

# Theoretical Study of Atomic Oxygen Adsorption on the Chlorine-Modified Ag(111) Surface

Lingling Jia, Yun Wang, and Kangnian Fan\*

Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Center for Theoretical Chemical Physics, Department of Chemistry, Fudan University, Shanghai 200433, P. R. China

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The adsorption of oxygen on the clean, chlorine-modified Ag(111) surface has been investigated by the *ab initio* pseudopotential total energy method based on density functional theory. The effects of chlorine on the adsorption of oxygen and the diffusion of surface oxygen have been studied. From the theoretical adsorption energies and structures of the adsorbate–surface system, we found that the existence of chlorine increases the adsorption energy of oxygen. Since the adsorbed chlorine atom will occupy the stable adsorption site for the oxygen atom, it will lead to the reduced adsorption of oxygen. We have calculated the barrier for the diffusion of atomic oxygen on the silver surfaces, and the results show that the diffusion of the surface oxygen atoms into bulk Ag is easier on the chlorine-modified Ag(111) surface than on the clean surface.

## 1. Introduction

The interaction of oxygen with silver surfaces has received much attention during the last few years because silver is the best catalyst for two important industrial reactions: the epoxidation of ethylene to ethylene epoxide and the partial oxidation of methanol to formaldehyde.<sup>1–8</sup> In the process of the epoxidation of ethylene, the presence of chlorine can promote the selectivity of ethylene epoxide rather than total combustion leading to H<sub>2</sub>O and CO<sub>2</sub>.<sup>9,10</sup> Both the mechanism of ethylene epoxidation and the promotion effect of chlorine are still unresolved. For the mechanism of ethylene epoxidation, the unanswered question is whether atomic oxygen or molecular oxygen is involved in the epoxidation process. Several research groups have performed studies on this system with surface science techniques or by the theoretical calculations. These studies led to two conflicting interpretations regarding whether adsorbed O or O<sub>2</sub> is the active oxygen agent in forming epoxide.<sup>2,3,11–14</sup> Except for these two different opinions, Van den hoek et al. have suggested by their theoretical calculations<sup>15</sup> that subsurface oxygen plays an important role in ethylene epoxidation. They showed that the presence of subsurface oxygen reduced the bond energy between silver and adsorbed oxygen and converted the repulsive interaction between adsorbed oxygen and (gas-phase) ethylene into an attractive one, thus making the epoxidation reaction possible. Another elusive question is the promotion action of chlorine. In the past, the adsorption of chlorine on silver surfaces has been studied by various research groups with a wide array of surface science techniques including LEED, thermal desorption, work function changes, XPS, AES, SEXAFS, and UPS.<sup>16–20</sup> However, there are still many unanswered questions such as different adsorption patterns and adsorption structures observed in different experiments.<sup>16,18,19</sup> Knowledge of chlorine adsorption on silver surfaces can provide important information about the effect of chlorine modification on the interaction between oxygen and silver surfaces, which is prerequisite to ideas on how chlorine adsorption accelerates ethylene epoxidation. The interaction

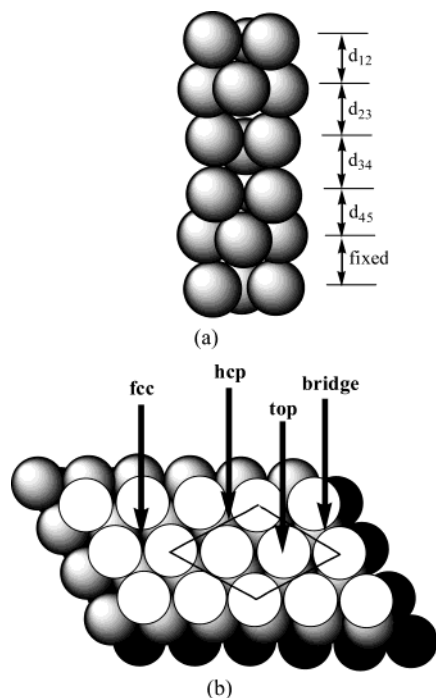
between chlorine and oxygen on silver surfaces has been extensively reviewed, and much discussion centers on the effects of chlorine on the adsorption of oxygen.<sup>10,21–24</sup>

However, in terms of theoretical research, very little work has been reported on chlorine–oxygen interactions over silver surfaces. Harrison et al. have studied the adsorption of chlorine on the Ag(111) surface with potential-gradient-corrected density functional calculations, and they obtained some information on the interaction between chlorine and the silver surface<sup>26</sup> such as the most favorable adsorption site, the energies and related properties of bulk Ag, the value of the Ag–Cl bond length, and so forth. Previous work in our laboratory<sup>27</sup> has been performed to study the effects of Cl on the structure and catalytic behavior of Ag(111) with the cluster model using the DFT method. Also, there are other theoretical studies on the promotion action of chlorine on silver surfaces,<sup>28,29</sup> but to the best of our knowledge, there is no systematic theoretical work on the effect of chlorine on oxygen adsorption over silver surfaces. The purpose of our present theoretical studies is to investigate the oxygen adsorption on the clean and chlorine-preadsorbed Ag(111) surfaces to obtain some information about the modification effect of chlorine on the adsorption of oxygen over the Ag(111) surface. The roles of chlorine in the diffusion of surface oxygen into the subsurface are also investigated.

## 2. Calculation Method

We performed the first-principles calculations within the framework of density functional theory (DFT) by using the *ab initio* total-energy and molecular-dynamics program VASP that was developed at the Institut für Theoretische Physik of Technische Universität Wien. The electron–ion interaction is represented by optimized Vanderbilt ultrasoft pseudopotentials,<sup>31</sup> which were supplied by Kresse and Hafner.<sup>32</sup> The residual minimization technique<sup>33,34</sup> is used to calculate the electronic ground state. Forces on atoms are all calculated according to the Hellmann–Feynman theorem with the conjugated-gradient technique. The generalized gradient approximation (GGA) proposed by Perdew and Wang,<sup>35</sup> named PW91, is employed. The cutoff energy of plane waves is 300.0 eV. The Monkhost–Pack net of special points is used for Brillouin zone sampling.

\* Corresponding author. E-mail: knfan@fudan.edu.cn. Fax: +86-21-65642978.



