuV)$ is close to $D_0^{0/-}(AuO)$ within 0.14 eV (Table 1), while $D_0^+(AgV)$ is smaller than $D_0^{0/-}(AgO)$ by more than 0.7 eV. From this point of view, it is expected that the V and O sites are competitive for Au adsorption while the O site is favoured for Ag adsorption.

	D_0^-	D_0^0	D_0^+	R^-	R^0	R^+
AuV	1.20	2.28	1.87	2.708	2.519	2.378
AuO	2.01	1.99	1.42	1.876	1.899	1.905
AgV	1.07	1.41	1.17	2.819	2.644	2.583
AgO	2.02	1.87	0.63	1.910	2.011	2.221
VO	6.10	6.29	5.58	1.601	1.580	1.537

Table 1 Calculated dissociation energy ($D_0^{-/0/+}$, in eV) and bond length ($R^{-/0/+}$, in Å) of anionic, neutral and cationic diatomic molecules AuV, AuO, AgV, AgO, and VO.

3.4 Population analysis

Natural Population Analysis (NPA) was performed on MV_3O_y clusters. The natural charges on Au_1/Ag_1 (Q) are plotted in Figure 3 to show the possible charge transfer between Au/Ag and the V oxide clusters. Each curve represents an adsorption site V or O for M = Au or Ag. The oscillation of the curves is due to the net charges of the clusters, and it is apparent that Q(cationic) > Q(neutral) > Q(anionic) for each curve. For each V oxide cluster (except $V_3O_7^-$), $Q(Ag\_o) > Q(Au\_o) > Q(Ag\_v) > Q(Au\_v)$. It is not unexpected that metal atoms (Au and Ag) often possess positive charges. For anionic clusters $AgV_3O_7^-\_v$ and $AgV_3O_7^-\_o$, Q(Ag) is close to zero. More interestingly, Au atoms on the V sites of V_3O_6, $V_3O_7^-$, and $V_3O_8^-$ have

Table 2 Calculated natural charges (q, in |e|) and bond lengths (R, in Å) of the [M-V] or [M-O] moiety in MV_3O_y clusters (M = Au, Ag) with M on V and O adsorption sites, respectively.

	[Au-V]		[Au-O]		[Ag-V]		[Ag-O]	
	q	R	q	R	q	R	q	R
V_3O_6	0.77	2.438	−0.22	2.017	0.84	2.605	−0.06	2.051
$V_3O_6^+$	1.00	2.414	0.15	2.014	1.24	2.678	0.25	2.097
$V_3O_7^-$	0.59	2.533	−0.66	2.244	0.73	2.613	−0.62	2.362

V_3O_7	0.81	2.436	−0.28	2.044	1.01	2.608	0.04	2.053
$V_3O_7^+$	1.44	2.646	0.17	2.033	1.53	2.944	0.26	2.144
$V_3O_8^-$	0.63	2.483	−0.01	2.073	0.77	2.610	0.12	2.182
V_3O_8	0.81	2.435	0.00	1.989	1.01	2.606	0.26	2.186

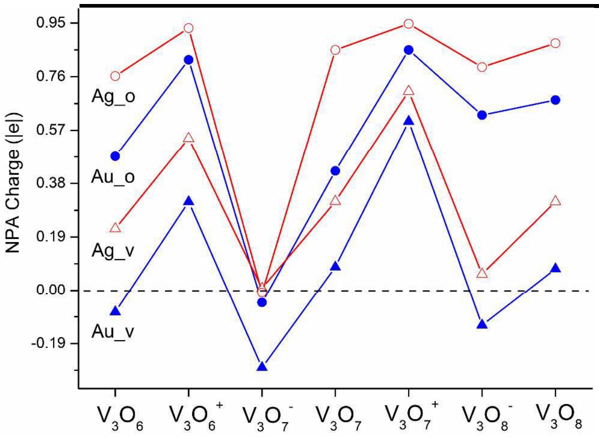

Figure 3. The natural charges on Au or Ag (Q) in MV_3O_y clusters (M = Au, Ag). Labels _v and _o indicate the adsorption sites of V and O, respectively.

significant negative charge populations as −0.08, −0.28, −0.12 |e|, respectively, and even on the O site of $V_3O_7^-$, the Au atom possesses −0.04 |e| charges. This suggests that metal atoms, such as Au, who has very large relativistic effect and shows the highest electron affinity of all metal atoms (approaching the values of halogens), can be negatively charged in the bimetallic oxide clusters.

Bond order is a quantitative description of chemical bonds and has been widely used to figure out the nature of the electronic structure and predict the stability and reactivity of the bonds. The values of Wiberg bond order (WBO),[57] which is an important indicator for the strength of covalent bonds, are listed in Table 3 for the M-V and M-O bonds in MV_3O_y clusters (M = Au, Ag) with M on V and O adsorption sites, respectively. It can be seen that WBO values for Au-V are generally larger than those for Ag-V, which is in agreement with the binding energies E_b(Au_v) > E_b(Ag_v). However, for the O adsorption sites, WBO(Au-O) > WBO(Ag-O) while E_b(Au_o) < E_b(Ag_o). This may be explained by that WBO is more suitable for covalent bonds while M-O bonds have high ionic character. To show this more clearly, a newly defined bond order, Laplacian bond order (LBO), was also calculated and listed in Table 3. The LBO was defined as a scaled integral of negative parts of the Laplacian of electron density in the fuzzy overlap space, and demonstrated to have a direct correlation with the bond polarity and the binding energy.[58] For example, the LBO values of H-H, H-Cl, and Na-Cl decrease as 0.887, 0.643, and 0.151 calculated by B3LYP/Def2-TZVP, along with the degressive covalent character of these bonds. The values of LBO for Au-V are much larger (more than twice for most cases) than those for the other three types of bonds (Au-O, Ag-V, and Ag-O), indicating the relatively high covalent character between Au and V, and the high polarity for the other three bonds. Now the values of LBO(Au-O) are no larger than those of LBO(Ag-O), consistent with E_b(Au_o) < E_b(Ag_o). The Au-V bond order in $AuV_3O_6^+$ has the largest value among all the M-V and M-O bonds (M = Au, Ag) in the studied clusters, no matter WBO or LBO is used, suggesting that the covalent interaction between Au and V in $AuV_3O_6^+$ is very strong, which agrees with the fact that the bond length of Au-V in $AuV_3O_6^+$ is the shortest among all Au-V or Ag-V bonds.

