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Electron transfer and back-transfer in the partial oxidation of ethylene on an Ag surface: dipped adcluster model study

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Abstract

The crucial step in catalyst design to increase the overall selectivity of epoxidation of ethylene on a silver surface is the reaction of atomically adsorbed oxygen with ethylene to give ethylene oxide, as shown previously. The energy diagram is recalculated using the dipped adcluster model combined with MP2 geometry optimizations. The previous result is confirmed. At the key transition state (TS), one-electron is back-transferred from the admolecule to the bulk Ag surface. The energy barrier is calculated to be 41 kcal/mol, comparable with the energy barrier of 39 kcal/mol in the complete oxidation path. The energy barrier of this electron-transfer type TS must be lowered to obtain a higher overall selectivity of ethylene oxide.
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1. Introduction

The heterogeneous selective oxidation of ethylene to ethylene oxide by promoted silver catalysts is an important catalytic reaction in the chemical industry and has attracted academic and industrial interest [1,2]. Though a great deal of research has been undertaken to try to understand the mechanism of the reaction [3–14], the origin of this unique catalytic activity of silver has not yet been fully clarified. One of the main questions still debated is the role of the different adsorbed oxygen species in the mechanisms of epoxidation and complete oxidation of olefins on a silver surface. This question is of crucial importance, since its solution not only leads to an understanding of the uniqueness of silver as a selective oxidation catalyst, but also provides a way to pursue higher selectivity of epoxide yield, by further refining the epoxidation catalyst.

Several different mechanisms have been proposed for this reaction. One mechanism attributes the total combustion to the reaction with the atomic oxygen species and the epoxidation to the reaction with the molecular oxygen species [3–9]. This mechanism is appealing since it gives a reasonable explanation of the well known homogeneous reaction in which olefins are epoxidised by the peracids in solution [10]. Another mechanism attributes both combustion and epoxidation to atomic oxygen species [11–14]. If only the molecularly adsorbed oxygen is involved in the partial oxidation, then the maximum selectivity of ethylene oxide formed from ethylene should be less than 85.7% [7]. However, some recent experi-

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ments have reported the selectivity as high as 85–87% [15–18]. This fact can not be explained if only the molecular oxygen species are involved in the partial oxidation process. Further, we regard the fact that the selectivity to ethylene oxide can be raised by the addition of alkali halides as important for identifying the mechanism.

We have been studying the oxidation mechanisms of olefins on silver surfaces [19–22]. We have studied the electronic mechanisms of the reactions of ethylene both with molecularly and atomically adsorbed oxygen on a silver surface [19]. The end-on adsorbed superoxide species was shown to be highly active and selective, leading to the formation of ethylene oxide, while the atomically adsorbed oxygen is not selective but leads to both ethylene oxide and the complete oxidation products. However, the transition state (TS) from the intermediate to ethylene oxide in the reaction of atomically adsorbed oxygen was not determined despite much computational effort. The nature of this TS is quite interesting as it was expected that the electron back-transfer from the adsorbate to the surface would occur near this TS [19].

In this Letter, we study in more detail the electronic mechanism of the partial oxidation process by the atomically adsorbed oxygen species, since this is the key step in designing a selectivity higher than 6/7 [19]. The electronic structure and the geometry of the TS in relation to the electron transfer between the admolecule and the Ag surface is studied using the dipped adcluster model (DAM) [23–25], which was proposed to investigate the surface reactions for which the electron transfer between admolecule and surface is important. This model has been successfully applied to the adsorption of O_2 on Pd and Ag surfaces [23,26–28] and recently to the oxidation reactions of ethylene and propylene on a silver surface [19–21]. The activation mechanisms of O_2 on Cu and Au surfaces were also studied using the DAM [22]. A review of DAM studies has been published [25].

