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Density Functional Study of Ethylene Oxidation on Ag(111) Surface. Mechanism of Ethylene–Oxide Formation and Complete Oxidation with Influence of Subsurface Oxygen

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Density Functional Study of Ethylene Oxidation on Ag(111) Surface. Mechanism of Ethylene–Oxide Formation and Complete Oxidation with Influence of Subsurface Oxygen[#]

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Abstract

Motivation. Ag catalysts oxidize ethylene to epoxide. This reaction is one of the most important reactions in chemical industry. Although the catalysts have been intensively improved for years, small portion of ethylene leads to combustion. The reaction mechanisms including the role of molecular and atomic oxygen are not yet clear, and have been investigated using the density functional method using a Ag_5 cluster model. Industrial catalysts include several dopants as co–catalysts, and one of them is oxygen atom under the surface layer. The effects of subsurface oxygen have also been examined with a Ag_5O cluster.

Method. The hybrid type density functional method with Gaussian basis set was used for computations.

Results. In the reaction between ethylene and oxygen molecule, the activation energy for ethylene epoxidation was much lower than those for acetaldehyde formation and for hydrogen abstraction from ethylene, which led to complete oxidation. This suggests that the oxygen molecule should oxidize ethylene to epoxide with a very high selectivity (almost 100%). The oxygen atom, which was formed by dissociative adsorption of oxygen molecule or as a "by–product" when one oxygen atom of the molecule was consumed, oxidizes ethylene into epoxide and acetaldehyde with a similar selectivity, since the difference in activation energies is very small (3.7 kcal/mol). The oxygen atom may, therefore, play a main role in ethylene epoxidation, because successive oxidation by both atoms of adsorbed oxygen molecule means to give higher selectivity at zero conversion than upper limit (85.7%) according to the active oxygen molecule mechanism. Subsurface oxygen slightly increased a difference in activation energies for epoxidation and acetaldehyde formation (up to 4 kcal/mol) with the atomic oxygen mechanism, suggesting a slight enhancement of the epoxidation selectivity, while adsorbed oxygen molecule maintained a very high selectivity again (difference was from 24 to 22 kcal/mol).

Conclusions. On the Ag surface containing subsurface oxygen, the oxidizing agent for ethylene epoxidation was, therefore, supposed to be adsorbed oxygen atom on Ag catalysts, similar to a Ag surface without subsurface oxygen.

Keywords. Ethylene oxidation; epoxidation; Ag catalyst; Hybrid DFT; catalyst design; reaction mechanism.

[#] Dedicated to Professor Haruo Hosoya on the occasion of the 65th birthday.

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Abbreviations and notations

DFT, density functional theory	TS, transition state
CS, coadsorbed state	HF, Hartree–Fock
MP, Møller–Plesset	ECP, effective core potential
CI, configuration interaction	

1 INTRODUCTION

There is a long history of research for ethylene oxide (epoxide) formation, because the epoxidation is known to be one of the most important industrial processes and so unique that silver is nearly the only element to catalyze ethylene oxide formation. Its catalyst development and basic research for the reaction mechanism are, therefore, still continuing intensively in these days [1–4]. In early works on the reaction mechanism, researchers have tried to take into account suitable heat of formation of silver oxide (Ag_2O) [5] and specific oxygen species on silver [6]. Then, much attention has been paid to oxygen species for a long time.

Two distinctive oxygen species have been proposed to produce ethylene oxide. One is adsorbed oxygen molecule, and the other is oxygen atom formed from dissociative adsorption of the molecule. IR measurements of intermediates to ethylene oxide and chemisorption studies of O_2 on Ag surfaces have suggested that one atom of oxygen molecule plays a decisive role for ethylene epoxidation, and the other brings about by–products (CO_2 and H_2O), which was reported by Killty *et al*. [6]. Ethylene selectivity for epoxide can not be higher than 85.7% (6/7), if adsorbed oxygen molecule is not reproduced from the remainder of oxygen atoms after ethylene epoxidation and ethylene oxide produced is not oxidized successively. The concept of molecular oxygen responsible for ethylene epoxidation was also supported by the fact that ethylene was mainly oxidized into combustion by N_2O, indicating the ethylene combustion by oxygen atom [7]. Since this report, reaction mechanisms to ethylene oxide and combustion (CO_2 and H_2O) have been studied with kinetics, adsorption experiment, TPD, TPR, ESR, XPS, AES, HREELS and LEED, which was reviewed in detail [8]. On the other hand, oxygen atoms below Ag surface (namely, subsurface oxygen) were also reported with an XPS measurement [9], and the subsurface oxygen was supposed to play an important role in ethylene epoxidation [10]. The adsorbed oxygen atom has been concluded as active species with similar analysis (XPS, AES, HREED) [11]. However, the oxygen species responsible for ethylene epoxidation was still in controversy because detectable species may not be active under real reaction conditions. Actually, ESR signals of O_2^- on Ag surfaces were observed, but the concentration of the O_2 species was supposed to be very low (only 3 % of totally chemisorbed O_2) and inactive from its g–value [12]. Moreover, oxidation by N_2O into ethylene oxide was reported in several studies [13].

Recently, new methods of scanning tunnel microscope (STM) [14] and temporal analysis of products (TAP) [15] have been employed to clarify the active oxygen species. STM images directly showed that oxygen atom was immediately produced from the oxygen molecule adsorbed on the

Ag(110) surface at room temperature [14]. TAP studies indicated that ethylene oxide was produced from the oxygen atom after all oxygen molecules were completely converted into their atoms on Ag surfaces [15]. Thus, both of the reports suggested that adsorbed oxygen atom could oxidize ethylene into epoxide in disagreement with the early reports on active molecular oxygen mechanism [15].

Several theoretical approaches have been presented by means of the extended Huckel [16], LCAO–Xα [17], HF+ MP3 [18], GVB–CI [19], and DFT method [20]. McKee supported the molecular oxygen mechanism [18]. But Carter and Goddard III suggested a surface atomic oxyradical as the active oxygen species [19], and Hoek *et al*. supported the atomic oxygen mechanism [20]. The role of subsurface promoters of oxygen or chlorine was also examined [18,20]. However, the reaction energetics was not investigated in detail in these reports [18–20].

Recently, the energetics on the molecular and atomic oxygen mechanisms were studied in detail with the HF+MP2 and SAC–CI method, by Nakatsuji and co–workers [21]. They concluded that the epoxidation took place selectively by adsorbed oxygen molecule, while both of selective and complete oxidation were competing by adsorbed oxygen atom. However, they used a very small cluster, Ag dimer, and the dipped adcluster method, in which the total energy was estimated over the systems with different number of electrons along the reactions. The effects of subsurface oxygen have not been considered there.

