This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Adsorption of a single gold or silver atom on vanadium oxide clusters

Xun-Lei Ding,*, Dan Wang, Rui-Jie Li, Heng-Lu Liao, Yan Zhang, and Hua-Yong Zhang

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$_2$O$_y$ (M = Au or Ag, q = 0, ±1, 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. 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, anionic, and zerovalent) or with low coordination numbers 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. 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.

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. 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. 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. 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. 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$_{2,11}$, AuFeO$_3$$_{12}$, and AuAl$_2$O$_{2,13}$ as well as the activation of H$_2$ on AuCeO$_3$$_{14}$ and multiple C-H bonds on AuNbO$_{15}$. 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. 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 and a strong synergistic effect between Au and vanadia was found in some catalytic reactions.
The studied V oxide clusters were selected according to the Δ value which clarifies the oxygen-richness or poorness of an oxide cluster. The Δ = 2y − nx + q for M,Oₙⁿ, where q is the charge number and n counts the highest oxidation state of element M (n = 5 for M = V). We studied neutral, cationic, and anionic V₃O, clusters with Δ = −3 (V₃O₆), −2 (V₃O₆⁺ and V₃O₇⁻), −1 (V₃O₇⁺), 0 (V₃O₈ and V₃O₈⁻), and +1 (V₃O₈), respectively. The adsorption of Ag⁺ on these clusters was also studied for comparison.
2. Computational methods

DFT calculations were performed using the Gaussian 09 program\textsuperscript{20} with the hybrid B3LYP functional.\textsuperscript{21-23} This functional has been demonstrated by several research groups to produce reasonably good results for homonuclear V oxide clusters,\textsuperscript{24-27} as well as some V-M (M = Si, P, Al, Ag, Ce) heteronuclear oxide clusters,\textsuperscript{22-25} compared with various experimental results. Global optimization was carried out for all studied clusters by a home-made Fortran code\textsuperscript{26} 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)\textsuperscript{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)\textsuperscript{,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\textsuperscript{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\textsubscript{y}O\textsubscript{z}\textsuperscript{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\textsubscript{y}O\textsubscript{z} and V\textsubscript{y}O\textsubscript{z}\textsuperscript{−}), chain (V\textsubscript{y}O\textsubscript{z}−), and ring (V\textsubscript{y}O\textsubscript{z}\textsuperscript{−}), which are generally consistent with previous works.\textsuperscript{24-26,46-52} The exceptions are that the ring structures were suggested as the ground states for V\textsubscript{y}O\textsubscript{z}\textsuperscript{−}\textsuperscript{0/−1}, V\textsubscript{y}O\textsubscript{z}\textsuperscript{−}\textsuperscript{0/−1}, V\textsubscript{y}O\textsubscript{z}\textsuperscript{−}\textsuperscript{0/−1} and V\textsubscript{y}O\textsubscript{z}\textsuperscript{−}\textsuperscript{0/−1} in some previous works, while they were found to be low-lying isomers or not stable in our calculations and some other works (V\textsubscript{y}O\textsubscript{z}\textsuperscript{−}\textsuperscript{0/−1}, V\textsubscript{y}O\textsubscript{z}\textsuperscript{−}\textsuperscript{0/−1} and V\textsubscript{y}O\textsubscript{z}\textsuperscript{−}\textsuperscript{0/−1}). For example, we found that the ring structure of V\textsubscript{y}O\textsubscript{z}\textsuperscript{−} 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),\textsuperscript{24-27,54} collision-induced dissociation (CID),\textsuperscript{28-50} and photoelectron spectroscopy (PES).\textsuperscript{1,55-56}

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\textsubscript{y}O\textsubscript{z}\textsuperscript{−s} (M = Au or Ag, and _s = _v or _o for the adsorption site V or O). In a few oxygen-rich clusters (AuV\textsubscript{y}O\textsubscript{z}\textsuperscript{−v} and AgV\textsubscript{y}O\textsubscript{z}\textsuperscript{−o}), Au/Ag is bound to two O atoms. Geometric structures do not change much during adsorption, except those for V\textsubscript{y}O\textsubscript{z}\textsuperscript{−} (the chain structure of V\textsubscript{y}O\textsubscript{z}\textsuperscript{−} to ring structures of MV\textsubscript{y}O\textsubscript{z}\textsuperscript{−} and some _v structures of oxygen-rich clusters (such as AgV\textsubscript{y}O\textsubscript{z}\textsuperscript{−v}) for which the atoms need rearrangement to form a V site for Au/Ag adsorption.