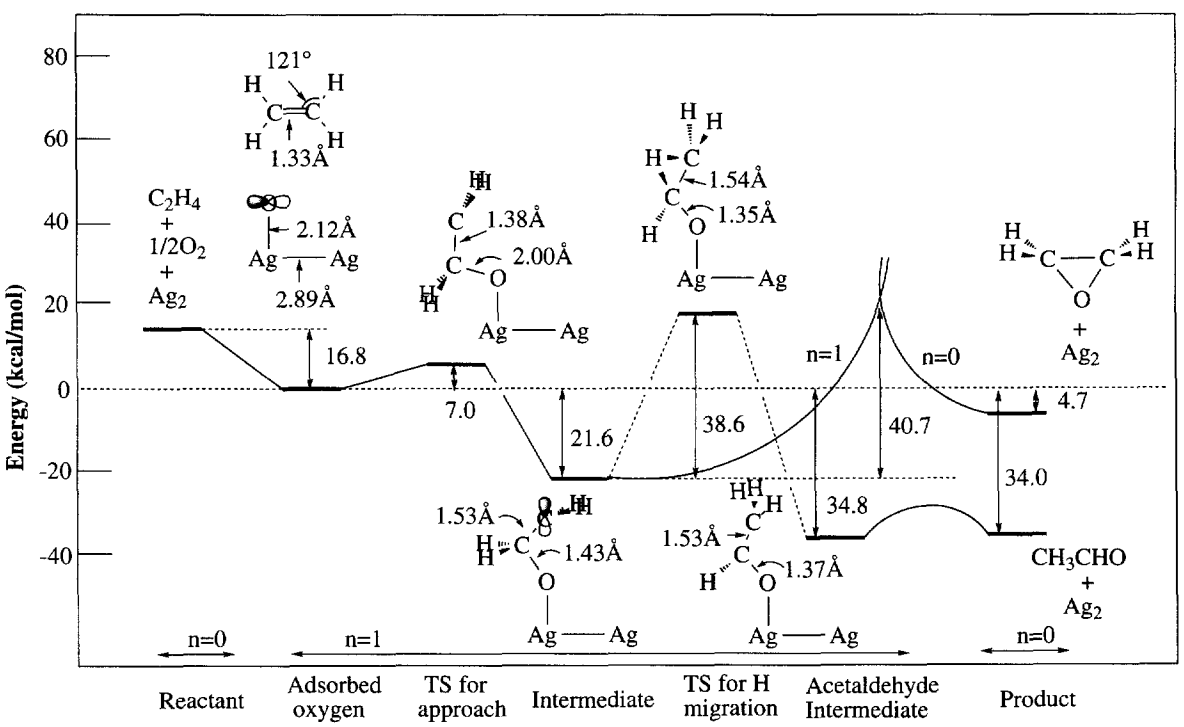

Fig. 1. Energy diagram for the reaction between ethylene and atomically adsorbed oxygen on an Ag surface calculated by the MP2 optimization method.

2. Computational details

The energy diagram for the reaction of ethylene with atomically adsorbed oxygen on an Ag surface reported in a previous paper [19] has been recalculated using a full MP2 geometry optimization procedure, to examine the reliability of the former MP2 energy calculations based on the UHF optimized geometries. The result is given in Fig. 1.

We calculate the potential energy curve (PEC) of the adcluster between the intermediate and ethylene oxide by considering electron transfer of $n = 0.0$, 0.25, 0.5, 0.75 and 1.0, where n is the number of the electrons transferred from the bulk metal into the adcluster. The geometry of the adcluster is sketched in Fig. 2. The reaction coordinate between the intermediate and the product is defined by linearly changing the C_a–C_b, C_a–O bond lengths and the C_bC_aO, C_aOAg_a angles, with the Ag_a–O, Ag_a–Ag_b bond lengths and the Ag_bAg_aO angle fixed at 2.1803 Å, 2.8894 Å and 90.0°, respectively, throughout the calculations.

The energy curves for $n = 0.0$, 0.25, 0.5, 0.75 and 1.0 are first calculated by the ab initio unrestricted HF (UHF) method. The MP2 method is used to give the final potential energy curves for the states corresponding to $n = 0$ and 1, respectively. The electrostatic image force between the admolecule ($C_2H_4O^-$) and surface was estimated by using the image force correction [24]. The calculations were performed by using the HONDO8 [29] and the Gaussian '92 program packages [30].