Thanks to the recent progress in the DF methods, the total energy and the energy gradients are evaluated accurately, and the DFT methods are suitable for the systems including several heavy atoms and/or electron correlation. We applied it to elucidate the reaction mechanism. In our approach, the system remains neutral and reserves the constant number of electrons throughout reactions.

In our previous work (referred as Paper I), we examined the O_2 adsorption to several Ag clusters and drew the following conclusion [22]. At first, the larger adsorption energy comes from the higher HOMO level of Ag clusters, which depends on cluster geometry as well as on the size. The charge–transfer from the Ag cluster to O_2 molecule is responsible for the stabilization. Secondly, the diamond shaped Ag_5 cluster is found to be a good model. Finally, both of oxygen molecule and atom can oxidize ethylene to ethylene oxide with acceptable reaction barriers (within 6 kcal/mol). However it remained unclear whether adsorbed oxygen molecule and atom selectively produce ethylene oxide, compared with ethylene combustion, since complete oxidation was not considered in Paper I [22]. In the present work we investigated the reaction profile more extensively not only for the ethylene oxide formation but also the combustion. The influence of subsurface oxygen on selectivity with both oxygen species was also discussed in detail.

On ethylene epoxidation, ethylene combustion proceeds simultaneously to some degree under reaction conditions in industry and laboratory. Thus, the highest selectivity of ethylene for epoxidation is 70–90 % actually. It is widely believed that a part of the combustion comes from the

oxidation of the produced ethylene oxide, and that the other takes place via direct oxidation of ethylene. Though the combustion mechanism was unclear, we assumed that the essential part of combustion should be initiated by hydrogen migration in epoxide intermediates to acetaldehyde, and/or hydrogen abstraction from ethylene to vinyl radical.

2 MATERIALS AND METHODS

2.1 Model of Ag Cluster for Catalyst

The diamond shaped Ag_5 cluster, which consists of four atoms of the (111) facet and one atom of the second layer, is used in this work again. This cluster satisfies the electronic necessities giving a moderate amount of O_2 adsorption energy (16 kcal/mol) and the geometrical necessities having an area for coadsorption of O_2 and C_2H_4 and for their mutual interactions, as discussed in Paper I. When the subsurface oxygen atom is considered, an oxygen atom is added to the Ag_5 cluster in the second layer. That model is represented as Ag_5O_s (the subscript "s" means subsurface).

The Ag_5 and Ag_5O_s clusters have the symmetry plane perpendicular to the "surface", and epoxidation is assumed to conserve this (C_s) symmetry. However, in the course of acetaldehyde formation, the TS structures are obtained without symmetry constraint, *i.e.*, C_1 symmetry, since H–atom migration needs to break this symmetry. Likewise, the symmetry constraint is not imposed on H–atom abstraction from ethylene.

2.2 Method of Calculation

The hybrid HF–DF method is used in this work [23,24]. This method is implemented in the Gaussian 98 program [25]. The parametrization is the one suggested by Pople *et al*. [24], *i.e.*, 0.2, 0.8, and 0.72 for the HF, Slater [26], and Becke [27] exchange functionals, and 0.19 and 0.81 for the Vosko–Wilk–Nusair [28] and Lee–Yang–Parr [29] correlation functionals. The Los Alamos ECP is used for the 1*s* to 4*p* electrons of Ag atoms along with the corresponding valence basis sets [30]. For H, C, and O atoms, Dunning–Huzinaga full double zeta (D95) basis set is used, (10*s*5*p*)/[3*s*2*p*] and (4*s*)/[2*s*], respectively [31]. First, the structures of local minima and TS's are optimized using the mentioned basis sets. Then, at the equilibrium structures, the energies are reevaluated with a larger basis set, in which the diffuse *s* and *p* functions of $\alpha = 0.059$ and the polarization d functions of $\alpha = 2.704$ and 0.535 are added on the O atoms, as used by Nakatsuji *et al*. [21].

Throughout this work, the structure of Ag clusters is fixed, and the structure and relative orientation of ethylene and oxygen with respect to the cluster is optimized. The stabilization energy was defined as follows:

$$\Delta E = E(\text{combined system}) - \{E(\text{Ag cluster}) + E(C_2H_4) + x\,E(O_2)\}\ ,$$

where x is 1 or 1/2 depending on molecule or atom of oxygen, respectively. Negative values in ΔE means exothermic adsorption or reaction, *i.e.* thermodynamically easy step to proceed.

