Oxygen adsorption on the Ag(111) surface: a quantum chemical study by the NDDO/MC method

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Abstract

The forms of the atomic oxygen adsorbed on the Ag(111) face were investigated using the semi-empirical NDDO/MC method within the modified cluster approximation. Two oxygen positions — surface (over the octahedral hollow) and the subsurface (in the hollow) one — between the first two layers of (111) face were studied. A cross-section of the potential energy for the oxygen penetration into subsurface positions has been computed. A new approach was applied to take into account the lattice relaxation caused by the interaction with adsorbate. The doubly-excited-CI-like correlation corrections to the diffusion and desorption barriers were estimated. The barrier of the oxygen atom diffusion through the surface was shown to be substantially lower than that of the desorption. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The molecular mechanism of the ethylene epoxidation using the silver catalyst is still unclear despite the numerous experimental and theoretical investigations. It is widely accepted that the knowledge of the high-temperature 'epoxidating' oxygen species structure is the key point in understanding of this mechanism. There is a number of reasons which make it difficult to assign such species experimentally. One of them is the dissolution of oxygen in the bulk. This process seems to be responsible for multiple oxygen 1s energies detected by XPS [1] at elevated temperatures. The major experimental problem is that the O1s energy could not be undoubtedly assigned to specific oxygen form on silver. There is a great dispute even on whether the high-temperature epoxidating oxygen is molecular one. The 'molecular' challenging hypothesis has been supported in the recent works of Boronin et al. [2].

In this work we have studied the atomic oxygen adsorption on Ag(111) making a special accent on penetration of oxygen through the surface into some subsurface positions. To our knowledge, despite that the dissolution of oxygen into the silver bulk is a well-known effect, no direct experimental or theoretical estimation of barrier height has been done yet. To avoid some artifacts caused by frozen cluster approximation routinely used by quantum chemists for such type of systems, we have applied some

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new approaches which allow (1) to take into account the metallicity of the system and (2) to reduce the inherent stress on the 'active' atoms of cluster that originates from artificial boundary conditions. This technique was developed on the base of semi-empirical NDDO/MC method [3–5].

Atomic oxygen adsorption on the Ag(111) surface was calculated [5] to be three-fold one. There are two types of such adsorption positions. The first one is that above an octahedral hollow between the first and second layer. The second position is the face of a tetrahedron. In our previous work, we showed that the octahedral hollow position is the most energetically stable [5]. In this paper, we calculated such surface position along with subsurface atomic oxygen positions located on the C_3 symmetry axis of octahedron. The energy barrier of penetration through the first and second layer was also estimated.

2. Computational details

All calculations have been done in the cluster approximation using the NDDO/MC semi-empirical Hamiltonian [3]. To take into account the metallicity of silver surface, we used an effective procedure that allows to keep the Fermi level of cluster equal to predefined value independently on the adsorption. Such procedure has been developed on base of NDDO/MC program [4,5] and could be applied within the assumption of very low adsorbate coverage.

Four-layer cluster (12/12/7/3) was chosen to model the Ag(111) surface (Fig. 1a). This cluster possesses of the 3rd-order rotation axis and thus all three atoms of the ''active'' triangle on the top 12-atom layer are equivalent. This allows one to consider the oxygen adsorption on the octahedral hollow between two first layers.

