

XPS of Oxygen Atoms on Ag(111) and Ag(110) Surfaces: Accurate Study with SAC/SAC-Cl Combined with Dipped Adcluster Model

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O1s core-electron binding energies (CEBE) of the atomic oxygens on different Ag surfaces were investigated by the symmetry adapted cluster-configuration interaction (SAC-Cl) method combined with the dipped adcluster model, in which the electron exchange between bulk metal and adsorbate is taken into account properly. Electrophilic and nucleophilic oxygens (O_{elec} and O_{nuc}) that might be important for olefin epoxidation in a low-oxygen coverage condition were focused here. We consider the O1s CEBE as a key property to distinguish the surface oxygen states, and series of calculation was carried out

by the Hartree–Fock, Density functional theory, and SAC/SAC-Cl methods. The experimental information and our SAC/SAC-Cl results indicate that O_{elec} is the atomic oxygen adsorbed on the fcc site of Ag(111) and that O_{nuc} is the one on the reconstructed added-row site of Ag(110) and that one- and two-electron transfers occur, respectively, to the O_{elec} and O_{nuc} adclusters from the silver surface. © 2013 Wiley Periodicals, Inc.

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Introduction

Ethylene oxide (EO) is one of the largest volume chemicals produced by chemical industry, and currently EO is almost exclusively produced by silver-catalyst supported on α -Al₂O₃. EO is widely used as chemical raw materials for detergents, polymers, and for many other purposes. According to its importance, this procedure is extensively studied both experimentally and theoretically.^[1–6] A main purpose of these studies was to improve catalyst's activity and selectivity; the selectivity of EO is 40–50% for unpromoted silver catalyst, but it increases to more than 80% when promoters such as Cs or Cl are used.^[7–9] Owing to extensive researches, much advance has been made in the understanding of this reaction, but detailed mechanism of this reaction is still far from complete understanding. One of the main difficulties arise from the diversity of surface oxygen species, that is, oxygen adsorbed on silver surface takes various forms such as atomically or molecularly adsorbed oxygen, subsurface oxygen, and silver substituting oxygen adatoms.^[7,10–12]

There have been long arguments on the active oxygen species for epoxidation, that is, atomic oxygen or molecular oxygen.^[1–3,13] For example, Grant and Lambert^[14] and Carter and Goddard^[15] thought that the atomic oxygen made by the dissociative adsorption of gaseous O₂ is the active species for the ethylene epoxidation.^[14,15] On the other hand, Campbell, Ayame and other researchers^[16–20] have proposed that superoxide (O₂[−]) adsorbed on silver surface is the active species for the ethylene epoxidation, because a O—O stretching vibrational mode is observed in the IR spectrum.^[16] About 15 years ago, we carried out theoretical studies on the ethylene and propylene epoxidation reactions on a silver surface,^[21,22] in which O₂[−] was assumed as active species. Our studies have provided natural explanations for the ethylene and propylene

partial oxidation reactions on silver: both have similar epoxidation routes, but for propylene, the activation barrier for the total combustion route is lower, because the stable allylic intermediate is formed in this route. Recent experimental studies, however, indicated that the atomic oxygen is much more stable in the reactive condition and, therefore, should be considered as the active species of the olefin epoxidation. For example, in 2004, Lambert and coworkers investigated styrene epoxidation reaction on the Ag(100) surface by synchrotron X-ray photoelectron spectroscopy (XPS) and found that the formation of the atomic oxygen was necessary for the epoxidation.^[23] In addition, recent experiments have shown that the selectivity limit (85.7%) of the molecular oxygen-based mechanism, so-called 6/7 rule, can be exceeded.^[1,2] These experiments strongly indicate the atomic oxygen-based mechanism on the clean silver surface rather than the molecular oxygen-based one. However, we note that the reaction mechanism under different reaction conditions like in the industrial operating condition is still unclear. Recent experiments strongly suggest that silver surface takes different configuration from the clean silver surface,^[3,11,24–26] and the molecular oxygen-based mechanism cannot be ruled out for such conditions. In addition, there is a strong possibility of O₂[−] as active species for the reactions on step or kink surface sites or nano-sized clusters.^[27,28]