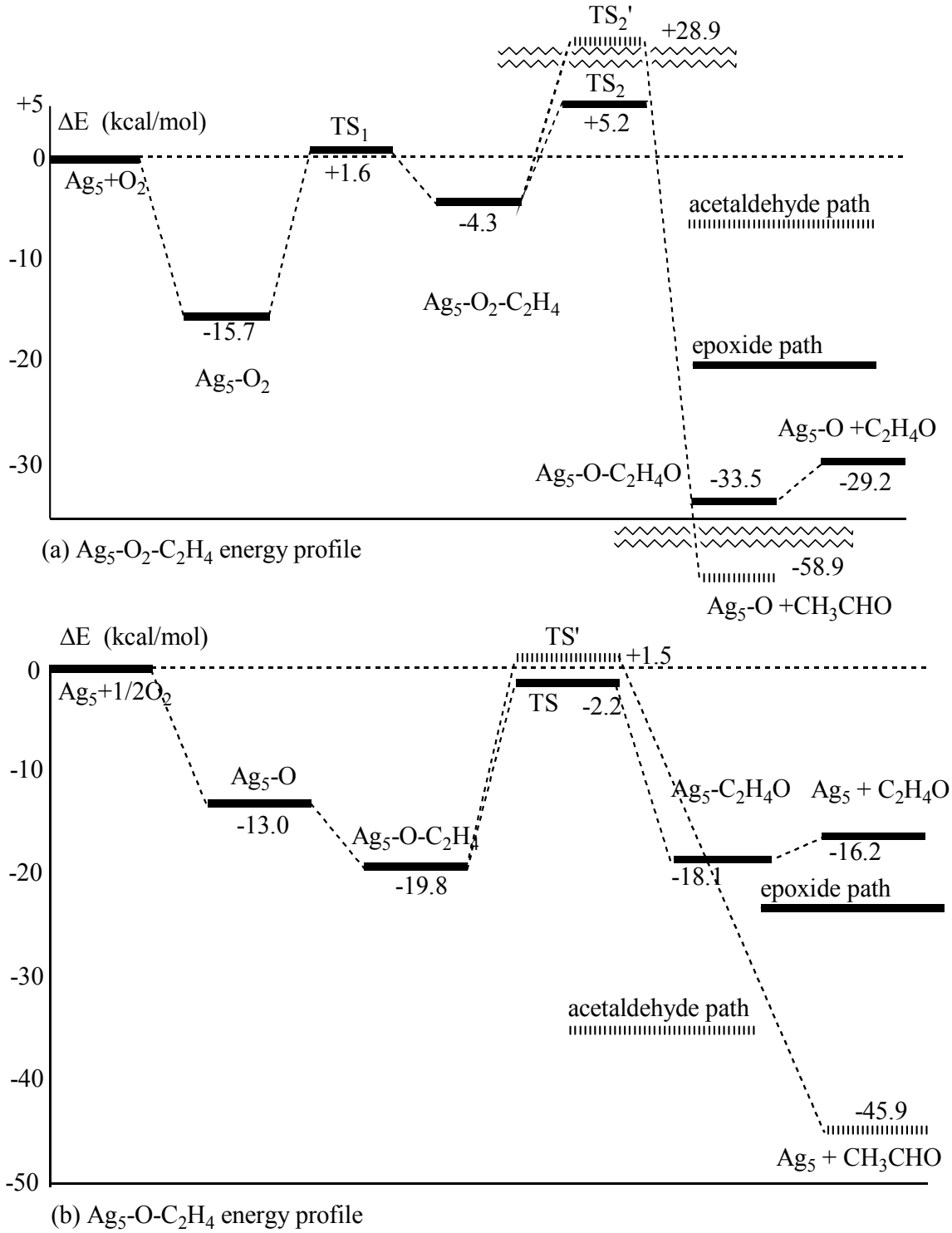


Figure 1. Energy profiles for epoxidation and acetaldehyde formation with oxygen molecule (a) and oxygen atom (b) on Ag_5 cluster.

3 RESULTS AND DISCUSSION

3.1 Reaction of Ethylene and Oxygen Molecule Adsorbed on Ag_5 Cluster

The energy profiles of epoxide and acetaldehyde formations are shown in Figure 1. On reaction with the adsorbed oxygen molecule (Figure 1 (a)), the O_2 adsorption on the Ag_5 cluster occurs with a stabilization energy of 16 kcal/mol. The successive ethylene adsorption over the O_2–Ag_5 cluster is considered as an activating process. After the first TS (TS_1), the coadsorbed state (CS) is observed with a stabilization energy of 4 kcal/mol in comparison with that of corresponding reactants. It should be noticed that up to the CS, the reaction path is common for epoxidation and acetaldehyde formations. After the CS, the second TS's (TS_2, TS_2') are observed toward epoxide and acetaldehyde, respectively. Both structures are shown in Figure 2 (The structures for O_2 adsorption, TS_1, and CS have been presented in Paper I). The energy of TS_2 is slightly higher by 5 kcal/mol than that of the reactant, while that of TS_2' is very high (29 kcal/mol).

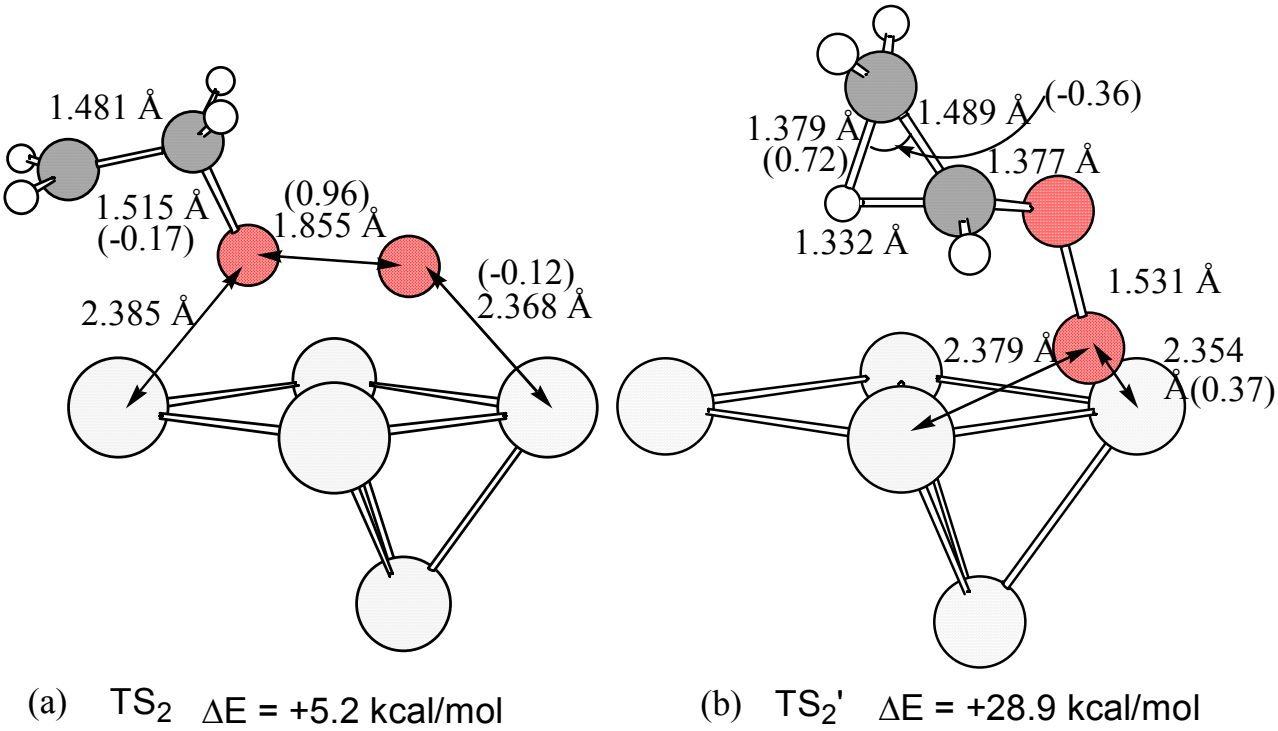


Figure 2. TS structures (TS_2 and TS_2') of $Ag_5O_2C_2H_4$ from CS to epoxide (a) and to acetaldehyde formation (b) with oxygen molecule. Values in parentheses are the leading coefficients of the normal mode corresponding to the imaginary frequency.