3.5 Comparison with the practical SAC

The comprehensive understanding and tuning of the strong metal-support interactions are great challenges in practical SAC.[9] Some studies on SAC have paid some attention on this issue. The Au_1/FeO_x catalyst was found extremely stable for CO oxidation at a wide temperature range,[16] in which the Au_1 atom occupies the Fe-vacancy and is bound to three or two oxygen atoms and thus have positive charges. The strong Au-O covalent bonding was suggested to be partially responsible for the ultra-stability of the Au_1/FeO_x catalyst during heating and catalytic cycles in comparison to the Au clusters/nanoparticles with weak metallic Au-Au interactions. In our calculations, the Au_1 atom can be bound to one O atom with quite large E_b, as in the oxygen-rich bimetallic oxide clusters $AuV_3O_7^+$_o (1.87 eV) and AuV_3O_8_o (2.28 eV). Additionally, the Au_1 atom can also make strong bonds with the V atom in some oxygen-poor clusters, such as in AuV_3O_6_v (1.99 eV) and $AuV_3O_6^+$_v (1.51 eV). So we may conclude that Au_1 atoms can be highly stabilized on the oxide surfaces

Table 3 Calculated Wiberg and Laplacian bond orders for the M-V and M-O bonds in MV_3O_y clusters (M = Au, Ag) with M on V and O adsorption sites, respectively.

	Wiberg bond order				Laplacian bond order			
	Au-V	Au-O	Ag-V	Ag-O	Au-V	Au-O	Ag-V	Ag-O
V_3O_6	0.998	0.522	0.852	0.323	0.238	0.079	0.073	0.109
$V_3O_6^+$	1.107	0.390	0.684	0.166	0.259	0.088	0.061	0.099

$V_3O_7^-$	0.818	0.237	0.869	0.130	0.183	0.036	0.071	0.036
V_3O_7	1.041	0.483	0.887	0.282	0.241	0.075	0.073	0.107
$V_3O_7^+$	0.610	0.345	0.421	0.135	0.136	0.083	0.031	0.083
$V_3O_8^-$	0.885	0.357	0.881	0.204	0.211	0.058	0.072	0.057
V_3O_8	1.040	0.565	0.886	0.170	0.243	0.089	0.074	0.058

with or without oxygen-vacancy by bonding with O or metal atoms. On the other hand, the binding between the Ag_1 and two O atoms in AgV_3O_8_o is particularly strong (E_b = 2.99 eV), indicating that Ag_1 atoms prefer to be adsorbed on oxygen-rich surfaces by making Ag-O bonds.

The charge states of the Au_1 atom have been investigated on various thin oxide films (MgO, FeO, SiO_2, and $Al_{10}O_{13}$) grown on metal single crystals.[59] It was found that the Au_1 atom might be adsorbed on top of oxygen ions of MgO films with positive charge state, on the oxygen vacancies with negative charges, or on the Mg ions also with negative charges if the film is thin enough. Here, we demonstrated that the Au_1 atom can be positively (for most _o cases and some _v cases) or negatively (for some _v cases and one _o case) charged, depending on its binding atoms (_v or _o) and the charge state of the clusters, while the Ag_1 atom always has positive (or nearly zero) charges. Studies on surfaces and clusters both demonstrate that the charge states of the Au_1 atom are dependant on its bonding atoms, which implies that in the catalytic reactions, the Au_1 atom could store or release electrons by making bonds with different atoms and thus facilitate the redox reactions.[15]

4. Conclusions

We systematically investigated the adsorption behaviour of Au_1 or Ag_1 on V_3O_y clusters by using DFT calculations. The Au/Ag atom tends to be adsorbed on the periphery of the V oxide clusters, and both the V and O atoms are possible adsorption sites. Au prefers V sites for oxygen-poor clusters and prefers O sites for oxygen-rich clusters, while Ag prefers O sites for most cases and prefers V sites only for limited oxygen-poor clusters. Although metal atoms often possess positive charges in the oxide clusters, there could be negative charges on Au_1 especially when it is bound to a V atom. The bonding between Au and V has relatively high covalent character. The unique bonding properties of Au in AuV_3O_y are expected to be represented in some other AuM_xO_y clusters, while further studies are required to reveal the influence on these properties by the cluster size, bond strength of M-O/M-Au, the electron affinity of M, and so on. Based on these results, reactivity of Au_1 or Ag_1 doped V oxide clusters towards typical small molecules (such as CO and CH_4) will be studied in future to reveal the detailed mechanisms in single-atom catalysis.

Acknowledgements

This work is supported by the National Natural Science Foundation of China (Nos. 91545122 and 21173233) and the Fundamental Research Funds for the Central Universities (Nos. JB2015RCY03, 13ZD24, and 2014ZZD10). We gratefully acknowledge the use of HPC cluster at School of Mathematics and Physics in NCEPU.

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