**Figure 1.** Schematic representation of the Ag(111) surface. (a) Side view of the slab model.  $d_{12}$ ,  $d_{23}$ ,  $d_{34}$ ,  $d_{45}$  represent the distances between different silver layers, respectively. “Fixed” means that the bottom two layers of the slab are fixed at their ideal positions. (b) Top view of the slab model. The  $\sqrt{3} \times \sqrt{3} 30^\circ$  unit cell is displayed inside the solid lines. The four distinct high-symmetry adsorption sites on the Ag(111) surface are also illustrated.

In our calculations, the  $\sqrt{3} \times \sqrt{3} 30^\circ$  unit cell is chosen with a coverage of  $\Theta = \frac{1}{3}$  ML, according to the observed experimental chlorine adsorption pattern on the Ag(111) surface.<sup>19</sup> Monkhorst–Pack meshes with  $8 \times 8 \times 1$  k-point sampling in the surface Brillouin zone is used for the unit cell. The silver surface systems are modeled by periodically repeated elongated supercells with six silver layers separated by a vacuum region corresponding to six layers. Figure 1 illustrates the unit cell of the slab model, which contains three Ag atoms per layer. Adsorbed atoms are placed on one side of the slab only. Both the adsorbed atoms and the upper four silver layers are allowed to relax. The bottom two layers are fixed at their bulklike position (calculated lattice constant =  $4.18 \text{ \AA}^{36}$ ).

### 3. Results and Discussion

**3.1. Clean Ag(111) Surface.** Calculations for clean surfaces were first performed in our study. The relaxation of the distances between the upper five layers is given as a percentage of the unrelaxed ideal interlayer distance in Table 1. It is found that the relaxation is very small. The values are  $-0.25$ ,  $-0.24$ ,  $0.11$ ,  $-0.14\%$ . (The minus sign means a contraction of the interlayer distance compared to the bulk distance.) The value of the work function  $\Phi$  calculated in the present work is  $4.63 \text{ eV}$ , in comparison with the result of  $4.65 \text{ eV}$  from Wang’s work.<sup>36</sup> The experimental value is  $4.46 \pm 0.02 \text{ eV}$ .<sup>37</sup> All of the calculated results demonstrate that the structure of the clean Ag(111) surface is little changed during the relaxation, which well agrees with the LEED (low-energy electron diffraction) and HEIS (high-energy ion scattering) experiments.<sup>37,45,46</sup>

**3.2. Cl Adsorption on Clean Ag(111) Surface.** For the Ag(111) surface, we have investigated four distinct high-symmetry sites at which chemisorption is considered. They are

**TABLE 1: Structural and Energetic Properties of the Cl/Ag(111) Surface Cell**

	clean Ag	Fcc	Hcp	bridge	top
$\Delta_{12}^a (\%)$	$-0.25$	$-1.29$	$-1.10$	$-1.30$	$-1.38$
$\Delta_{23}^a (\%)$	$-0.24$	$0.18$	$0.25$	$0.16$	$-0.24$
$\Delta_{34}^a (\%)$	$0.11$	$0.24$	$0.32$	$0.22$	$-0.13$
$\Delta_{45}^a (\%)$	$-0.14$	$-0.33$	$-0.32$	$-0.32$	$-0.47$
$d_{\text{Cl-surface}}^b (\text{\AA})$		$2.00$	$2.01$	$2.06$	$2.30$
$d_{\text{Cl-Ag}}^c (\text{\AA})$		$2.64$	$2.64$	$2.56$	$2.39$
$\text{AE}^d (\text{eV})$		$3.124$	$3.117$	$3.044$	$2.684$
$\Phi^e (\text{eV})$	$4.63$	$5.64$	$5.68$	$5.82$	$6.41$
$\Delta\Phi^f (\text{eV})$		$1.01$	$1.05$	$1.20$	$1.78$

<sup>a</sup>  $\Delta_{ij}$ : interlayer relaxation. <sup>b</sup>  $d_{\text{Cl-surface}}$ : distance between a Cl atom and the top layer of silver. <sup>c</sup>  $d_{\text{Cl-Ag}}$ : distance between a Cl atom and the nearest-neighbor silver atom. <sup>d</sup> AE: adsorption energy. <sup>e</sup>  $\Phi$ : work function value. <sup>f</sup>  $\Delta\Phi$ : change in the work function.

the top site, bridge site, fcc hollow site (the 3-fold hollow site with a third-layer Ag atom beneath), and hcp hollow site (the 3-fold hollow site with a second-layer Ag atom beneath). A top view of the model and the  $\sqrt{3} \times \sqrt{3} 30^\circ$  unit cell consisting of three atoms in each layer are displayed in Figure 1b. The calculated results of the chlorine-modified Ag(111) surface are also listed in Table 1. The symbols  $\Delta_{12}$ , ...,  $\Delta_{45}$  in Table 1 stand for the changes in interlayer spacing between the uppermost layers relative to the bulklike value. The value of  $d_{\text{Cl-surf}}$  is the distance between the adsorbed chlorine layer and the center of mass of the first layer on the silver surface; the value of  $d_{\text{Cl-Ag}}$  equals the distance between chlorine atom and the nearest-neighbor silver atom. The adsorption energy (AE) is defined by the equation  $\text{AE} = E_{\text{Cl-substrate}} - E_{\text{substrate}} - E_{\text{Cl}}$ , where  $E_{\text{Cl-substrate}}$  and  $E_{\text{substrate}}$  are the total energy of the system with or without the adsorbate, respectively.  $E_{\text{Cl}}$  represents the energy of the isolated chlorine atom. For the calculation of the isolated chlorine atom, the spin polarization is considered. The change in the work function value is calculated by  $\Delta\Phi = \Phi_{\text{Cl-substrate}} - \Phi_{\text{substrate}}$ .  $\Phi_{\text{substrate}}$  is the work-function value of the clean silver surface, and  $\Phi_{\text{Cl-substrate}}$  represents the work-function value of the system with the adatom. The work-function value  $\Phi$  is calculated from the equation  $\Phi = E_{\text{vac}} - E_{\text{fermi}}$ , in which  $E_{\text{vac}}$  is the vacuum energy and  $E_{\text{fermi}}$  represents the Fermi energy of the system. The vacuum energy is estimated by averaging the electrostatic potential over the middle plane of the vacuum layers.