As another mechanism for ethylene combustion, hydrogen abstraction from ethylene by O_2–Ag_5 cluster is also suggested. Table 1 summarizes all the activation energies examined in this work. Comparing the energy consisting of Ag_5OOH and vinyl radical (28 kcal/mol) with the TS energy of acetaldehyde formation (29 kcal/mol), it is concluded that hydrogen abstraction by an adsorbed oxygen molecule is as a difficult path to combustion as acetaldehyde formation. A large difference

in activation energies (22–24 kcal/mol) suggests that the selectivity for epoxide should be as high as 100%. After the TS_2 and TS_2', adsorbed epoxide and acetaldehyde are formed on the Ag_5O cluster with stabilization energies of 34 and 59 kcal/mol, respectively. The desorption energy of epoxide from the Ag_5O cluster is calculated to be 4 kcal/mol. A relatively large energy of 29 kcal/mol is due to the change in the heat of formation from ethylene to epoxide (16 kcal/mol) and the stabilization energy of O atom to Ag_5 cluster (13 kcal/mol).

Table 1. Comparison of activation energies for epoxide formation and ethylene combustion with and without subsurface oxygen.[a]

CSor TS	chemical formula	type of reaction	relative energy (barrier height[b])
TS_2	$Ag_5O – OC_2H_4$	epoxide formation	+5.2 (9.5)
TS_2'	$Ag_5O – CH_3CHO$	acetaldehyde formation	+28.9 (33.2)
CS	$Ag_5OOH + CH_2CH•$	H atom abstraction	+27.5 (31.8)
TS	$Ag_5 – OC_2H_4$	epoxide formation	–2.2 (17.6)
TS'	$Ag_5 – CH_3CHO$	acetaldehyde formation	+1.5 (21.3)
CS	$Ag_5OH + CH_2CH•$	H atom abstraction	+2.4 (22.2)
TS_2	$Ag_5O_s – O – OC_2H_4$	epoxide formation	+10.6 (18.2)
TS_2'	$Ag_5O_s – O – CH_3CHO$	acetaldehyde formation	+33.0 (41.2)
TS	$Ag_5O_s – OC_2H_4$	epoxide formation	–0.9 (25.3)
TS'	$Ag_5O_s – CH_3CHO$	acetaldehyde formation	+3.1 (29.3)

[a] Energy is in kcal mol^{-1}
[b] Barrier height is defined as the energy increase at TS compared to the preceding local minimum, *i.e.*, CS.

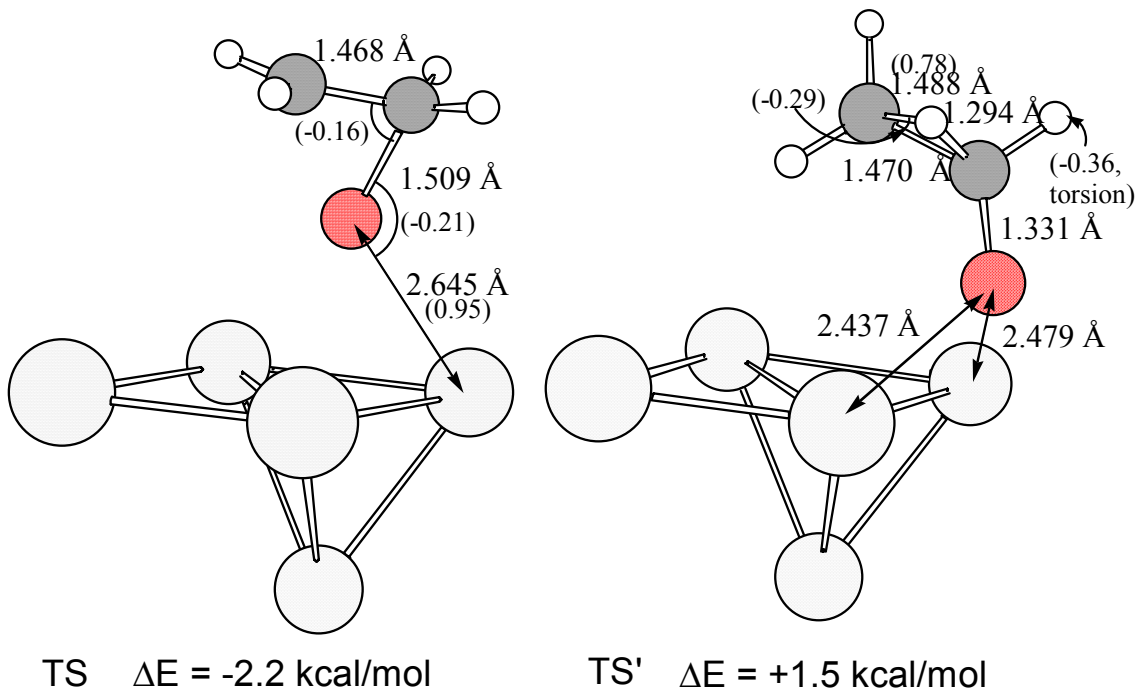


Figure 3. TS structures (TS and TS') of $Ag_5OC_2H_4$ from CS to epoxide (a) and to acetaldehyde formation (b) with oxygen atom. The values in parentheses are the leading coefficients of the normal mode corresponding to the imaginary frequency.

3.2 Reaction of Ethylene and Oxygen Atom Adsorbed on Ag_5 Cluster

The reactivity of oxygen atom adsorbed on Ag_5 cluster for ethylene is different from that of oxygen molecule. Coadsorption of ethylene occurs without a barrier and is further stabilized by 7 kcal/mol, as presented in Figure 1(b). The TS structures toward epoxide and acetaldehyde are shown in Figure 3. The energy of TS for epoxide is slightly (2.2 kcal/mol) below the reactant (zero) energy level, whereas that for acetaldehyde (TS') is slightly (1.5 kcal/mol) above it, as listed in Table 1. A difference in their energies is very small (3.7 kcal/mol), showing that both of the reactions compete, in other words, some portion of ethylene should be combusted. The energy of acetaldehyde formed on the Ag cluster is much lower than that of epoxide again. The desorption energy of epoxide is calculated to be 2 kcal/mol.

In summary, it is found from our hybrid DF calculations that adsorbed oxygen molecule is very high selective oxidant for epoxide but adsorbed oxygen atom is low. This conclusion is in accordance with Nakatsuji and co–worker studies using a Ag dimer, the dipped adcluster model and the HF method [21].