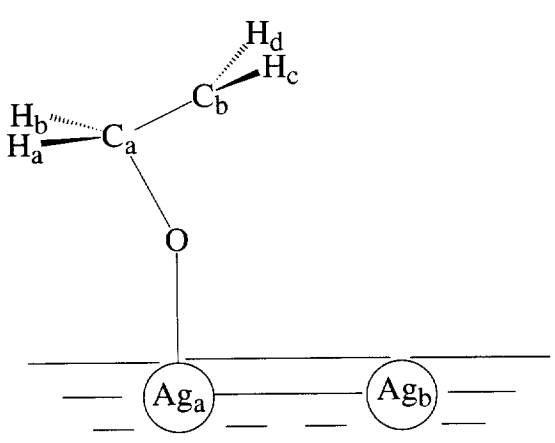

Fig. 2. Model adcluster used.

The Gaussian basis set for the silver atom was (3s3p4d)/[3s2p2d] with the Kr core replaced by a relativistic effective core potential [31]. For oxygen, we used the (9s5p)/[4s2p] set of Huzinaga–Dunning [32,33] augmented by diffuse s and p functions of exponent $\alpha = 0.059$ as anion bases [34] in the UHF calculation and d polarization functions of exponents $\alpha = 2.704$ and 0.535 [35] were added for the MP2 calculation. For carbon and hydrogen, the (9s5p)/[4s2p] and (4s)/[2s] basis sets, respectively, of Huzinaga–Dunning were adopted [32,33]. These basis sets are the same as those used previously [19] and were shown to give reliable thermochemical data [19].

3. Results and discussion

Fig. 1 shows the energy diagram for the reaction of ethylene with atomically adsorbed oxygen on an Ag surface calculated by the MP2 geometry optimization procedure. The net charge and the frontier density (spin population) of each atom in the reaction path are listed in Table 1. These results are similar to those reported in fig. 5 and table 4 of our previous paper [19], in which the MP2 calculations were done for the UHF optimized geometries. Thus, the present result supports the argument given in Ref. [19] on the reactions of ethylene with the atomically adsorbed oxygen. In particular, the energy barriers from the intermediate to ethylene oxide and to the acetaldehyde intermediate are 40.7 and 38.6 kcal/mol, in comparison with ≈ 36 and 39.1 kcal/mol in the previous calculations [19]. Thus, we estimate the selectivity to ethylene oxide by atomically adsorbed oxygen to be about 50%. This is in marked contrast to the selectivity of almost 100% of the molecularly adsorbed superoxide species [19]. The geometries of the intermediates and the transition states obtained by the MP2 optimization procedure (Fig. 1) are similar to the previous results. The same is true for the net charges and the frontier densities shown in Table 1.

The PECs between the intermediate and the product calculated for different amounts of electron trans-

Table 1
Net charge and frontier density (spin population) (in atomic units) of the $Ag_2OC_2H_4$ adcluster at various structures shown in Fig. 1 calculated by the MP2 optimization procedure

	Adsorbed oxygen	TS for approach	Intermediate	TS for H migration	Acetaldehyde intermediate
net charge					
Ag_a	−0.078	−0.177	−0.205	−0.133	−0.174
Ag_b	−0.307	−0.270	−0.277	−0.246	−0.278
O_a	−0.615	−0.533	−0.623	−0.629	−0.576
C_a	−0.356	−0.222	+0.015	+0.033	0.069
C_b	−0.356	−0.448	−0.422	−0.665	−0.668
H_a	+0.178	+0.167	+0.104	+0.125	0.113
H_b	+0.178	+0.167	+0.104	+0.161	0.215
H_c	+0.178	+0.158	+0.152	+0.151	0.149
H_d	+0.178	+0.158	+0.152	+0.204	0.149
frontier density					
Ag_a	−0.097	−0.039	+0.041	−0.124	−0.015
Ag_b	+0.076	+0.043	−0.013	0.130	0.001
O_a	+1.021	+0.805	+0.023	+0.121	0.154
C_a	0.0	−0.340	−0.084	+0.394	0.980
C_b	0.0	+0.560	+1.182	+0.545	−0.121
H_a	0.0	+0.017	+0.002	−0.003	−0.080
H_b	0.0	+0.017	+0.002	−0.033	0.002
H_c	0.0	−0.032	−0.076	−0.001	0.035
H_d	0.0	−0.032	−0.076	−0.030	0.035