3.2 Binding energies

The binding energies (\(E_b\)) of neutral Au or Ag atom on V\textsubscript{y}O\textsubscript{z}\textsuperscript{−} clusters are listed in Figure 1, which is calculated by

\[
E_b = E(M) + E(V\textsubscript{y}O\textsubscript{z}) - E(MV\textsubscript{y}O\textsubscript{z})
\]

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\textsubscript{y}O\textsubscript{z}\textsuperscript{−v}, AgV\textsubscript{y}O\textsubscript{z}\textsuperscript{−v}, and AgV\textsubscript{y}O\textsubscript{z}\textsuperscript{−v}, which have negative values of \(E_b\), indicating that the dissociations of them into Au/Ag and V\textsubscript{y}O\textsubscript{z}\textsuperscript{−} 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\textsubscript{y}O\textsubscript{z}\textsuperscript{−} and AgV\textsubscript{y}O\textsubscript{z}\textsuperscript{−}, since the calculated ionic potential of Ag (7.93 eV) is less than those of V\textsubscript{y}O\textsubscript{z} and V\textsubscript{y}O\textsubscript{z} (8.09 and 9.32 eV, respectively), the dissociation channels into Ag\textsuperscript{+} and neutral V oxides are more exothermic than into Ag and cationic V oxides. Taking these channels into account, AgV\textsubscript{y}O\textsubscript{z}\textsuperscript{−} is also thermodynamically unstable by dissociation into Ag\textsuperscript{+} and V\textsubscript{y}O\textsubscript{z} (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\(_3\)O\(_y\)\(_z\) cluster (M = Au, Ag), Figure 2 plots the energy difference of the two sites (\(\Delta E_{o,v}\)), which was calculated by \(\Delta E_{o,v}(M) = E(MV_3O_y)_o - E(MV_3O_y)_v\) (E is the total energy), or alternatively, \(\Delta E_{o,v}(M) = E_q(M \text{ on } V) - E_q(M \text{ on } O)\). As the \(\Delta\) (i.e., the oxidation degree of a cluster) increases, \(\Delta E_{o,v}\) 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 \(\Delta E_{o,v}\) indicate that V site is preferred for most oxygen-poor clusters (\(\Delta = -3, -2,\) and \(-1\) clusters, i.e., \(V_3O_6, V_3O_5, V_3O_4,\) and \(V_3O_3\)), except the cases of Ag on \(V_3O_6^+\) and \(V_3O_5^+\), while the O site is preferred for oxygen-rich clusters (\(\Delta = 0\) and \(+1\), i.e., \(V_3O_7\), \(V_3O_6^-,\) and \(V_3O_5^-\)) with negative \(\Delta E_{o,v}\). 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. Au prefers O site to V site even for the oxygen-poor clusters \(V_3O_6^+\) and \(V_3O_5^+\), and the curve of \(\Delta E_{o,v}(Au)\) is always above that of \(\Delta E_{o,v}(Ag)\), 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, \(E_q(Au) > E_q(Ag)\) for V sites while \(E_q(Au) < E_q(Ag)\) for O sites (except \(V_3O_7^-\) and \(V_3O_5^-\)) from the data of \(E_q\) 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/Ag on V oxide clusters. The dissociation energy into thermodynamically most stable products (\(D_0\)) and the bond length of these diatomic molecules are also listed in Table 1. The \(D_0\) values of AuV (or AuO) are generally larger than those of AgV (or AgO), except that \(D_0(AuV)\) 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 \(V_3O_7\) clusters to avoid breaking the strong V-O bonds.

When the Au atom is adsorbed on the V site of \(V_3O_6^-\), 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 \(E_q([Au-V])\) values in Table 1 Calculated dissociation energy (\(D_0\)) and bond length (\(R\), in Å) of the [MV\(_3\)O\(_y\)\(_z\)] moiety may be similar to diatomic AuO or AuO\(^+\). The \(E_q([Au-O])\) values for AuV\(_3\)O\(_6^-\)\(_o\) (1.87 eV) and AuV\(_3\)O\(_6^-\)\(_o\) (2.28 eV) are close to those of \(D_0(AuO)\) or \(D_0(AuO^+)\), ca. 2.0 eV. Analogously, in AgV\(_3\)O\(_6^-\)\(_o\) clusters, [Ag-V] moiety is similar to AgV\(^+\), and [Ag-O] is to AgO or AgO\(^+\). Note that \(D_0([Au-V])\) is close to \(D_0([O-Au])\) within 0.14 eV (Table 1), while \(D_0([Ag-V])\) is smaller than \(D_0([Ag-O])\) 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.