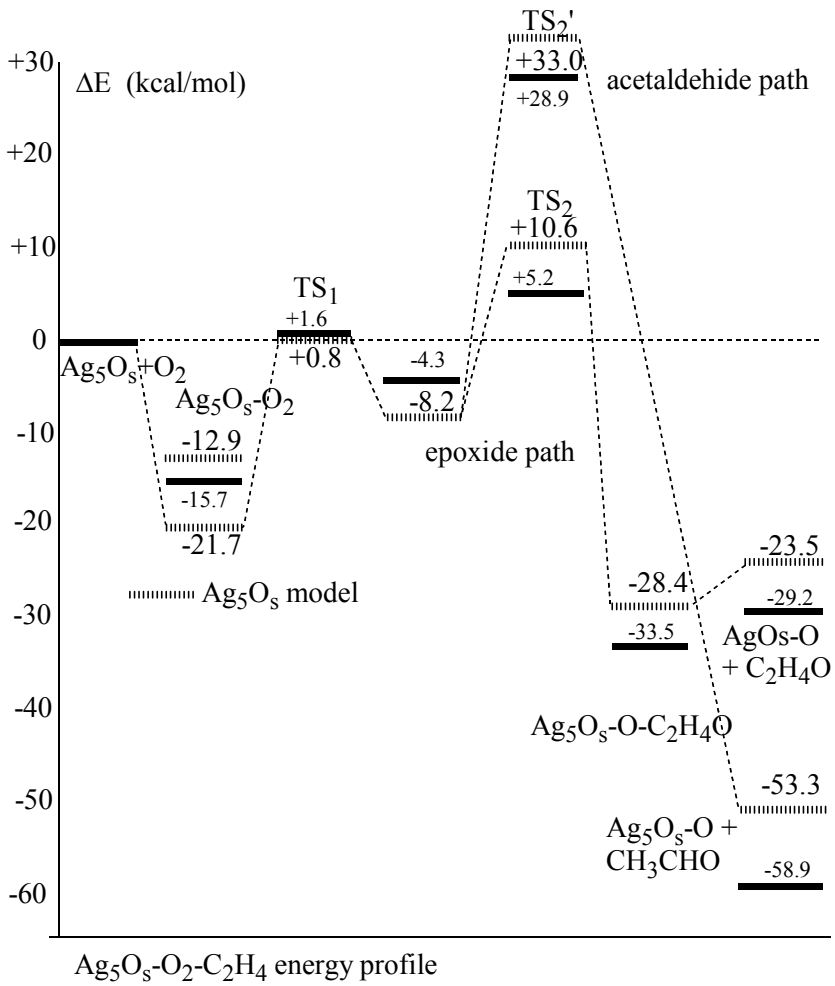


Figure 4. Energy profiles for epoxidation and acetaldehyde formation with oxygen molecule on the Ag_5O_s cluster.

3.3 Effects of Subsurface Oxygen on Ethylene Oxidation

3.3.1 Reaction of ethylene and oxygen molecule adsorbed on Ag_5O_s cluster

The co–existence of subsurface oxygen seems to be important for ethylene oxide formation [10]. We examined the influence of subsurface O atom (abbreviated as O_s) on ethylene epoxidation and combustion. The structure of the Ag_5O_s cluster was determined by optimizing the position of O_s atom only in the neighborhood of the tetrahedral vacancy below the (111) surface, and then the structure of Ag_5O_s cluster was fixed in the following studies. Using the Ag_5O_s cluster, we again evaluated reactivity of adsorbed oxygen molecule and atom with ethylene.

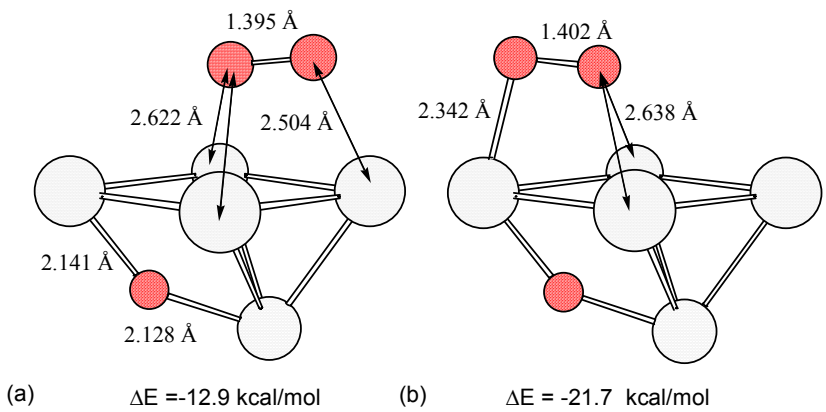


Figure 5. Two optimized structures for O_2 adsorption on Ag_5O_s cluster. Long O_2–O_s configuration (a) and short O_2–O_s configuration (b).

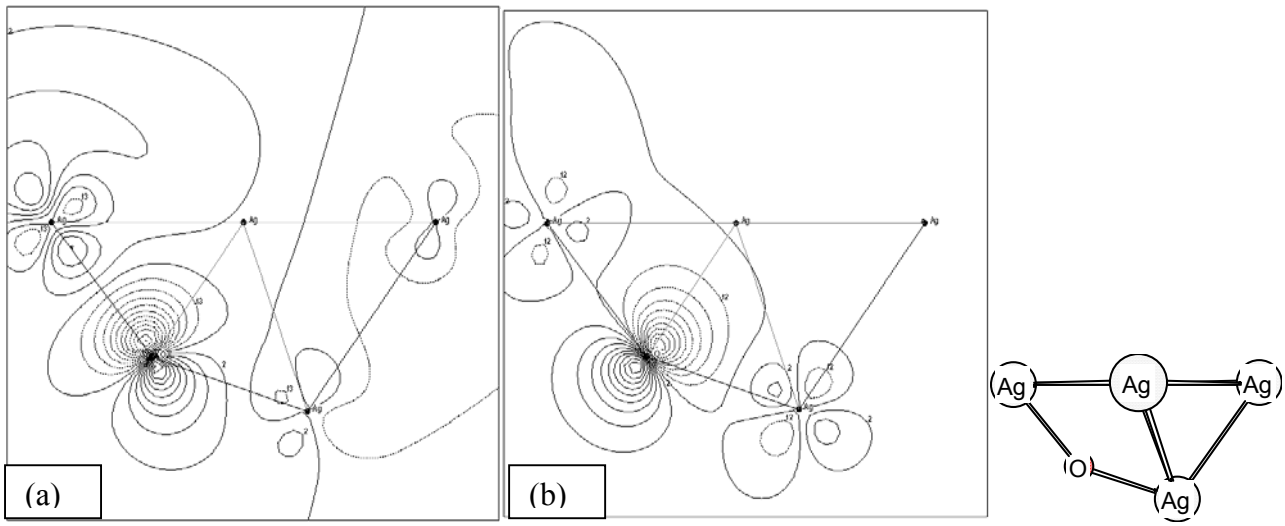


Figure 6. MO contour maps for α–HOMO (a) and β–HOMO (b) of the Ag_5O_s cluster. The configuration of atoms is also illustrated.