A special attention was paid to take into account the silver lattice relaxation caused by the oxygen adsorption. Any attempt of direct geometry optimization would lead to the artificially distorted cluster. This is a consequence of inherent high tension in cluster structure caused by non-periodical boundary conditions. To overcome this problem, we applied a new approach that can be called as ''shrinkage'' of cluster boundary method [6]. Since the boundary atoms of the cluster are not the subject of adsorption simulation, then one could change
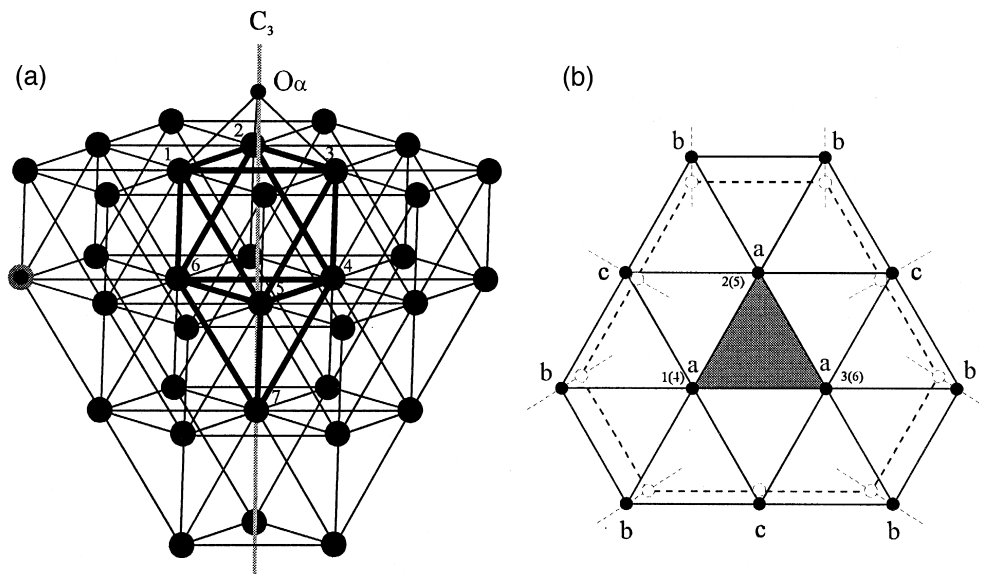

Fig. 1. (a) Ag$_{34}$ cluster with oxygen adsorbed in α-position; (b) scheme of cluster border treatment for first two layers.

their positions in order to remove a tension on the ''active'' site. For the cluster, we choose to model the Ag(111) surface, the scheme of the cluster boundary treatment is shown in Fig. 1b. We have minimized the gradient norm for the **a** atoms of top and second layers using coordinates of the **b** and **c** atoms as variables and freezing coordinates of the **a** atoms (Fig. 1b). This should be done for the cluster without adsorbate. Fortunately, new border for the top and second layers does not differ much from the initial one. It becomes a little shrunken and the corresponding Ag–Ag distances are decreased by about 0.1 Å. Despite that the normal forces remain quite high for the **a** atoms, their relaxation along the surface seems to be the most important for the determination of the barrier for oxygen penetration into subsurface positions.

3. Results and discussion

Using the techniques described above, the potential energy profile for penetration of atomic oxygen into the silver lattice has been calculated. The procedure of calculation consisted of the following steps.

The first one is minimization of the tangential tension at the **a** atoms (Fig. 1b) of top and second layers using the shrinkage of boundary. Such an optimization of the cluster boundary is not accompanied by the equalization of HOMO level since the latter does not affect the geometry and the binding energy of cluster without adsorbate.

The second step is calculation of the potential energy of oxygen atom along the 3rd-order rotation axis of cluster. All points along this line were obtained optimizing the positions of active silver atoms at the top and second layer in the respective planes. Oxygen–silver and other distances are given in Table 1 for minima and maxima of potential energy along the reaction coordinate. Corresponding curve of oxygen potential energy with respect to the oxygen position in cluster is given in Fig. 2. Zero oxygen coordinate is set to be that in the center of active silver triangle of the top layer. This position corresponds to a first barrier for penetration through the Ag(111) surface. As seen from Fig. 2, there are two stable adsorption positions above (the α surface position) and below (the β octahedral position) the top silver layer and one position below the second layer (the γ tetrahedral position). The β minimum appears to be lower in energy than the α one. The γ minimum is calculated to be highly unfavorable and lies above the desorption barrier. This seems to be related to a small room inside non-distorted tetrahedron — as seen from Table 1 in the tetrahedral hollow the O–Ag distances are about 0.1 Å less than those for the α and β positions.