To determine the active oxygen species for olefin epoxidation, the Ag surface structure in an operating condition [high temperature, non-ultra-high vacuum (UHV)] needs to be

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understood. This is because the Ag surface reconstruction occurs in the presence of O adatoms, thus the active phase may be different from the clean Ag surface. This issue is extensively studied both experimentally and theoretically, and it is widely known that the Ag-O surface structure strongly depends on the oxygen coverage.^[24] On high-coverage surface, Rovida et al.^[29] reported the formation of the $p(4 \times 4)$ low-energy electron diffraction pattern for O/Ag(111) system. Afterward, Campbell^[30] and Bare et al.^[31] suggested that the topmost Ag layer exists between two oxygen layers. Their "three-layer model" was corrected by Carlisle et al.^[32] based on the scanning tunneling microscope (STM) experiment. Furthermore, the " $(p-T)$ phase diagram" obtained by the density functional theory (DFT) calculations also supports the stability of their "Ag_{1.83}O layer model" under an operating condition for ethylene epoxidation.^[32,33]

In contrast to the high-oxygen coverage surfaces, the low-coverage surfaces are less understood, although researchers admit that the surface geometry is close to the clean Ag(111) with low-oxygen adatom concentration.^[34] Interestingly, this low-coverage surface is also stable surface in high-temperature condition, as shown from the $(p-T)$ phase diagram given by Scheffler and coworkers.^[35] Therefore, as proposed by many researchers,^[24,35] it is natural to think that high- and low-coverage surfaces may coexist in an operating condition, that is, the real active phase in olefin epoxidation is not yet fully determined. Clearly, the difficulty is related to the limitation in STM technique; it is not easy to have atomic resolution routinely, and more importantly, ultra-cold and UHV condition is usually required in STM measurements.

One of the promising approaches for understanding active phase under operating condition is *in situ* XPS. Recent advances in this technique have made it possible to clarify the nature of the atomic oxygens on a silver surface. For example, Schlögl and coworkers carried out the detailed XPS measurements on polycrystalline silver surface in the presence of O₂ and ethylene gas at reaction conditions (300–500 K and 0.07–1 millibar).^[36] In their spectrum, two atomic oxygen states called electrophilic oxygen (O_{elec}) and nucleophilic oxygen (O_{nuc}) were found. These can be clearly distinguished in XPS because they have different O1s core-electron binding energies (CEBEs); O_{elec} has 530.4 eV, whereas O_{nuc} has 528.3 eV.^[36–39] Their notable finding was that the EO yield was proportional to the peak intensity of O_{elec} , whereas O_{nuc} was irrelevant to the EO yield. This indicates that O_{elec} is an active species for ethylene epoxidation, although detailed information such as the adsorption sites of O_{elec} and O_{nuc} are not yet determined. The adsorption site is significantly important to understand the relationship between the surface oxygen states and the catalyst's activity or selectivity, which is the key information for new catalysts design. However, present experimental data are insufficient to fully determine the adsorption sites of O_{elec} and O_{nuc} on a silver surface, although some important clues were known, as follows; there is an experimental report that the appearance of the O1s signal with 528.4 ± 0.1 eV in XPS is accompanied with the formation of the Ag(110)-(2×1)-O added-row structure.^{[1,14,15,30],[31,37,39,40]} This structure is formed by the surface reconstruction of the Ag(110). Thus, this strongly indicates that

O_{nuc} , whose O1s CEBE is 528.3 eV, corresponds to the O atom in the added-row structure. The geometry of O_{elec} is less clear, but series of angle-resolved XPS have clarified that these are on-surface oxygen species.^[41,42] Based on these experimental data, possible adsorption sites were suggested by Schlögl and coworkers,^[43] although further studies are necessary to identify real adsorption sites.