The energetics along the reaction with oxygen molecule is shown in Figure 4. Two optimized structures of O_2–Ag_5O_s are obtained, as shown in Figure 5. One configuration where O_2 is close to the O_s atom is more stable by 9 kcal/mol than the other with a longer O_2–O_s distance (Figure 5 (b), (a), respectively). This result is curious from the point of chemical intuition, because the electrostatic interaction seems unfavorable for the shorter O_2–O_s distance. A possible explanation is that the Ag atom interposed between O_2 and O_s may become much positive, enough to stabilize the sandwich–like structure, though the O_2 and O_s moieties become negative. However, definite advantage is not recognizable in the atomic charges estimated by Mulliken population. Another explanation is based on the extension of the frontier orbitals, since the HOMO orbital is important for adsorption of oxygen molecule onto the Ag surface, as shown in Paper I. The contour maps of the HOMO with α and β spins for Ag_5O_s cluster are shown in Figure 6. At first, both the HOMO's localize on the O_s atom, and secondary the orbital lobes of Ag atom are much extending at the side close to O_s atom, which is favorable for the bonding with oxygen π orbitals. This result is interpreted as follows. The O_s 2*p* orbitals are main component of the HOMO, and antibonding to the neighboring Ag 4*d* orbitals on the surface. The Ag 4*d* orbitals have larger mixing components with the O_s 2*p* ones due to larger overlap, and extend out of the cluster. It causes larger stabilization at the configurations with shorter O_2–O_s distance, to which we restricted our calculations hereafter.

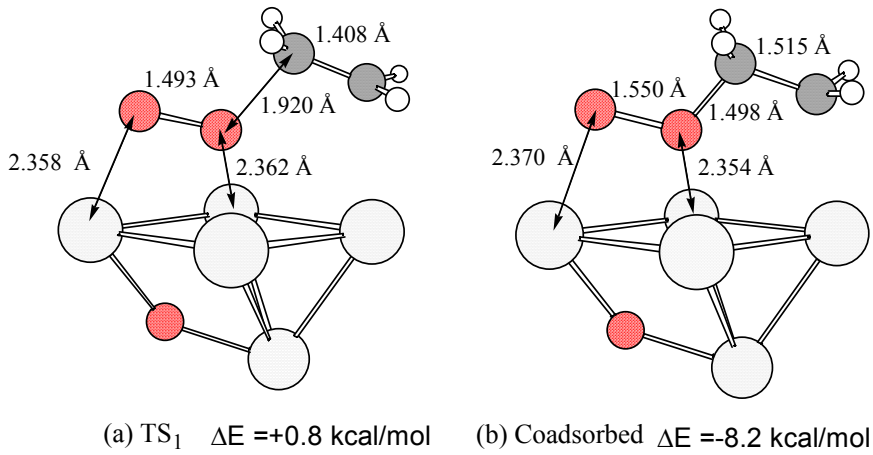
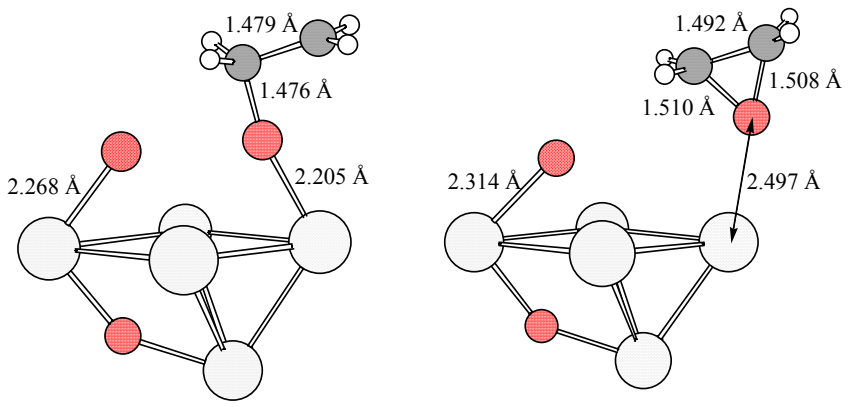


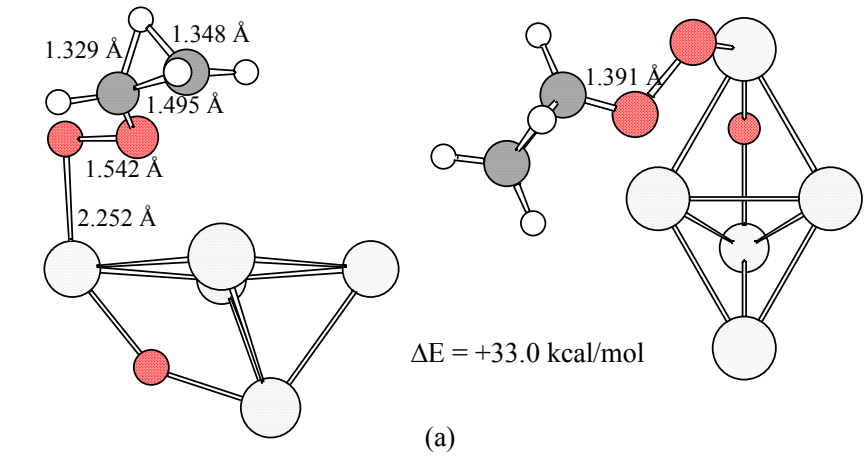
Figure 7. First TS structure (a) and coadsorbed structure (b) of $Ag_5O_sO_2C_2H_4$ for epoxide formation.

As shown in Figure 4, the Ag_5O_s cluster with shorter O_2–O_s configuration (Figure 5 (b)) further stabilizes the O_2 adsorption by 6 kcal/mol compared to the Ag_5 cluster. Figure 7 shows the structures of TS_1 and CS, and Figure 8 shows those of TS_2 and the product. These structural changes are similar to those obtained with the Ag_5 cluster (see paper I). Coadsorption of O_2 and ethylene on the Ag_5O_s cluster is more stabilized by 4 kcal/mol, whereas the energy of TS_1 is not changed. Following coadsorption, three states of TS_2, adsorbed and desorbed ethylene oxide on Ag_5O_s cluster are destabilized by 5 – 6 kcal/mol, compared to those on Ag_5 cluster.