In Table 1, the fcc hollow sites are the highest in adsorption energy whereas the hcp hollow sites are only  $0.007 \text{ eV}$  lower in energy. The small difference in the adsorption energy indicates that the energetic properties of the Ag(111) surface with the chlorine atom at the hcp and fcc sites are similar. Little theoretical work on the examination of the chemisorption of chlorine on silver surfaces has been reported in the literature. One elaborate theoretical study has been done by Harrison.<sup>26</sup> In their work, the value of AE (about  $3.04 \text{ eV}$ ) with the chlorine atom adsorbed at the fcc hollow site approaches our calculation of  $3.12 \text{ eV}$ . In Table 1, we have found that all of the values of the work function increase at the various adsorption sites after the adsorption of the chlorine atom, which indicates that part of the electronic density has transferred from the silver atoms to the chlorine atom. We also found that the difference of  $\Delta\Phi$  is small between the fcc and hcp hollow sites, with the latter being slightly smaller. This also demonstrates that the silver surfaces with chlorine atoms at the fcc and hcp hollow sites have very similar electronic character. Therefore, we can conclude that the chlorine atom may be adsorbed at the fcc and hcp hollow sites on the Ag(111) surface with almost the same probability.

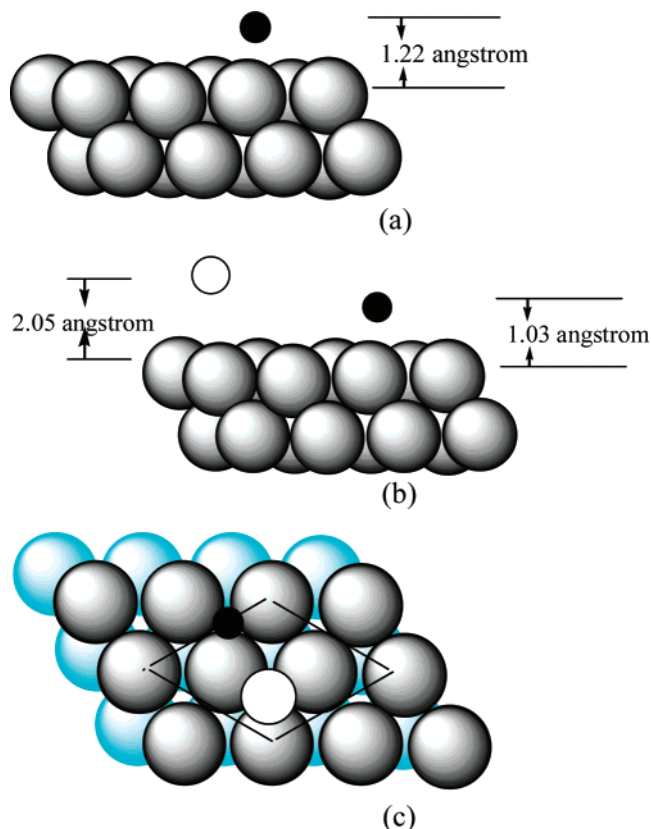
**TABLE 2: Structural and Energetic Properties of the O/Ag(111) Surface Cell**

	clean	Fcc	Hcp	Top	NDDO/ MC <sup>46</sup>	subsurface
$\Delta_{12}^a$ (%)	-0.25	-1.41	-0.16	1.23	fixed	17.76
$\Delta_{23}^a$ (%)	-0.24	-0.29	-0.16	0.27	fixed	-0.38
$\Delta_{34}^a$ (%)	0.11	-0.46	-0.12	0.03	fixed	-0.41
$\Delta_{45}^a$ (%)	-0.14	-0.71	-0.40	-0.40	fixed	-0.79
$d_{O-surface}^b$ (Å)		1.22	1.30	1.75	1.31	-1.42
$d_{O-Ag}^c$ (Å)		2.15	2.18	1.97	2.11	2.32
$d_{Ag-Ag}^d$ (Å)		2.96	2.91	2.96	2.87	
AE <sup>e</sup> (eV)		3.794	3.681	2.348		3.044
$\Phi^f$ (eV)	4.626	6.05	6.75	6.73		4.85
$\Delta\Phi^g$ (eV)		1.43	2.12	2.10		0.23

<sup>a</sup>  $\Delta_{ij}$ : interlayer relaxation. <sup>b</sup>  $d_{O-surface}$ : distance between an O atom and the top layer of silver. <sup>c</sup>  $d_{O-Ag}$ : distance between an O atom and the nearest-neighbor silver atom. <sup>d</sup>  $d_{Ag-Ag}$ : Ag–Ag distance on the top layer. <sup>e</sup> AE: adsorption energy. <sup>f</sup>  $\Phi$ : work function value. <sup>g</sup>  $\Delta\Phi$ : change in the work function.

The changes in the surface structure brought about by the chlorine atom adsorption are also shown in Table 1. On the basis of the values of  $\Delta_{12}$ , ...,  $\Delta_{45}$ , we find that the relaxation of the surface atoms is small after the chlorine atom adsorption. This may be due to the dense packing of the Ag(111) surface atoms. We have also found that at the hcp hollow sites  $d_{Cl-surf}$  is almost the same as the value at the fcc hollow sites. This means that at the hcp hollow sites the interaction of the chlorine atom with the second-layer silver atoms is very weak. For both of the hollow sites, the distance from the chlorine atom to the silver surface is much smaller than that at the bridge and top sites. However, the values of the Cl–Ag bond lengths that we calculated are 2.64 Å for the fcc and hcp hollow sites, 2.56 Å for the bridge site, and 2.39 Å for the top site. Shen et al. have determined the Ag–Cl bond length to be 2.73 Å by using cluster-model  $Ag_7(3,3,1)$ .<sup>27</sup> Harrison et al. have studied the adsorption of chlorine on the Ag(111) surface with full potential-gradient-corrected density functional calculations,<sup>26</sup> and they obtained a value of  $d_{Ag-Cl} = 2.62$  Å according to the most stable fcc hollow adsorption site. In experiments, Lambel et al. gave a Ag–Cl bond length of 2.70 Å at a coverage of  $1/3$ ,<sup>16</sup> but Shard et al. observed a value of 2.48 Å also for a nominal coverage of  $1/3$ .<sup>19</sup> Therefore, the experimental results need to be reinterpreted. According to our calculations for the simulation study of this system, our results support Lambel's work, which gave a Ag–Cl bond length of 2.70 Å, rather than Shard's work, which gave a value of 2.48 Å.