When low-coverage Ag-O surface was assumed to be the active phase of olefin epoxidation, O_{elec} and O_{nuc} are obviously key oxygen species for catalysis. To determine the adsorption sites of O_{elec} and O_{nuc} , we believe that theoretical method is quite helpful, provided that the theoretical method is accurate enough to be the complement to experimental data. Among various theoretical approaches to study the adsorbate-metal surface system, the dipped adcluster model (DAM) proposed by Nakatsuji is highly reliable.^[44,45] Various types of adsorbate-surface systems were investigated using this model; the results were in good agreement with experiments and at the same time, some fundamental insights were provided.^[44,45] In the DAM, electron exchange between the bulk metal and the adcluster (i.e., admolecule plus metal cluster) is taken into account. Such electron exchange is particularly important in adsorption of oxygen species. For example, the DAM properly describes the adsorption of O₂, whereas the usual cluster model (CM) does not.^[21,22,46–49] To present theoretical XPS, the O1s CEBE of the adsorbates should be calculated. These are accurately calculated with the symmetry adapted cluster (SAC) and SAC-configuration interaction (SAC-CI) methods^{[45],[50–53]} combined with the DAM, which is referred to as SAC-CI/DAM method. As previously shown in various examples, XPS experiments were well understood by the SAC/SAC-CI method.^[45,53]

In this study, we carry out the investigation on the atomic oxygen species adsorbed on the clean Ag(111) and the Ag(110) surfaces, which corresponds to the low-oxygen coverage surface. Our main focus is on the XPS. As discussed earlier, the active species of olefin epoxidation is still under debate. Here, we investigate the properties of atomic oxygens on silver surface, which were not fully examined in our previous study. Our aim is to present some information on O_{elec} and O_{nuc} , such as their adsorption sites and surface geometry of the oxygen-silver system. These are important to newly design the epoxidation catalyst, but it was not determined yet from experiments alone.

Computational Details

We used Ag₁₃(9,4) cluster for clean Ag(111) and Ag(110) surfaces, and Ag₂₁(3,12,6) cluster was used for the Ag(110) with added-row structure, where the number of Ag atoms in the first and the second layers are shown in parentheses; see Figure 1 for their geometries. These surface models are based on the models proposed by Schlögl and coworkers.^[43] Electron exchange between the bulk metal and the adcluster was taken into account by the DAM with the highest spin-coupling model. For highest spin-coupling model, an integral number of electron transfer naturally arises; for details, see Ref. [45]. The DAM with no electron transfer corresponds to the CM.

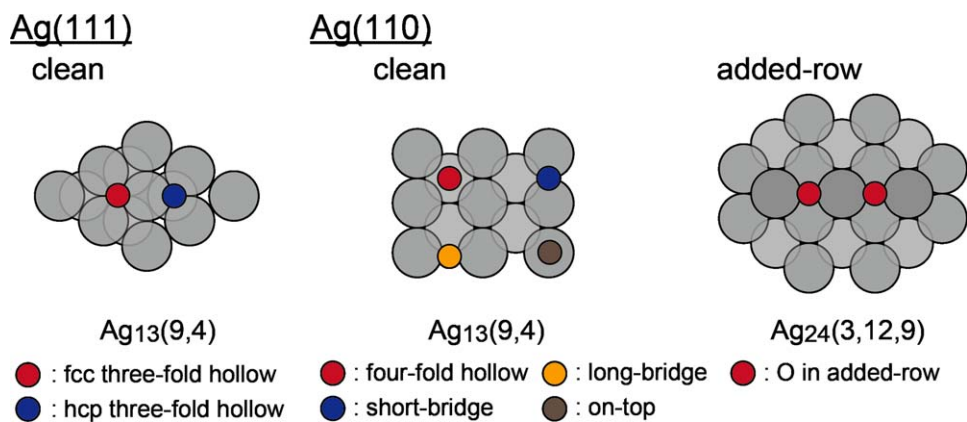


Figure 1. Geometries of Ag(111) and Ag(110) surfaces and O atom adsorption sites are considered in the CEBE calculations.

The DAM ($n = 1$) and the DAM ($n = 2$) were used, where n represents the number of transferred electrons from the bulk metal to the adcluster. The C_{3v} , C_1 , and C_{2v} symmetry was assumed for the clean Ag(111), clean Ag(110), and the added-row Ag(110) surfaces, respectively.