fer from the bulk metal to the adcluster are shown in Fig. 3. At the geometry of the intermediate, the state with $n = 1.0$ has the lowest energy. The PECs on the left-hand side are rising curves with the order of stability $n = 1.0 > 0.75 > 0.5 > 0.25 > 0.0$. However, the PECs on the right-hand side have a different order of stability $n = 0.0 > 0.25 > 0.5 > 0.75 > 1.0$. Interestingly, the crossing of the lowest two curves on the left- and right-hand sides occurs between $n = 1.0$ and $n = 0.0$ both being integers. The geometry at the crossing point is $R_{Ca-Cb} = 1.486$ Å, $R_{Ca-O} = 1.453$ Å, $R_{Cb-O} = 1.751$ Å and $\angle C_bC_aO = 73.6°$ and $\angle C_aOAg_a = 147.3°$. Though this is not the lowest energy state along the crossing seam between $n = 1.0$ and $n = 0.0$, we approximate this structure as the TS in this reaction pathway. At this TS, one electron is transferred back from the adcluster to the bulk Ag metal.

At the TS electron transfer may occur in decimal. However, the result presented in Fig. 3 shows that decimal electron transfer does not occur in the present reaction pathway. The PECs and the crossings corresponding to decimal electron transfer are always higher than that for the one electron transfer. Therefore, we conclude that *one* electron transfer occurs directly between the adcluster and the bulk metal. In the intermediate, the state with one electron transferred from the bulk to the adcluster is stable. In the TS, the states with one electron ($n = 1.0$) and no-electron ($n = 0.0$) transferred have the same energy. After the TS, the no-electron transferred state has the lowest energy, leading to the ethylene oxide product.

Next we investigate the electronic structure of the adcluster along the reaction pathway shown in Fig. 3. Table 2 shows the net charges. We see that the electronic structures along the reaction pathway are divided into two groups, i.e. ones similar to the intermediate and the others similar to the product. The electronic state changes from the former to the later at around the TS. Furthermore, the change in the net charge of the C_2H_4O system is continuous, except for that of C_b, in spite of a sudden change in n between b and c. The charges of the two Ags are always small as they should be. The bond indices listed in Table 3 show that the Ag_a–O bond changes from bonding to anti-bonding at around the TS state, implying that the product ethylene oxide leaves auto-