**3.3. Chemisorption of Oxygen Atoms on the Clean Silver Surface.** The chemisorption properties of oxygen on the silver surface are very important to the adsorption and epoxidation of ethylene on the silver surface; therefore, we intensively investigated the chemisorption of oxygen at different adsorption sites on the Ag(111) surface. In our calculations, the  $\sqrt{3} \times \sqrt{3}R30^\circ$  surface unit cell is also used, and the coverage of oxygen atoms is  $1/3$  ML. The adsorption energy is defined by the equation  $AE = E_{O-substrate} - E_{substrate} - E_O$ , where  $E_{O-substrate}$  and  $E_{substrate}$  are the total energy of the system with or without adsorbate, respectively.  $E_O$  represents the energy of a free O atom. The calculated chemisorption energies and equilibrium distance of an adsorbed oxygen atom from the surface are listed in Table 2. From our calculated results, we find that among our considered adsorption sites the fcc hollow sites are the most preferred adsorption sites and the hcp hollow sites are the next most preferred. The adsorption energies of oxygen at fcc and hcp sites are 3.79 and 3.68 eV, respectively. Comparing our calculated results with that of experiment<sup>2</sup> (about 3.68 eV), we



**Figure 2.** Schematic representation of atomic oxygen adsorption on the Ag(111) surface. (a) O/Ag(111) surface (side view). (b) O/Cl/Ag(111) surface (side view). (c) O/Cl/Ag(111) surface (top view). The black balls represent oxygen atoms; the white balls represent chlorine atoms; and the others represent silver atoms.

find that our calculated results are very consistent with the experimental value. From Table 2, we find that adsorption at the top sites is the most unstable. When the oxygen atom is placed at bridge sites on the silver surface as the initial geometry, we find that it always moves to the fcc hollow sites after the structure optimization, so the bridge site is not an energetically stable site for the oxygen atom on the Ag(111) surface.

The geometry of the Ag(111) surface with the oxygen atom adsorbed at the fcc hollow site is shown in Figure 2a. It can be seen in Table 2 that our calculations for the position of the adsorbed oxygen agree with those of other theoretical studies. The calculated O–Ag bond length is 2.15 Å, which agrees with the experimental value of  $2.05 \pm 0.03$  Å.<sup>40</sup> The first Ag–Ag interlayer spacing is found to be contracted by 1.41% with respect to the bulk value, but for the clean silver surface, the contraction of the top interlayer spacing is 0.25% (see Table 1) with respect to the bulk value. Therefore, the adsorption of oxygen increases the contraction of the top interlayer spacing. There are no experimental data for the interlayer distance of the oxygen adsorbed on the silver surface in the literature. Therefore, we suggest that additional experiments should be done to determine the interlayer distances of the silver surface and the adsorption position of the oxygen atom for a confirmation of the theoretical calculations.

**3.4. Oxygen Adsorption on the Chlorine-Modified Ag(111) Surface.** To investigate the effect of chlorine on oxygen adsorption over the Ag(111) surface, we have studied the oxygen adsorption on the chlorine-modified Ag(111) surface. The calculated equilibrium geometries and adsorption energies of oxygen adsorbed on the chlorine-modified Ag(111) surface are presented in Table 3. In the geometry optimization, we have



**TABLE 3: Structural and Energetic Properties of the O/Cl/Ag(111) Surface Cell**

	fcc	hcp	subsurface
$\Delta_{12}^a$ (%)	-0.93	-0.72	13.50
$\Delta_{23}$ (%)	-0.09	-0.31	-0.531
$\Delta_{34}$ (%)	-0.01	-0.13	-0.369
$\Delta_{45}$ (%)	-0.65	-0.01	-0.742
$d_{\text{Cl-surf}}^b$ (Å)	2.056	2.057	2.043
$d_{\text{O-surf}}^c$ (Å)	1.033	1.404	-1.223
AE <sup>d</sup> (eV)	5.618	5.178	6.269

<sup>a</sup>  $\Delta_{ij}$ : interlayer relaxation. <sup>b</sup>  $d_{\text{Cl-surf}}$ : distance between a Cl atom and the top layer of silver. <sup>c</sup>  $d_{\text{O-surf}}$ : distance between an O atom and the top layer of silver. <sup>d</sup> AE: adsorption energy.

considered two adsorption sites for the chemisorption of oxygen, which are fcc and hcp hollow sites, and the preadsorbed chlorine is located at the fcc hollow site. The configuration of oxygen adsorbed on the chlorine-modified Ag(111) surface is shown in Figure 2b and c.