The O–Ag distances calculated for the α and β adsorption positions are very close to the

Table 1
Surface and subsurface positions of oxygen on Ag(111)

Oxygen position	Oxygen coordinate[a] (Å)	O–Ag$_a$ distance (Å)	Ag$_a$–Ag$_a$ distance (Å)		Potential energy (kcal/mol)
			Top layer	Second layer	
Desorbed	10.000	10.138	2.882	2.883	0.0
α	1.306	2.109	2.869	2.852	-53.0 (-77.9)[b]
Barrier 1	0.292	1.884	3.224	2.921	-29.1 (-58.6)[b]
β	-1.052	2.045	3.038	2.930	-77.5
Barrier 2	-2.264	1.847	2.840	3.196	24.7
γ	-2.788	1.870	2.838	3.150	7.8

[a] Origin of coordinates corresponds to the plane of the top layer.
[b] Values in parentheses are calculated using DCIP method.
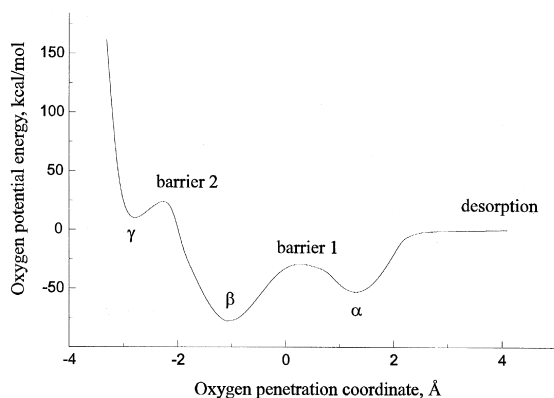
Fig. 2. Potential energy curve for oxygen atom penetration into the silver lattice along the 3rd-order rotation axis of cluster.

O–Ag distance of 2.063 Å obtained for Ag(110) in our previous paper [4] and to the SEXAFS data of 2.06–2.17 Å for Ag(110) surface [7].

The barrier between the α and β position is calculated to be 24.0 kcal/mol (if going from the surface position), whereas the calculated desorption barrier is 53.0 kcal/mol. The barrier of penetration through the second layer is much higher than that for first layer and lies above the desorption barrier.

The energy barrier for oxygen penetration through silver layer seems to be mostly determined by the Pauli repulsion between occupied 3d orbitals of silver atoms and oxygen p_π orbitals. Therefore, the height of the barrier may be reduced by taking into account the electron correlation. In order to estimate the effect of correlation, we have calculated the correlation correction using the doubly-excited-CI method. To simplify calculation we used the perturbative version of the method, in which all the non-diagonal matrix elements between the doubly excited configurations are neglected [8]. As shown in the table, oxygen potential energy drops down significantly after the correlation has been accounted. It appears that the relative energy of 19 kcal/mol for barrier 1 is just 5 kcal/mol less than that without correlation account. Nevertheless, such decrease of the penetration barrier seems to display physically evident effect of the electron correlation.

4. Conclusions

To summarize all, the following main points could be marked. Firstly, two new methods, namely equalization of HOMO energy to the Fermi level of pure metal surface and shrinkage of cluster boundary, were applied to obtain more reasonable energetics for the process of oxygen penetration into the silver lattice. In general, these new techniques could also be applied to other metallic systems. Secondly, as follows from our calculations, the barrier for oxygen penetration through the first layer of the Ag(111) surface appeared to be much lower than that of the desorption. Taking into account the correlation effects somewhat reduces this barrier and, at the same time, increases substantially the desorption barrier. This allows us to predict that at the elevated temperatures, atomic oxygen does not desorb from the surface but most likely diffuses into the silver bulk occupying octahedral hollows. Because of that, we suppose that subsurface β-oxygen plays an important (if not the key) role in the epoxidation reactions.

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