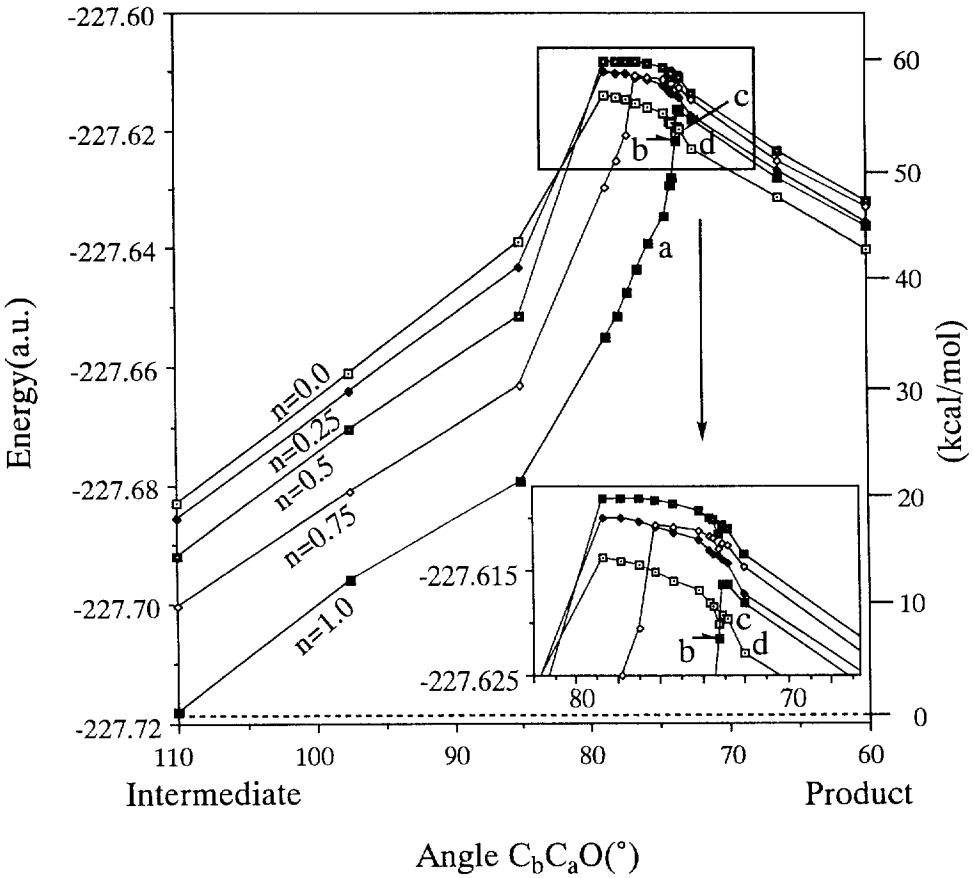

Fig. 3. Potential energy curves calculated by the UHF method between the intermediate and the product for different numbers of electrons transferred from the bulk Ag metal to the adcluster. The inset shows the TS region more clearly.

matically from the surface, while the C_b–O bond changes suddenly from anti-bonding to bonding between points b and c, as it should do.

We calculate the PECs by the MP2 method for the lowest state shown in Fig. 3 and the result is given in Fig. 4. The energy barrier for the formation

Table 2
Net charge (in atomic units) of the $Ag_2OC_2H_4$ adcluster at intermediate ($n = 1$), point-a ($n = 1$), point-b ($n = 1$), point-c ($n = 0$), point-d ($n = 0$) and product (ethylene oxide + Ag_2) ($n = 0$), calculated by the UHF method

Atom	Intermediate ($n = 1$)	Point-a ($n = 1$)	Point-b ($n = 1$)	Point-c ($n = 0$)	Point-d ($n = 0$)	Product ($n = 0$)
Ag_a	−0.161	−0.194	−0.238	−0.017	−0.009	+0.022
Ag_b	−0.157	−0.168	−0.192	−0.148	−0.157	−0.183
O	−0.758	−0.688	−0.594	−0.456	−0.483	−0.452
C_a	+0.043	−0.029	−0.071	−0.077	−0.078	−0.138
C_b	−0.417	−0.430	−0.473	−0.161	−0.134	−0.112
H_a	+0.084	+0.102	+0.122	+0.199	+0.199	+0.212
H_b	+0.084	+0.102	+0.122	+0.199	+0.199	+0.212
H_c	+0.140	+0.153	+0.162	+0.231	+0.232	+0.219
H_d	+0.140	+0.153	+0.162	+0.231	+0.232	+0.219

Table 3
Bond indices of the $Ag_2OC_2H_4$ adcluster at intermediate ($n = 1$), point-a ($n = 1$), point-b ($n = 1$), point-c ($n = 0$), point-d ($n = 0$) and product (ethylene oxide + Ag_2) ($n = 0$), calculated by the UHF method