In comparing Table 3 with Table 2, it can be seen that the adsorption energy of oxygen on the Cl-modified Ag(111) surface is greatly enhanced for both at the fcc and hcp hollow sites. The adsorption energy of oxygen at the fcc hollow site is 5.618 eV, which is higher than that at the hcp hollow site (5.178 eV). This indicates that the fcc hollow site is also the more energetically stable adsorption site for the oxygen atom on the Cl-modified Ag(111) surface. From Table 3, we can see that the distances between the oxygen and the first silver layer are 1.033 and 1.404 Å for the oxygen atom adsorbed at the fcc and hcp hollow sites, respectively. The distance of the adsorbed oxygen atom from the silver surface at the fcc hollow site is much smaller than that at the hcp hollow site, which indicates that oxygen atoms interact with the silver surface more strongly when they are adsorbed at the fcc hollow sites than when they are adsorbed at the hcp hollow sites. Furthermore, when we compare the results with the value of the oxygen atom adsorbed at the fcc hollow site on the clean silver surface, we find that the distance decreases by about 0.2 Å, which means that the oxygen atom can be adsorbed more stably on the Cl-modified silver surface. According to these results, we can conclude that the fcc hollow site is the more stable adsorption site for the chemisorption of oxygen on the Ag(111) surface. In addition, the great increase in the adsorption energy of the oxygen atom adsorbed on the chlorine-modified silver surface compared with that on the clean silver surface confirms that the existence of chlorine can promote the adsorption of oxygen on the silver surface. However, it should be noticed that the more preferred adsorption site for the oxygen on the Cl-modified Ag(111) surface is the fcc hollow site, which is also the more stable adsorption site for chlorine adsorbed on the Ag(111) surface. This means that the preadsorbed chlorine atoms on the surface will take up some stable adsorption sites for the oxygen atoms. Furthermore, there is a higher activation energy for the surface migration of chlorine compared to that of oxygen,<sup>9</sup> so the adsorption of oxygen will be reduced. Another result is that oxygen atoms may move to or directly adsorb on other less stable adsorption sites such as the top sites etc. on silver surface in the presence of chlorine atoms. It has been shown that it is the weakly adsorbed oxygen that yields the epoxide in the process of ethylene epoxidation,<sup>22,43</sup> and very recently, Hu et al. have found theoretically that there is one crucial event in oxidation reactions on transition-metal surfaces.<sup>48,49</sup> Namely, O atoms must be activated from the most stable hollow site to the bridge site. In their work, they investigate the manner of the O atom binding to metal surfaces and find that the O 2p

orbitals in the 3-fold hollow site are saturated. Consequently, the O atom is reluctant to bond with another species when it is on the hollow site. Their calculations can be used to explain the promotion effects of chlorine on the epoxidation of ethylene: the preadsorbed chlorine atoms occupy the most stable hollow site for the oxygen adsorption, so oxygen has to be adsorbed at other less stable sites (e.g., the bridge or top sites). However, oxygen atoms on these sites are more active than those on the hollow site in oxidation reactions. For the ethylene epoxidation process, the reactivity will be improved. In summary, according to our calculations combined with previous experimental observations and Hu's theoretical work, the effect of chlorine can be explained as suppressing the formation of strongly adsorbed atomic oxygen that is inactive in the epoxidation of ethylene. These promotion effects of chlorine on the adsorption of oxygen are considered to be the reason that the chlorine atom is one of the best modifiers in this significant industrial reaction.

**3.5. Diffusion of Oxygen Atoms.** Many experiments<sup>22,41-43</sup> show that subsurface oxygen may play an important role in catalytic oxidation processes. Lambert et al. have observed ethylene oxide production from  $\text{C}_2\text{H}_4 + \text{O}_2$  via a single-crystal Ag(111) surface under highly controlled conditions.<sup>42</sup> They found that chemisorbed atomic oxygen and the presence of subsurface oxygen are necessary and sufficient conditions for the catalytic epoxidation of  $\text{C}_2\text{H}_4$  by silver. van Santen et al. also found from their experiments<sup>43</sup> that subsurface oxygen atoms become incorporated in the epoxide upon exchange with surface-adsorbed oxygen atoms. van den Hoek et al. have found that the presence of subsurface oxygen reduces the bond energy between silver and adsorbed oxygen and converts the repulsive interaction between adsorbed oxygen and (gas-phase) ethylene into an attractive interaction,<sup>15</sup> thus making the epoxidation reaction possible. This conclusion was obtained from the electronic structure calculations of the chemisorption of atomic oxygen on the silver surface and on the subsequent reaction of this chemisorbed oxygen with ethylene. The fact that subsurface oxygen is necessary for epoxide formation is one of the most important characteristics of the process of ethylene epoxidation, but the mechanism is still poorly understood. We know that the Ag(111) surface is more active for the epoxidation of ethylene than other surfaces such as (110) and (100). But it is also well known that the Ag(111) surface is the most densely packed surface. Can the chemisorbed oxygen atom diffuse into bulk silver to become subsurface oxygen from this compact surface? What role does chlorine play in this process? To clarify these questions, we considered the diffusion process of the surface oxygen atom and the adsorption system of the subsurface oxygen. The considered diffusion pathway is that in which the oxygen atom adsorbed at the fcc hollow site enters the subsurface. The results calculated here are also listed in Table 2. We have found that on the clean silver surface the adsorption energy of the subsurface oxygen is 3.04 eV, which is lower than that of the oxygen adsorbed on the surface at the fcc and hcp sites. From the structural parameters listed in Table 2, we have also found that the distance between the top layer and the second layer of silver atoms increases enormously by 17.76% when the oxygen atom diffused into bulk silver on the clean Ag(111) surface. The subsurface oxygen atom is 1.42 Å below the top layer of the silver surface. In Table 2, we find that the work function  $\Phi$  increases to 4.85 eV when the oxygen atom diffused into bulk Ag compared with 4.63 eV for the clean surface. Above all, we conclude that the configurable properties and the electronic character of the Ag(111) surface have undergone

**TABLE 4: Calculated Structural Parameters of Ag Surfaces with Subsurface O**

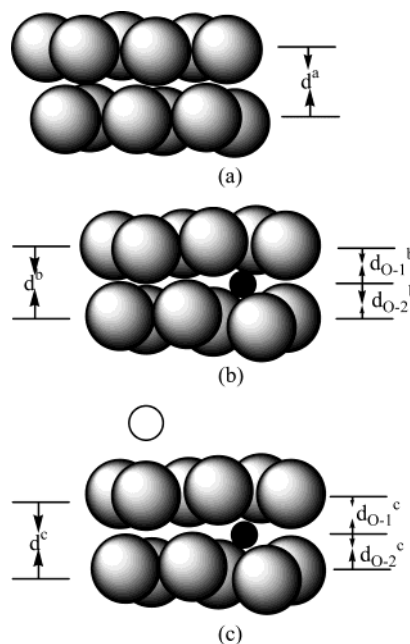
	clean Ag surface	O/Ag surface	O/Cl/Ag surface
$d^a$ (Å)	2.40	2.84	2.73
$\Delta d^b$ (%)	-0.250	17.76	13.54
$d_1^c$ (Å)		1.42	1.22
$d_2^d$ (Å)		1.42	1.51

<sup>a</sup>  $d$ : distance between the top layer and the second layer of the silver surface. <sup>b</sup>  $\Delta d$ : interlayer relaxation. <sup>c</sup>  $d_1$ : distance between the subsurface O and the top layer of the silver surface. <sup>d</sup>  $d_2$ : distance between the subsurface O and the second layer of the silver surface.

enormous changes when the oxygen atom diffuses into bulk silver to become subsurface oxygen. Therefore, the diffusion of the surface oxygen atom into bulk Ag is difficult because the oxygen atom must overcome a tremendous spatial resistance in this process.