For Ag atom, its Kr core was replaced by Los-Alamos effective core potential (ECP) and (331/321/31) basis set was used to represent the valence electrons.^[54] For O atom, 6-31G(d) with s and p diffuse functions with $\zeta = 0.0845$ were used for geometry optimizations,^[55] and aug-cc-pVTZ basis was used for the calculations of the CEBE.^[56] Geometry optimizations and energy evaluations were carried out by using the DFT with B3LYP functional.^[57,58] In geometry optimization, the coordinates of the Ag atoms were frozen and the Ag-Ag distances were determined by the lattice constant (4.0857 Å).^[59] We carried out geometry optimizations for all the adsorption sites, as shown in Figure 1, with the DFT + DAM method. The CEBEs were evaluated at these stable adsorption sites. Adsorption energy (E_{ads}) is defined as $E_{\text{ads}} = E(\text{Ag-O adcluster}) - \{E(\text{Ag cluster}) + E(\text{O})\}$ and calculated by the DFT method. Atomic charges were evaluated by the Mulliken and natural bond orbital (NBO) population analysis methods.^[60] All calculations were carried out using Gaussian09 Revision C01.^[61]

The O1s CEBEs were evaluated by the Hartree-Fock (HF), DFT, and the SAC/SAC-Cl methods. In HF and DFT methods, the CEBE was estimated by the O1s molecular orbital energy, that is, the Koopmans' theorem was assumed, though this approximation is known to be not so reliable. We tried to calculate CEBEs with the so-called delta self consistent field (SCF) method, by taking energy difference between the neutral and the O1s ionized states. However, the SCF convergence toward the O1s ionized state was not successful. The SAC/SAC-Cl calculations were carried out by the singles and doubles (SD)-R method. Direct algorithm was used ("direct" keyword), and ionization from the O1s core orbital is allowed ("CorePrWindow" keyword). 1.0×10^{-6} and 1.0×10^{-7} thresholds ("LevelThree" keyword) were used for perturbative selection of S2 and R2 operators, respectively.

For closed shell systems, ionized states were calculated by the SAC-Cl by applying the electron-subtracting operator to the ground state (by "CationDoublet" keyword). For open shell

systems, this procedure is not appropriate because the ground state is not a closed shell system. Instead, we evaluated the ionization energy of N -electron open shell system by the following two calculations: (i) calculate singlet excited state of $N-1$ electron systems (by "Singlet" keyword) and (ii) calculate electron affinity for $N-1$ electron systems (by "AnionDoublet" keyword). The procedures of calculating the SAC-Cl ionization energies for closed and open shell systems are summarized in Figure 2.

O1s CEBE on Ag(111) and Ag(110) Surfaces

In Table 1, the adsorption energies (E_{ads}) and O1s CEBEs on Ag(111) and Ag(110) surfaces were summarized. The adsorption sites of O_{elec} and O_{nuc} are determined based on these results, as will be shown in this section.

Ag(111)

First, we discuss E_{ads} of the O atom on the Ag(111) surface. Geometry optimizations with the DFT + DAM have shown that the fcc and hcp are stable adsorption sites in both cases of DAM ($n = 1$) and DAM ($n = 2$). E_{ads} of O atom on these sites are evaluated with DAM ($n = 1$) to be 56.29 and 52.02 kcal/mol for the fcc and hcp sites, respectively. These are larger than the E_{ads} with DAM ($n = 2$; 54.93 and 51.13 kcal/mol for fcc and hcp) and are close to the experimental E_{ads} (59.04 kcal/mol). The plane-wave DFT calculation gave E_{ads} of 72.18 kcal/mol.^[34,62] For this reason, we conclude that the one-electron transfer from the bulk metal to the adcluster favorably occurs when the O atom is adsorbed on the Ag(111) surface.

Next, we discuss the nature of the O atom adsorbed on the Ag(111) surface. As shown earlier, the larger E_{ads} indicates that the O atom on Ag(111) is better represented by DAM ($n = 1$) than DAM ($n = 2$). This implies that the O atom on Ag(111) is O_{elec} that shows electrophilic nature. Actually, the CEBEs calculated by the SAC-Cl for the DAM ($n = 1$) are 530.3 and 530.2 eV for the fcc and hcp sites, respectively. These reproduce the experimental value for O_{elec} (530.0–530.4 eV) very well.^[36,39] On the other hand, the CEBEs evaluated for the DAM ($n = 2$) are 528.0 and 528.6 eV for the fcc and hcp sites, respectively,