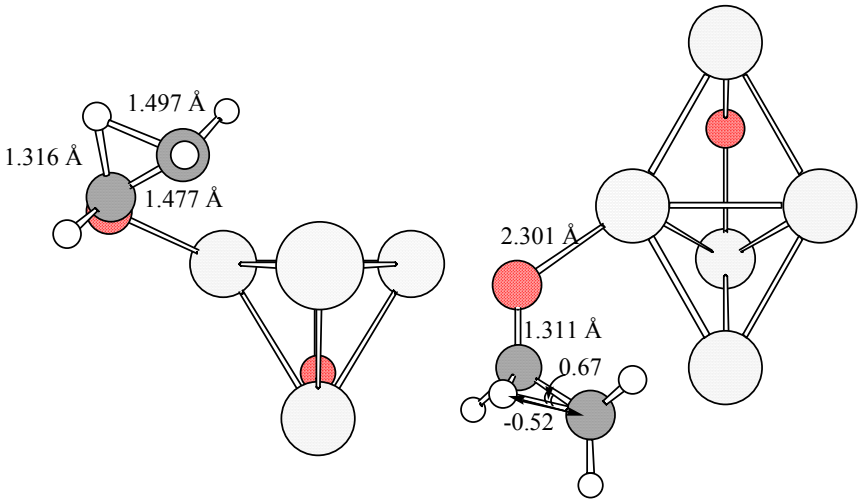


(a) TS_2 ΔE = +10.6 kcal/mol (b) Product ΔE = -28.4 kcal/mol

Figure 8. Second TS structure (a) and product structure (b) of $Ag_5O_sO_2C_2H_4$ for epoxide formation.



(a)



ΔE = +3.1 kcal/mol

(b)

Figure 9. TS structures to acetaldehyde formation with oxygen molecule, $Ag_5O_sO_2C_2H_4$ (a) and with oxygen atom, $Ag_5O_sOC_2H_4$ (b).

We then examined the energies in the course of acetaldehyde formation. The energetics is also shown in Figure 4. The TS_2' is destabilized by O_s coexistence as much as TS_2 (4 – 5 kcal/mol), showing that high epoxide selectivity should be unchanged because the difference in both TS energies is not changed. The TS_2' structure is described in Figure 9(a). In the TS_2' structure, an O_2 moiety on the Ag_5O_s cluster is almost parallel to the plane of the cluster facet and bonded to the Ag atom close to the O_s atom, whereas an O_2 moiety on the Ag_5 cluster is rather perpendicular against the Ag_4 plane (see Figure 2(b)).

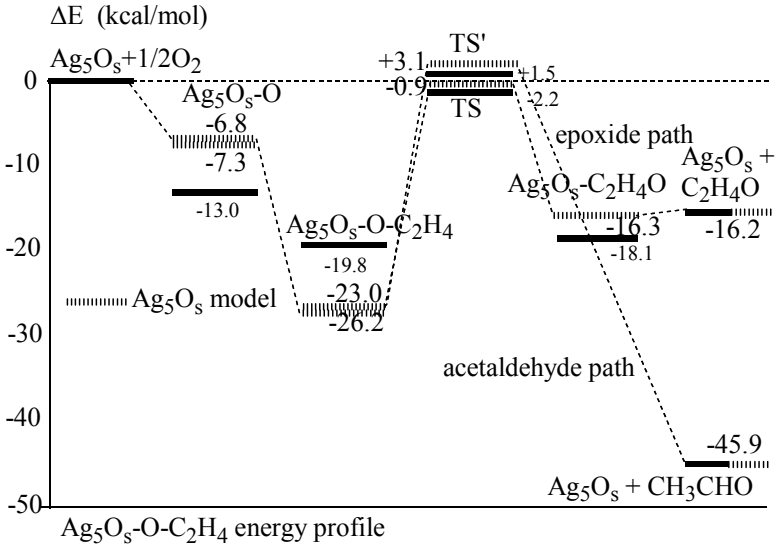


Figure 10. Energy profiles for epoxidation and acetaldehyde formation with oxygen atom on the Ag_5O_s cluster.

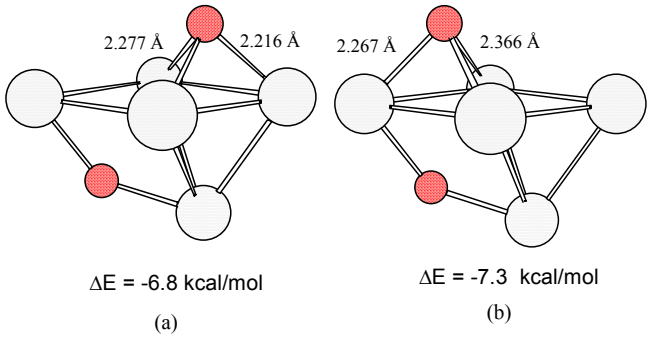


Figure 11. Two optimized structures for O atom adsorption on Ag_5O_s cluster. Long O–O_s configuration (a) and short O–O_s configuration (b).

3.3.2 Reaction of ethylene and oxygen atom adsorbed on Ag_5O_s cluster

The energetics along the reaction with oxygen atom is shown in Figure 10. Two optimized structures for O adsorption on the Ag_5O_s cluster are obtained, as shown in Figure 11. The two structures differ in a position of the adsorbed O atom, although both of the energies are almost the same. The stability of the O–Ag_5O_s cluster with a shorter O–O_s configuration is larger contrary to intuition and similar to the case of O_2–Ag_5O_s cluster. Therefore, the structure of ethylene

coadsorption is also optimized on the O–Ag_5O_s cluster with a shorter O–O_s configuration. Two structures of C_2H_4–O coadsorption on the Ag_5O_s cluster are obtained, as presented in Figure 12. More stable structure of C_2H_4–O coadsorption is a configuration with a shorter H_2C–Ag distance (Figure 12 (b)). The difference is ascribed to the H_2C–Ag electrostatic interaction: in more stable structure, the negatively charged CH_2 group has a shorter distance to the positively charged Ag atom. The distance between the CH_2 group and Ag atom in the C_2H_4–O–Ag_5O_s structure is reduced than that on the O–Ag_5 cluster. This shorter distance may be responsible for increase in the adsorption energy on the Ag_5O_s cluster. The TS and product structures are shown in Figure 13.