The oxygen atom hardly diffuses into bulk silver to become subsurface oxygen from the Ag(111) surface. How can we explain the experimental fact that subsurface oxygen may play an important role in the process of ethylene epoxidation? Wu et al. have found that coadsorbed chlorine can enhance the transport of chemisorbed oxygen on the Ag(111) surface from the surface to the subsurface.<sup>23</sup> They suggested that the chlorine atom acts through a structural effect in this process rather than an electronic one. To validate this experimental finding, we have studied the effect of chlorine on the diffusion of the surface chemisorbed oxygen atom on the Ag(111) surface.

The calculated results are listed in Table 3. It can be seen in Table 3 that the adsorption energy for the subsurface oxygen increases from 3.04 eV at a clean surface to 6.27 eV at the chlorine-modified Ag(111) surface. The great increase in the adsorption energy indicates that preadsorbed chlorine can enhance the transport of chemisorbed oxygen from the Cl-modified Ag(111) surface to bulk silver more than that from the clean Ag(111) surface. For the subsurface oxygen, the calculated structural parameters are listed in Table 4, and the geometry of the Ag(111) surface with a subsurface oxygen atom is displayed in Figure 3. In Table 4,  $d$  means the distance between the top layer and the second layer of the clean or modified silver surface.  $\Delta d$  represents the change in the interlayer spacing between the upper two layers relative to the bulklike value.  $d_1$  equals the distance between the top silver layer and the subsurface oxygen atom layer when the subsurface oxygen atoms exist whereas  $d_2$  represents the distance between the subsurface oxygen atom layer and the second layer of the silver surface. From the calculated results, it can be seen that the subsurface oxygen is 1.42 Å below the clean silver surface and 1.22 Å below the chlorine-modified silver surface. The distance between the top two silver layers increases from 2.40 to 2.84 Å after the oxygen atom has diffused into the subsurface from the clean Ag surface. However, on the Cl-modified silver surface, the distance between the top two layers is 2.73 Å, which is smaller than the value over the clean surface with the subsurface oxygen. We know that the accretion of the distance is due to the repulsion between the oxygen atom and the nearest-neighbor silver atoms, so from the calculated results of oxygen adsorption on the clean and chlorine-modified silver surfaces, we can deduce that there may exist much weaker repulsion in the process of the oxygen atom diffusing into the subsurface from the chlorine-modified silver surface than from the clean silver surface. To obtain thorough evidence for the promotion effects of the diffusion of the surface oxygen atom caused by the adsorbed chlorine over the silver surface, we explored the barriers of the penetration of the oxygen atom to form subsurface



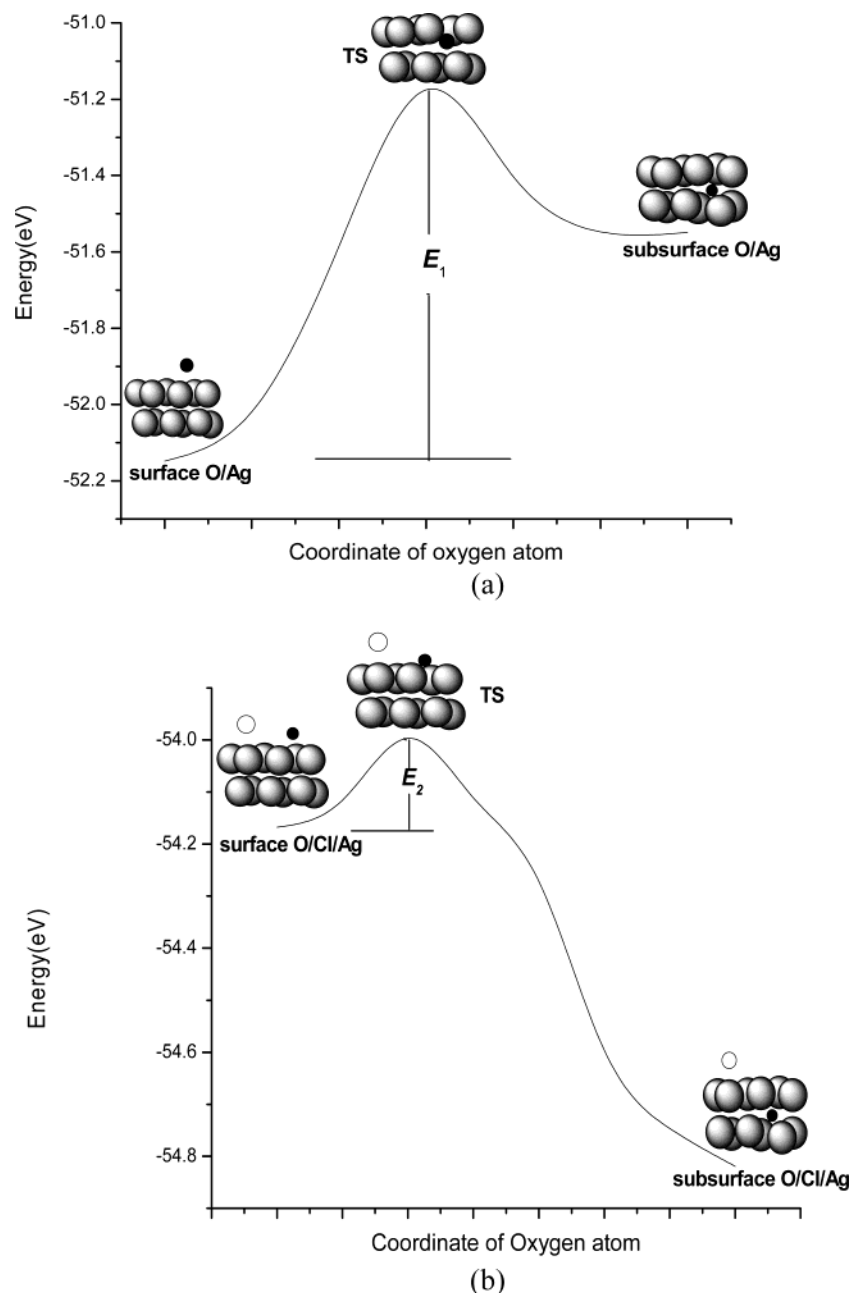
**Figure 3.** Illustrations of the Ag(111) surface with or without the subsurface oxygen atom. (a) Clean Ag(111) surface. (b) O(subsurface)/Ag(111) surface. (c) O(subsurface)/Cl/Ag(111) surface. The black balls represent oxygen atoms; the white balls represent chlorine atoms; and the others represent silver atoms.