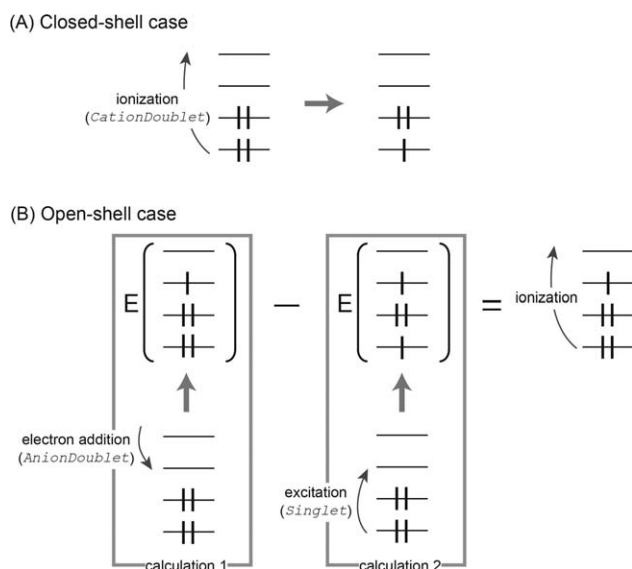


Figure 2. Procedure of calculating the CEBE for closed and open shell ground states by SAC/SAC-CI. Words written in italics are SAC/SAC-CI keywords in Gaussian.

deviating from the experimental value by ~ 2 eV. Therefore, not only the E_{ads} but also the CEBEs support the DAM ($n = 1$) rather than the DAM ($n = 2$). The difference between the CEBEs of the fcc and hcp sites are quite small (0.1 eV), but the E_{ads} on the fcc site (56.29 kcal/mol) is larger than that on the hcp site (52.02 kcal/mol). According to these results, we conclude that the stable adsorption site of O_{elec} is the fcc site. However, the difference in E_{ads} between the fcc and hcp sites is calculated to be only 4.3 kcal/mol, which indicates that the hcp site would also be occupied for high-coverage and/or high-temperature conditions. Note that the O atoms on the fcc and hcp sites are difficult to be distinguished using the XPS, because our calculation shows that their CEBEs are quite similar.

We also carried out the CEBE calculation by the HF and DFT Koopmans methods; however, these largely deviate from the

experimental values; for example, the HF + DAM ($n = 1$) gave 552.5 eV for both fcc and hcp sites, whereas the DFT + DAM ($n = 1$) gave 515.6 and 515.5 eV for fcc and hcp, respectively; the Koopmans-HF method overestimates the experimental CEBE by ~ 22 eV, whereas the DFT method underestimates it by ~ 15 eV. We consider their large errors come from (i) the relaxation energy of the ionized state and (ii) the lack of electron correlation in ground and ionized states. The relaxation energy has larger contribution, as the effect of electron correlation on CEBE is known to be a few eV.^[63,64] Underestimations of CEBEs by the DFT method would come from the lack of self-energy, as reported in Ref. [65]. These methods are not reliable enough to be used to determine the adsorption site of O_{elec} and O_{nuc} , because their CEBEs are out of the experimental range of the CEBEs of the O atoms on various surfaces (528–531 eV).^[36] Further, it is difficult to find a reasonable relation between the O atomic charges (Mulliken and NBO) and the CEBEs. Therefore, we omitted discussion based on electron populations, although these are often used for the CEBE analysis. Finally, we note that the CM is almost useless in both of the calculations of E_{ads} and CEBE. This model is rather dangerous for the proper understanding of the oxygen adsorption on a metal surface where the electron transfer from the bulk metal to the adcluster is essential. This effect is considered only in the DAM.

Ag(110)

Experimentally, O_{nuc} is proposed to be formed on the Ag(110) facet of polycrystalline silver catalyst. An interesting observation of the surface science experiments is that the surface reconstruction to added-row structure is facilitated by oxygen adsorption.^[40,66] Thus, we considered not only clean Ag(110) surface but also reconstructed Ag(110) surfaces in which the added-row structure is formed. On the clean Ag(110) surface, four adsorption sites are possible; four-fold hollow, on-top, short- and long-bridge sites; see Figure 1. Geometry