### 3.4 Population analysis

Natural Population Analysis (NPA) was performed on MV\(_3\)O\(_y\) clusters. The natural charges on Au and Ag atoms (Au\(_o\) and Ag\(_o\)) often possess positive charges. For anionic clusters, [AulV] and [AulO] is to AuV\(^-\) or AuO\(^-\), while the O site is preferred (\(Q_{(Au-V)}\) is close to zero). More interestingly, Au and Ag atoms on the V sites of \(V_3O_6, V_3O_5^-,\) and \(V_3O_4^+\) 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\(_3\)O\(_y\) clusters (M = Au, Ag) with M on V and O adsorption sites, respectively.

<table>
<thead>
<tr>
<th>[Au-V]</th>
<th>[Au-O]</th>
<th>[Ag-V]</th>
<th>[Ag-O]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(V_3O_6)</td>
<td>0.77</td>
<td>2.438</td>
<td>-0.22</td>
</tr>
<tr>
<td>(V_3O_6^+)</td>
<td>1.00</td>
<td>2.414</td>
<td>0.15</td>
</tr>
<tr>
<td>(V_3O_5^-)</td>
<td>0.59</td>
<td>2.533</td>
<td>-0.66</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.73</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-0.62</td>
</tr>
</tbody>
</table>
significant negative charge populations as −0.08, −0.28, −0.12 |e|, respectively, and even on the O site of V_{2}O_{5}^{+}, 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),\(^{37}\) 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_{2}O_{5} 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.\(^{38}\) 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 degenerative 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 LBOO(Ag-O), consistent with \(E_b(Au-O) < E_b(Ag-O)\). The Au-V bond order in AuV_{2}O_{5}^{+} 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_{2}O_{5}^{+} is very strong, which agrees with the fact that the bond length of Au-V in AuV_{2}O_{5}^{+} 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/FeO\(_x\) catalyst was found extremely stable for CO oxidation at a wide temperature range,\(^{16}\) in which the Au 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/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_{2}O_{5}^{+}\_O (1.87 eV) and AuV_{2}O_{5}^{+}\_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_{2}O_{4}^{+}\_V (1.99 eV) and AuV_{2}O_{4}^{+}\_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_{2}O_{5} clusters (M = Au, Ag) with M on V and O adsorption sites, respectively.

<table>
<thead>
<tr>
<th>M</th>
<th>V</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>Au</td>
<td>Ag</td>
</tr>
<tr>
<td>Au</td>
<td>0.998</td>
<td>0.522</td>
</tr>
<tr>
<td>Ag</td>
<td>1.107</td>
<td>0.390</td>
</tr>
<tr>
<td>Au</td>
<td>0.238</td>
<td>0.079</td>
</tr>
<tr>
<td>Ag</td>
<td>0.259</td>
<td>0.088</td>
</tr>
</tbody>
</table>

Figure 3. The natural charges on Au or Ag (O) in MV_{2}O_{5} clusters (M = Au, Ag). Labels _v and _o indicate the adsorption sites of V and O, respectively.
with or without oxygen-vacancy by bonding with O or metal atoms. On the other hand, the binding between the Ag1 and two O atoms in AgV3O8−o is particularly strong (E_b = 2.99 eV), indicating that Ag1 atoms prefer to be adsorbed on oxygen-rich surfaces by making Ag-O bonds.

The charge states of the Au1 atom have been investigated on various thin oxide films (MgO, FeO, SiO2, and Al2O3) grown on metal single crystals.29 It was found that the Au1 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 Au1 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 Ag1 atom always has positive (or nearly zero) charges. Studies on surfaces and clusters both demonstrate that the charge states of the Au1 atom are dependant on its bonding atoms, which implies that in the catalytic reactions, the Au1 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 Au1 or Ag1 on V3O7 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 Au1, 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 AuV3O7 are expected to be represented in some other AuM2O3 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 Au1 or Ag1 doped V oxide clusters towards typical small molecules (such as CO and CH3) 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.

References