**TABLE 5: Main Geometrical Parameters of the TSs Identified for the Diffusion of Oxygen Atoms on Clean and Preadsorbed Chlorine Ag(111) Surfaces and the Barriers Associated with These Two TSs**

	barrier (eV)	$d_{O-surface}$ (Å)	$d_{O-subsurface}$ (Å)	$d_{O-Ag}$ (Å)
TS <sup>a</sup>	0.973	-0.139	2.282	2.092
TS <sup>b</sup>	0.171	0.378	2.836	2.066

<sup>a</sup> On a clean silver surface. <sup>b</sup> On a chlorine-modified silver surface.

oxygen on the clean and the chlorine-modified Ag(111) surfaces, respectively. In our calculation, both the top layer of silver and the adsorbate were relaxed. The distance between the oxygen atom and the silver surface was fixed, and the rest of the degrees of freedom were optimized according to the forces based on the Hellmann–Feynman theorem. This procedure was repeated at different  $d_{O-silver\ surface}$  values until the atomic oxygen entered the bulk Ag and the stable configuration was reached. For the simulation of the diffusion process of the atomic oxygen on the clean and the chlorine-modified Ag(111) surfaces, two distinct transition states have been identified, as shown in Figure 4. The main structural parameters of these TSs are summarized in Table 5. It can be seen that these two TSs are very different from each other. On the clean silver surface, the oxygen atom of TS is below the first layer of silver with a distance of 0.139 Å. On the chlorine-modified silver surface, the oxygen atom is 0.378 Å above the silver surface. The calculated barriers associated with TSs on the clean and the Cl-preadsorbed silver surfaces were found to be 0.97 and 0.17 eV, respectively (Figure 4). Obviously, by overcoming a small barrier (about 0.17 eV), the adsorbed oxygen atom on the chlorine-modified silver surface diffuses into bulk Ag to become subsurface oxygen; meanwhile, the total energy of the system is decreased. However, on the clean silver surface, the barrier is about 1 eV, which is much higher than the barrier on the chlorine-modified silver surface, which indicates that the diffusion of the oxygen atom is much easier on the chlorine-modified Ag(111) surface than on the clean Ag(111) surface. We conceive that the



**Figure 4.** Energy diagram for the diffusion of the oxygen atom on clean (a) and chlorine-modified (b) Ag(111) surfaces. Transition-state structures are shown by the slab model. The black, white, and gray balls represent oxygen atoms, chlorine atoms, and silver atoms, respectively. Energy barriers:  $E_1 = 0.973$  eV,  $E_2 = 0.171$  eV.

promotion effect of Cl might be geometric (e.g., the adsorption of Cl increases the lateral relaxations of the Ag(111) surface, which can make the oxygen atom diffusing into bulk Ag much easier). In another paper, we will thoroughly discuss the penetration of the oxygen atom on the silver surface.

Hence, according to our theoretical study, we show that the adsorption of chlorine on the Ag(111) surface is advantageous to the diffusion of the surface oxygen atom. This is another reason that chlorine is one of the best modifiers in the process of ethylene epoxidation.

#### 4. Conclusions

The adsorption of oxygen on the clean and Cl-modified Ag(111) surfaces has been studied by using the first-principles local density functional method. We find that the fcc hollow sites are the most stable adsorption sites for both chlorine and oxygen atoms. For the adsorption of chlorine on the Ag(111)

surface, the calculated adsorption energy is 3.12 eV. The Ag–Cl bond length is predicted to be 2.64 Å, which confirms that the experimental result of 2.70 Å is more credible than another experimental value of 2.48 Å. From our calculated results of the adsorption of the oxygen atom on the clean and chlorine-modified Ag(111) surfaces, it can be seen that the presence of chlorine on the surface can enhance the adsorption energy of oxygen. However, adsorbed chlorine atoms could occupy some stable adsorption sites for oxygen atom, which would reduce the adsorption of oxygen or lead to the oxygen atoms being adsorbed on the less stable adsorption sites. According to experimental results and other theoretical studies, this is an advantage for the formation of epoxide in the partial oxidation of ethylene and is the reason that chlorine is one of the best modifiers in this important industrial reaction. We have also discussed the effects of chlorine on the diffusion of the oxygen atom from the silver surface into the bulk. From the calculated

adsorption energy, structural parameters, and barriers in the process of diffusion, we find that preadsorbed chlorine can promote the transport of the surface oxygen atom into bulk Ag to become subsurface oxygen distinctly. This may be considered to be another important reason that the chlorine atom is the best modifier in the reaction of ethylene epoxidation.