Table 1. Core electron binding energies (CEBEs) of O atom on Ag(111) and Ag(110) surfaces.						
Adsorption site	Surface model	Adsorption energy (kcal/mol) ^[a]	CEBE (eV)			
			DFT(B3LYP)	Hartree-Fock	SAC/SAC-CI	Experiment
Ag(111)						
fcc-hollow	CM	50.43	518.7	555.2	533.7	530.0, ^[b] 530.4 ^[c]
	DAM ($n = 1$)	56.29	515.6	552.5	530.3	
	DAM ($n = 2$)	54.93	512.7	549.5	528.0	
hcp-hollow	CM	46.29	518.6	556.6	533.4	
	DAM ($n = 1$)	52.02	515.5	552.5	530.2	
	DAM ($n = 2$)	51.13	512.7	549.5	528.6	
Ag(110)						
Four-fold hollow	CM	57.90	519.1	555.4	532.9	528.1, ^[d] 528.3 ^[c]
	DAM ($n = 1$)	58.31	516.2	553.4	530.5	
	DAM ($n = 2$)	54.77	513.7	550.8	528.0	
Added-row	CM	67.61	519.0	555.9	532.8	
	DAM ($n = 1$)	68.49	516.7	553.3	531.3	
	DAM ($n = 2$)	69.26	514.4	551.6	528.5	

[a] DFT(B3LYP) method was used. [b] Ref. [36]. [c] Ref. [39]. [d] Ref. [40].

optimization with the DFT + DAM method showed that the on-top site is not a stable adsorption site on the clean Ag(110). E_{ads} of four-fold hollow, short- and long-bridge sites are (i) E_{ads} (four-fold hollow) = 57.90, 58.31, and 54.77 kcal/mol for DAM ($n = 0, 1,$ and 2), (ii) E_{ads} (short-bridge) = 50.20, 49.66, and 51.10 kcal/mol for DAM ($n = 0, 1,$ and 2), and (iii) E_{ads} (long-bridge) = 44.67, 51.80, and 50.19 kcal/mol for DAM ($n = 0, 1,$ and 2). Thus, it is concluded that fourfold hollow site is the most stable adsorption site on a clean Ag(110) surface. On the reconstructed Ag(110) site, as widely known by experiments, the added-row sites are considered as the candidates of the stable adsorption sites. E_{ads} , oxygen atomic charge, and the O1s CEBEs were evaluated, and the results are summarized in Table 1.

On the fourfold hollow site, the E_{ads} is 58.31 and 54.77 kcal/mol for the DAM ($n = 1$) and ($n = 2$), respectively. Interestingly, the stability is larger with the DAM ($n = 1$) model than the DAM ($n = 2$) model, which indicates the formation of O_{elec} rather than O_{nuc} . Further, both values are larger than E_{ads} on the Ag(111) surface, indicating that O atom is more favorably adsorbed on the Ag(110) surface. When the added-row is formed by the surface reconstruction, the E_{ads} becomes even much larger; E_{ads} is 68.49 and 69.26 kcal/mol for the DAM ($n = 1$) and ($n = 2$), respectively. The value with DAM ($n = 2$) is larger than that of DAM ($n = 1$), indicating that O_{nuc} is formed, in accordance with the XPS experiment. Thus, our results show that the formation of the added-row structure is thermodynamically favorable process: first, oxygen is adsorbed on the four-fold hollow site of Ag(110), and then the surface reconstruction toward added-row structure is facilitated. The stabilization energy based on the difference in E_{ads} is as large as 11.0 kcal/mol and so, the oxygen adsorption may induce this surface reconstruction. Here, we did not consider the effect of surface reorganization and so on, and therefore further investigations are necessary on this issue.

Our E_{ads} indicates that one- and two-electron transfer favorably occurs on the fourfold hollow and the added-row site, respectively. Based on this result, we employ the DAM ($n = 1$) and DAM ($n = 2$) for the clean and reconstructed Ag(110) surfaces.