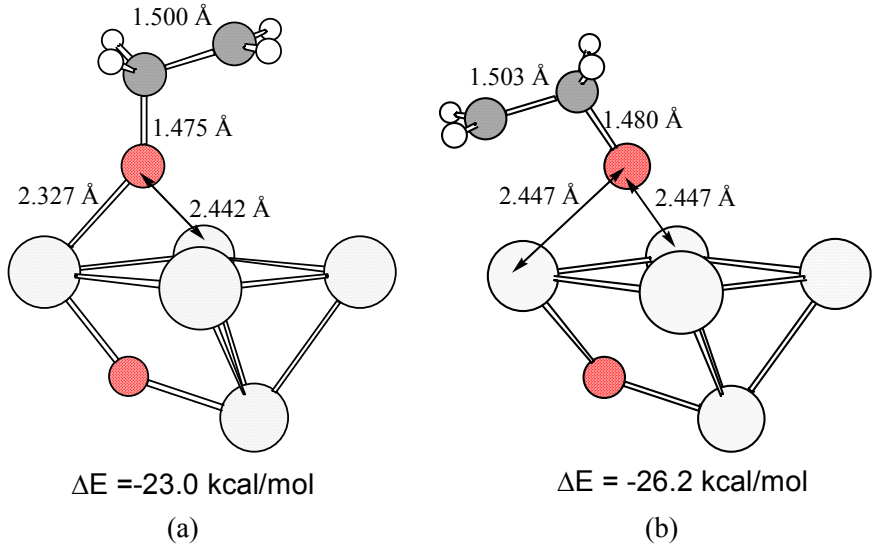


Figure 12. Two optimized structures for O–C_2H_4 coadsorption on Ag_5O_s cluster. Long H_2C–Ag configuration (a) and short H_2C–Ag configuration (b).

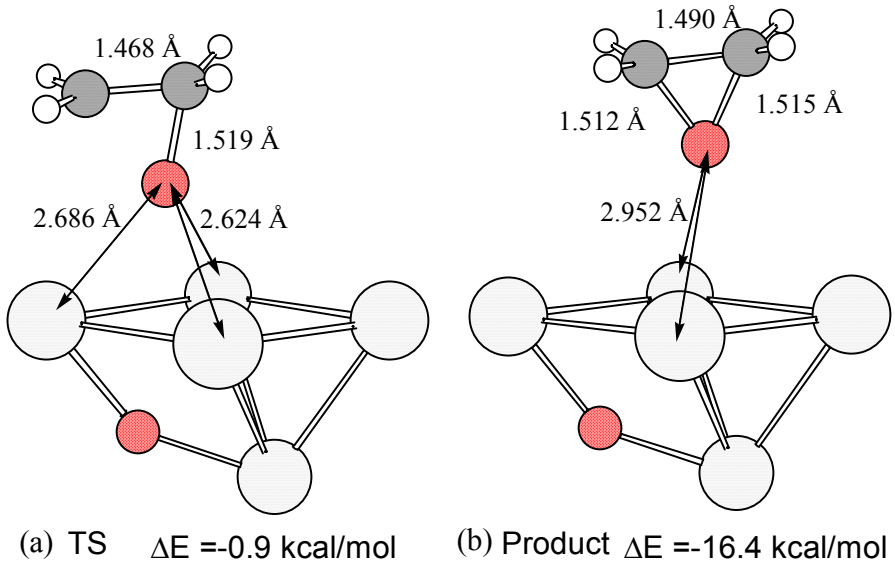


Figure 13. TS structure (a) and product structure (b) of $Ag_5O_sOC_2H_4$ for epoxide formation.

The energetics is summarized in Figure 10. The O_s atom destabilizes the O atom adsorption by 6 kcal/mol, and stabilizes ethylene by 6 kcal/mol, compared to that on the Ag_5 cluster. However the TS energy for epoxide formation is hardly changed by O_s coexistence compared to that on the Ag_5 cluster. The TS structure toward acetaldehyde is shown in Figure 9 (b). As is different from the TS structure on the Ag_5 cluster shown in Figure 3, the ethylene moiety is located far from the Ag_5O_s cluster. The negative eigenvalue of Hessian matrix is –0.369. Two leading components of this eigenvector are 0.67 for the H–C–C angle and –0.52 for the H–C distance, as shown in this figure, and their magnitude is discriminated from the third component, 0.26 for the C–O distance. Thus this structure is a really TS for acetaldehyde formation. The TS energy for acetaldehyde formation is increased by 1.6 kcal/mol by O_s coexistence. Eventually the difference in barrier heights between the two reactions increases from 3.7 to 4.0 kcal/mol. Though this increase is very small, the subsurface oxygen species may be shown to be a useful component for epoxide formation in agreement with the experimental results [10]. After the TS, epoxide is formed and desorbed from Ag_5O_s with an essentially zero binding energy. The much lower energy for acetaldehyde is due to a large heat of formation compared to that for epoxide. On desorption of the final products (CH_3CHO or C_2H_4O), the energies have the same value between the Ag_5O_s and Ag_5 clusters since the total energy is a sum of a free molecule and a free cluster on either cluster.

4 CONCLUSIONS

Using a Ag_5 cluster as a model for Ag catalysts, the mechanisms of ethylene oxide formation and complete oxidation, which could proceed via acetaldehyde formation or hydrogen abstraction from ethylene, were investigated using the hybrid DFT method. The influence of O_s (subsurface oxygen) on epoxide selectivity was also examined. Hydrogen abstraction did not show advantage over acetaldehyde formation. The energy profile showed high selective (nearly 100%) formation of epoxide with oxygen molecule adsorbed on the Ag_5 and Ag_5O_s clusters, while adsorbed oxygen atom oxidizes less selectively. The coexistence of O_s atom and Ag_5 cluster might enhance epoxide selectivity with adsorbed oxygen atom to some extent.

Based on the active oxygen molecule mechanism for epoxide, the selectivity of oxygen is 50% corresponding to ethylene selectivity of 85.7% (6/7). However this work indicates that the adsorbed oxygen atom can produce epoxide with/without O_s coexistence to some extent, showing ethylene selectivity higher than 85.7%. Therefore, an oxidizing agent for epoxide formation may be considered as adsorbed oxygen atom.

It is still unclear why adsorbed oxygen molecule can give a very high selectivity for epoxide in this work. Further studies are necessary to understanding this occurrence, and thus can contribute to epoxide catalyst development.

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