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## References and Notes

- (1) Kitson, M.; Lambert, R. M. *Surf. Sci.* **1981**, *109*, 60.
- (2) Campbell, C. T. *Surf. Sci.* **1983**, *137*, 43.
- (3) Nakatsuji, H.; Hu, Z. M. *Surf. Sci.* **1997**, *387*, 328.
- (4) Wang, J. H.; Dai, W. L.; Deng, J. F. *Appl. Surf. Sci.* **1998**, *126*, 148.
- (5) Buatier de Mongeot, F.; Valbusa, U.; Rocca, M. *Surf. Sci.* **1995**, *339*, 291.
- (6) Baird, J. K.; King, T. R.; Stein, C. J. *Phys. Chem. Solids* **1999**, *60*, 891.
- (7) Bukhtiyarov, V. I.; Kaichev, V. V. *J. Mol. Catal. A: Chem.* **2000**, *158*, 167.
- (8) Salazar, M. R.; Saravanan, C.; Kress, J. D.; Redondo, A. *Surf. Sci.* **2000**, *449*, 75.
- (9) Kilty, P. A.; Sachtler, W. M. H. *Catal. Rev. Sci. Eng.* **1974**, *10*, 1.
- (10) Campbell, C. T. *J. Catal.* **1986**, *99*, 28.
- (11) Worbs, H. Dissertation, Technischen Hochschule Breslau, 1942.
- (12) Ilty, P. A.; Rol, N. C.; Sachtler, W. M. H. In *Proceedings of the 5th International Congress on Catalysis*; Hightower, J. W., Ed.; North-Holland: Amsterdam, 1973; p 929.
- (13) Jorgensen, K. A.; Hoffmann, R. J. *Phys. Chem.* **1990**, *94*, 3046.
- (14) Avdeev, V. I.; Boronin, A. I.; Koscheev, S. V. *J. Mol. Catal. A: Chem.* **2000**, *154*, 257.
- (15) Van den Hoek, P. J.; Baerends, E. J.; van Santen, R. A. *J. Phys. Chem.* **1989**, *93*, 6469.
- (16) Lamble, G. M.; Brooks, R. S.; Ferrer, S.; King, D. A.; Norman, D. *Phys. Rev. B* **1986**, *34*, 2975.
- (17) Wu, K.; Wang, D. Z.; Deng, J. Z.; Wei, X. M.; Cao, Y. M.; Zei, M. S.; Zhai, R. S.; Guo, X. X. *Surf. Sci.* **1992**, *264*, 249.
- (18) Andryushechkin, B. V.; Eltsov, K. N.; Shevlyuga, V. M.; Yurov, V. Yu. *Surf. Sci.* **1998**, *407*, L633.
- (19) Shard, A. G.; Ghanak, V. R. *J. Phys. Chem. B* **2000**, *104*, 2743.
- (20) Staicu-Casagrande, E. M.; Lacombe, S.; Guillemot, L.; Esaulov, V. A.; Pasquali, L.; Nannarone, S.; Canepa, M. *Surf. Sci.* **2001**, *480*, L411.
- (21) Mukoid, H. C.; Badyal, J. P. S.; Lambert, R. M. *Surf. Sci.* **1989**, *219*, L615.
- (22) Van Santen, R. A.; Kuipers, H. P. C. E. *Adv. Catal.* **1987**, *35*, 265.
- (23) Wu, K.; Wang, D. Z.; Wei, X. M.; Cao, Y. M.; Guo, X. X. *J. Catal.* **1993**, *140*, 370–383.
- (24) Wu, K.; Wei, X. M.; Cao, Y. M.; Wang, D. Z.; Guo, X. X. *Catal. Lett.* **1994**, *26*, 109.
- (25) Tan, S. A.; Grant, R. B.; Lambert, R. M. *J. Catal.* **1986**, *100*, 383.
- (26) Doll, K.; Harrison, N. M. *Phys. Rev. B* **2001**, *63*, 16540.
- (27) Shen, B. R.; Fang, Z. G.; Fan, K. N. *Surf. Sci.* **2000**, *459*, 206.
- (28) Kramar, T.; Vogtenhuber, D.; Podlucky, R.; Neckel, A. *Electrochim. Acta* **1995**, *40*, 43.
- (29) Wang, Y.; Sun, Q.; Fan, K. N. *Chem. Phys. Lett.* **2001**, *334*, 411–418.
- (30) Walter, Eric J.; Rappe, A. M. *Surf. Sci.* **1999**, *427–428*, 11.
- (31) Vanderbilt, D. *Phys. Rev. B* **1990**, *41*, 7892.
- (32) Kresse, G.; Hafner, J. *J. Phys.: Condens. Matter* **1994**, *6*, 8245.
- (33) Wood, D. M.; Zunger, A. *J. Phys. A* **1985**, *18*, 1343.
- (34) Pulay, P. *Chem. Phys. Lett.* **1980**, *73*, 393.
- (35) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. *Phys. Rev. B* **1992**, *46*, 6671.
- (36) Wang, Y.; Wang, W. N.; Fan, K. N.; Deng, J. F. *Surf. Sci.* **2001**, *490*, 125.
- (37) Chelvayohan, M.; Mee, C. H. B. *J. Phys. C: Solid State Phys.* **1982**, *15*, 2305.
- (38) Kuk, Y.; Feldman, L. C. *Phys. Rev. B* **1984**, *30*, 5811.
- (39) Soria, F.; Sacedon, J. L.; Echenigire, P. M.; Titherington, D. *Surf. Sci.* **1977**, *68*, 448.
- (40) Pushmann, A.; Haase, J. *Surf. Sci.* **1984**, *144*, 559. Becker, L.; Aminpirooz, S.; Schmalz, A.; Hillert, B.; Pedio, M.; Haase, J. *Phys. Rev. B* **1991**, *44*, 13655.
- (41) Backx, C.; Moolhuysen, J.; Green, P.; Van Santen, R. A. *J. Catal.* **1981**, *72*, 364.
- (42) Grant, R. B.; Lambert, R. M. *J. Chem. Soc., Chem. Commun.* **1983**, 662.
- (43) van Santen, R. A.; de Groot, C. P. M. *J. Catal.* **1986**, *98*, 530.
- (44) Mikami, J.; Satoh, S.; Kabayshi, H. *J. Catal.* **1970**, *18*, 265.
- (45) Foils, S. M.; Baskes, M. J.; Daw, M. S. *Phys. Rev. B* **1986**, *33*, 7983.
- (46) Culberston, R. J.; Feldman, L. C.; Silverman, P. J.; Boehm, H. *Phys. Rev. Lett.* **1981**, *47*, 657.
- (47) Milov, M. A.; Zilberberg, I. L.; Ruzankin, S. Ph. *J. Mol. Catal. A: Chem.* **2000**, *158*, 309.
- (48) Zhang, C. J.; Hu, P. *J. Am. Chem. Soc.* **2000**, *122*, 2134.
- (49) Zhang, C. J.; Hu, P. *J. Am. Chem. Soc.* **2001**, *123*, 1166.