For the CEBE, likewise the Ag(111) surface, only the SAC-CI method combined with DAM gives the CEBEs within the experimental range of experimental XPS; again, the HF and DFT Koopmans calculations largely overestimate or underestimate experimental values. When the SAC-CI + DAM ($n = 1$) was used, O atoms in the fourfold hollow and the added-row sites give 530.5 and 531.3 eV, respectively. For the SAC-CI + DAM ($n = 2$), the fourfold hollow and the added-row sites give CEBE of 528.0 and 528.5 eV, respectively. As shown earlier, E_{ads} indicates the DAM ($n = 1$) and ($n = 2$) is appropriate for the fourfold hollow and the added-row site respectively, and in this case, their theoretical CEBEs are 530.5 and 528.5 eV for the fourfold hollow and the added-row sites. Among these two sites, we adopt the added-row site as the adsorption site of O_{nuc} by following reasons; (i) the E_{ads} of the added-row site is larger than the fourfold hollow site by ~ 15 kcal/mol, thus in reactive condition the O atoms on the clean Ag(110) would induce the added-row formation, (ii) experimentally, the XPS

peak for O_{nuc} is associated with the added-row formation,^[36,40] and (iii) the calculated CEBEs on the added-row site (528.5 eV) is much closer to the experimental value of O_{nuc} (528.1–528.3 eV) than that on the four-fold hollow site (530.5 eV). Therefore, both experimental and theoretical information is necessary to determine the adsorption site of O_{nuc} .

The difference in the CEBEs of O_{elec} and O_{nuc}

As shown earlier, we could successfully determine the adsorption site of O_{elec} and O_{nuc} as the Ag(111)-fcc and the Ag(110)-added-row sites, respectively, using the experimental and the present theoretical results. We observed that the O1s CEBEs of O_{elec} and O_{nuc} calculated by the SAC-CI + DAM method are highly accurate, and the difference in the theoretical CEBE of O_{elec} and O_{nuc} (1.8 eV) reproduces the experimental value (2.1 eV) very well. Therefore, detailed analysis on the CEBE difference between O_{elec} and O_{nuc} (denoted as $\Delta(O_{\text{elec}}-O_{\text{nuc}})$) is meaningful. $\Delta(O_{\text{elec}}-O_{\text{nuc}})$ can be divided into two contributions, as (i) the difference in the O1s orbital energy and (ii) the difference in the relaxation energy of ionized state. As mentioned in the previous section, the ionization energy calculated by the SAC/SAC-CI method includes both effects, while (ii) is not properly described by the HF and DFT Koopmans methods.

In Table 2, we summarized the O1s orbital energy and the relaxation energy in the ionized state calculated by the SAC-CI method. The fcc site is assumed as the adsorption site of O_{elec} , and the added-row site is considered for O_{nuc} . Experimentally, Schlögl and coworkers carried out detailed analysis on the O_{elec} and O_{nuc} XPS results, and they divided $\Delta(O_{\text{elec}} - O_{\text{nuc}})$ into the O1s orbital energy and the relaxation energy components based on Wagner's equation using their XPS and Auger results^[39,67]; these are also shown in Table 2. Our results indicate that both the orbital energy and the relaxation energy difference between the O_{elec} and O_{nuc} are 0.9 eV, in agreement with experimental results (1.2 eV for orbital energy component, and 0.9 eV for relaxation energy component). Therefore, our theoretical results by the SAC-CI + DAM support the experimental understanding that the orbital energy and the relaxation energy components are half and half of the total difference. Good agreement between experimental and theoretical results also supports our assignment of the adsorption sites of O_{elec} and O_{nuc} .

Conclusions

In the present article, we theoretically investigated atomic oxygen species adsorbed on clean Ag(111) and Ag(110) surfaces. Such clean Ag-O surface is proposed as one of the stable surface geometries in high-temperature condition. We focused on O_{elec} and O_{nuc} atomic oxygen species because these are experimentally known to promote or inhibit the EO formation, respectively. Thus, these atomic oxygen species are considered to control the catalytic function of silver. However, their adsorption sites were not yet determined, although several sites are suggested by experimentalists.^{[36], [43]} It is rather difficult to determine whether these models are correct or not, only from known experimental results. We believe theoretical method would be

Table 2. Difference in the orbital and correlation energy components in the O1s CEBEs of O_{elec} and O_{nuc} calculated by the SAC/SAC-Cl method.