	Intermediate ($n = 1$)	Point-a ($n = 1$)	Point-b ($n = 1$)	Point-c ($n = 0$)	Point-d ($n = 0$)	Product ($n = 0$)
Ag_a–O	+0.128	+0.142	+0.139	−0.073	−0.076	−0.062
C_a–O	+0.911	+0.822	+0.768	+0.719	+0.715	+0.706
C_a–C_b	+0.900	+0.949	+0.951	+0.929	+0.936	+0.935
C_b–O	−0.063	−0.055	+0.003	+0.597	+0.645	+0.691

of ethylene oxide, calculated to be 40.7 kcal/mol as shown in Fig. 1, is close to the energy barrier of 38.6 kcal/mol for the complete combustion reaction pathway. This result supports the previous result [19] that the oxidation reaction of ethylene with the atomically adsorbed oxygen species gives both ethylene oxide and the complete oxidation product. We note that the energy barrier of 40.7 kcal/mol should be the upper limit, since we did not do a complete optimization of the geometry at the TS. We estimate the selectivity of epoxide formation by atomically adsorbed oxygen to be about 50%.

For the partial oxidation of ethylene, promoters such as alkali halides are added in practical industrial processes. While some explanations have been presented [1–3,16–18], they are controversial. The roles of the promoters may indeed be complicated, but they are a key for pursuing higher selectivity. From our present and former studies, we have shown that molecularly adsorbed oxygen is highly selective, but atomically adsorbed oxygen can also give ethylene oxide, though the selectivity is low, about 50%. This means that to obtain higher overall selectivity, the

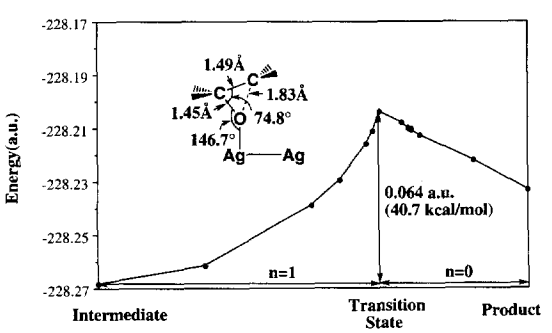

Fig. 4. Potential energy curves calculated by the MP2 method for the lowest reaction passway between the intermediate and the product.

step involving atomically adsorbed oxygen must be modified: the overall selectivity would become higher than 6/7, if we can lower the energy barrier from the intermediate to ethylene oxide in comparison with that from the intermediate to acetaldehyde in Fig. 1. A key difference between these two reactions is that the former involves the electron-transfer step in the TS, but the latter does not. We propose to investigate a method to lower the former TS, where one electron is back-transferred from the adcluster to the bulk Ag metal, and/or to increase the barrier of the latter H-migration step.

4. Conclusion

For the science and engineering of catalyst design, a clear understanding of the mechanism of the reaction under study is important and our series of studies on the reaction mechanisms of the oxidations of ethylene and propylene on the Ag surface have this aim [19–22]. In this Letter, we have investigated the reaction of atomically adsorbed oxygen in the partial oxidation of ethylene to ethylene oxide, since we have clarified in Ref. [19] that this step is the key in increasing the overall selectivity of the conversion from ethylene to ethylene oxide on a silver catalyst.

At the TS from the intermediate to ethylene oxide, one electron is back-transferred from the admolecule to the bulk Ag surface. We have shown the geometry and the electronic structure of the TS. The energy barrier of this TS, calculated to be 40.7 kcal/mol, is close to the barrier of 38.6 kcal/mol leading to the complete oxidation product. An essential difference between these two TSs is that the former involves one-electron back-transfer from the admolecule to the bulk metal, but the latter does not.

The role of the alkali-halide promoter may be interpreted in terms of the electron-transfer nature of the former TS. Methods which can lower the energy barrier in the ethylene oxide formation pathway and/or can increase the barrier for the H-migration step should lead to higher overall selectivity.

In the present series of studies, our aim has been to clarify the mechanism of the partial oxidation of ethylene to ethylene oxide [19,20,22]. The overall mechanisms were given in Ref. [19] but some uncertainties have been clarified in this Letter. The role of the Ag surface, in contrast to the Cu and Au surfaces, was investigated [22]. Based on these findings, we hope that catalyst design for the epoxidation of ethylene will be accelerated.

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