		O_{elec} (fcc hollow)	O_{nuc} (added row)	$\Delta(O_{\text{elec}}-O_{\text{nuc}})$
Orbital energy (eV)	Theory	552.5	551.6	0.9
	Experiment ^[a]	—	—	1.2
Correlation energy (eV)	Theory	-22.2	-23.1	0.9
	Experiment ^[a]	—	—	0.9
CEBE (eV)	Theory	530.3	528.5	1.8
	Experiment ^[a]	530.0–530.4	528.3	2.1

[a] Refs. [36] and [39].

helpful to determine the adsorption sites of O_{elec} and O_{nuc} , but for this purpose, accurate and reliable theory should be used. As the electron exchange between bulk metal and adsorbate is important for oxygen adsorption, we used the DAM to describe this effect properly. We consider the O1s CEBE as a key property to distinguish these surface oxygen states; series of calculation was carried out by the HF, DFT, and SAC/SAC-Cl methods.

On the Ag(111) surface, the O1s CEBEs were calculated on the fcc and hcp three-fold hollow sites because the DFT + DAM geometry optimization indicated these are stable adsorption sites. E_{ads} was larger in the DAM ($n = 1$) model than the DAM ($n = 2$) model, indicating that one-electron transfer favorably occurs on the Ag(111). The theoretical CEBEs for the fcc and hcp sites calculated by the SAC-Cl + DAM ($n = 1$) were 530.3 and 530.2 eV, respectively, both close to the experimental value of O_{elec} (530.0–530.4 eV). As the fcc site has the larger E_{ads} (56.29 kcal/mol) than the hcp site (52.02 kcal/mol), we concluded that O_{elec} is the atomic oxygen adsorbed on the fcc site of the Ag(111) surface. CEBEs calculated by the HF and DFT methods largely deviated from the experimental value by more than 10 eV, thus cannot be used for the XPS peak assignment.

We also investigated the O atom adsorbed on the Ag(110) surface. Both clean and reconstructed surfaces with the added-row structure are considered. Geometry optimization using the DFT + DAM shows the four-fold hollow and the added-row sites are stable adsorption sites. On the four-fold hollow site, E_{ads} with DAM ($n = 1$) (58.31 kcal/mol) was larger than the DAM ($n = 2$) (54.77 kcal/mol), indicating the one-electron transfer occurs on this site. On the other hand, the two-electron transfer was more favorable in the added-row site, and it gave much larger E_{ads} . The CEBE on the Ag(110) surface are calculated as 530.5 eV (SAC-Cl + DAM($n = 1$)) and 528.5 eV (SAC-Cl + DAM($n = 2$)) for the four-fold hollow and the added-row sites, respectively. We concluded that the adsorption site of O_{nuc} is the Ag(110) added-row site based on following experimental and theoretical facts; (i) the larger E_{ads} of the added-row site (69.26 kcal/mol) than the four-fold hollow site (54.77 kcal/mol), (ii) the experimental fact that the XPS peak for O_{nuc} is associated with the added-row structure formation, and (iii) the calculated CEBEs on the added-row site (528.5 eV) is close to the experimental value of O_{nuc} (528.1–528.3 eV).

The difference in the CEBEs of O_{elec} and O_{nuc} calculated by the SAC-Cl + DAM is 1.8 eV, which agrees with the experimental value of 2.1 eV. This shift was further analyzed by decomposing it into the difference in the orbital energy and the relaxation energy components, and these are both 0.9 eV.

These agree with the corresponding experimental values of 1.2 and 0.9 eV, thus the orbital and relaxation energy decomposition of the $O_{\text{elec}} - O_{\text{nuc}}$ difference also supports our assignment of the adsorption sites.

In this study, the experimental XPS spectra were successfully reproduced by the SAC-Cl method based on the DAM, indicating the proposed adsorption sites and the DAM were correct. This is possible because the SAC-Cl + DAM method is reliable so that the calculated results can be used as complementary data for experiment: The present study has shown that based on both the theoretical and experimental results, we could successfully determine the adsorption site of O_{elec} and O_{nuc} and obtain the insight on the nature of these oxygens on the silver surfaces with low oxygen-coverage conditions. This information might be valuable in elucidating the nature of the atomic oxygen that may be a key player in olefin epoxidation reactions.

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Keywords: *ab initio* method · O1s X-ray photoelectron spectroscopy · metal surface · symmetry adapted cluster/symmetry adapted cluster-configuration interaction · dipped adcluster model

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