

Ab initio studies on the reaction of O₂ with Ba_n (n=2,5) clustersS. F. Li^{a)}

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Ab initio theoretical calculations have been performed to study the reaction of O₂ with Ba_n (n=2,5) clusters. Our results show that O₂ can easily chemisorb and dissociate on small Ba_n clusters and there is no obvious energy barrier in the process of the dissociation. The local magnetic moment contributed by oxygen must vanish during the intermediate states before the O₂ dissociation. Correspondingly, local magnetic moment only decreases from 2μ_B to about 1μ_B if O₂ molecularly adsorbs onto Ba₅ cluster. The electronic structure analysis indicates that the charge transfer from Ba_n cluster to O₂ as well as the orbital hybridization between the cluster and the oxygen molecule may play a key role in O₂ dissociation. © 2006 American Institute of Physics.
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I. INTRODUCTION

In the past decades, the adsorption of molecules on metal and semiconductor surfaces has been an active field of experimental and theoretical research.^{1–11} Among them, the adsorption of O₂ and the associated oxidization of surfaces may be one of the most important subjects of modern surface science.^{3–8,10,11} Owing to the large surface-volume ratio and the unique size effect, the atomic clusters provide the optimal environment to investigate the reaction of O₂ with metal in different local atom and electronic structures.^{12–23} The study of oxidation reaction, on one hand, can test the stability of these clusters^{12–17,21} in the presence of O₂, which is much important for the growth of quantum dots. On the other hand, it can shed light on the corresponding bulk surface adsorption, catalysis, corrosion, and oxidization reaction with cluster model approach.²²

To date, a few metal clusters have been studied in the presence of oxygen. Bulk gold is chemically inert; however, gold nanoparticles and gold clusters show high activity and can be used as catalysts.²³ Salisbury *et al.*¹³ and Mills *et al.*¹⁴

found that O₂ can bind strongly with some gold anion clusters with odd-number electrons, concluding that the charge transfer from the gold cluster to the O₂ plays a crucial role for the O–O activation. Hoshino *et al.*²⁰ studied the lowest energy reaction path for the oxidation of an Al₆ nanocluster with an O₂ molecule and found that the spin state of O₂ may play a key role in the reaction process for O₂ reacting with Al nanocluster.

For alkali-earth metal barium atom, the outermost electronic shell is occupied by two *s* electrons, which is very different from that of gold and aluminum atoms. The binding between the two atoms of Ba₂ molecule is weak van der Waals interaction. With the cluster size increasing, Ba_n clusters begin to display metal character²⁴ and present very different properties from that of general transition metals. As for the oxidization of barium clusters, Chen *et al.*²⁵ studied the geometrical and electronic configurations of Ba_mO_n clusters. Their results show that if the number *n* of oxygen atoms is much fewer than that of barium atoms, then the oxygen atoms will occupy the interstices of Ba_m clusters and Ba_mO_n keep almost the same geometries with that of the corresponding Ba_m clusters. When the number difference between the Ba and O atoms is reduced to four (*m*–*n*=4), the geometry

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of Ba_mO_n will transform from close-packed structure of Ba_m to cubiclike: at the same time, the electronic structure will change distinctly from that of the pure Ba_m clusters. Once the number of oxygen atoms is equal to that of the Ba atoms, Ba_mO_n will prefer to cubic symmetry and the electronic structure will evolve entirely to ionic character, which is in solid agreement with experimental results.²⁶ The structures of Ba_mO_n clusters have been clarified by the work of Chen *et al.*²⁵ however, the detailed oxidization process of Ba_n clusters is far from understood. Many fundamental questions are still open. For instance, how does the O_2 dissociate when interacting with Ba_n clusters? How does the charge transfer as well as the spin state change in the oxidization process? In this paper, we investigate the reaction of O_2 with Ba_2 molecule and Ba_5 cluster in detail by using *ab initio* calculations to provide valuable insight into the oxidization mechanism of Ba_n clusters.

The remainder of the paper is organized as follows. The methodology is described in Sec. II. The results and discussions are presented in Sec. III. The main conclusions are summarized in Sec. IV.

II. CALCULATION DETAILS

Our calculations are based on the density functional theory^{27,28} (DFT) with the generalized gradient approximations^{29,30} (GGA) for the exchange correlation functional, as implemented in the code of VASP.³¹ Spin-polarized calculations have been adopted after considering the spin-triplet ground states of both O_2 molecule and oxygen atom. The interaction of the valence electrons with the core is described with projected augmented wave (PAW) method,³² and the wave functions are expanded in a plane wave basis set with an energy cutoff of 400 eV. In our calculations, simple cubic supercells with the sizes of 15 and 17 Å are used for Ba_2 and Ba_5 clusters, respectively, to make the interaction between the periodic images negligible. As the supercells are large enough, only the Γ point is used in the summation of the Brillouin zone of the simulation cell.

To test the accuracy of the plane wave basis set and the PAW potential used in VASP code, we have calculated the interatomic distances of Ba_2 and O_2 molecules, which are 4.75 and 1.23 Å, in agreement with experimental results of 4.60 and 1.21 Å, respectively.^{26,33} The calculated lattice constant of Ba solid is 4.99 Å, which is also in close agreement with the experimental value of 5.02 Å.³⁴ The calculated binding energy of 6.27 eV for the spin-triplet O_2 is overestimated compared to the corresponding experimental result of 5.11 eV;³³ however, such overestimation of the binding energy will not make much effect on the adsorption energy for O_2 on Ba_n ($n=2,5$) clusters with different initial configurations.

The structures of the clusters are optimized by the conjugated gradient³⁵ (CG) method with an energy convergence up to 0.001 eV. The obtained structure of Ba_5 cluster has D_{3h} symmetry in spin-singlet state. In order to study how an oxygen molecule oxidizes the Ba cluster, we put one oxygen molecule on the cluster about 3.5 Å away, with which the interaction between oxygen molecule and the cluster is very

TABLE I. The calculated properties for products of O_2 reaction with Ba_2 and Ba_5 cluster. Adsorption energy is defined as $\Delta E = -(E[\text{Ba}_n\text{O}_2] - E[\text{Ba}_n] - E[\text{O}_2])$ (eV), where E is the total energy. $R_{\text{O-O}}$ (Å) is the distance between two O atoms in the products. $M(\text{tot}/\text{Bo}/\text{O})$ (μ_B) refers to the total magnetic moment and the local moment of Ba atom and O atom, respectively. $Q_{(\text{O})}$ is the number of electrons transferred to per oxygen atom obtained by VDD (Ref. 36) analysis.

		ΔE	$R_{\text{O-O}}$	$M(\text{tot}/\text{Ba}/\text{O})$	$Q_{(\text{O})}$
Ba ₂ O ₂		6.639	7.65	0.00/0.00/0.00	-0.80
Ba ₅ O ₂	(1)	2.053	1.36	0.00/0.87/-0.87	-0.38
	(2)	1.610	1.36	0.00/-0.87/0.87	-0.34
	(3)	2.963	1.47	0.00/1.00/-1.00	-0.30
	(4)	2.534	1.45	0.00/0.85/-0.85	-0.31
	(5)	4.590	1.46	0.00/0.00/0.00	-0.53
	(6)	4.309	1.45	0.00/0.00/0.00	-0.52
	(7)	10.991	3.10	2.00/2.00/0.00	-1.03
	(8)	11.349	3.20	2.00/2.00/0.00	-1.06
	(9)	10.939	3.11	0.00/0.00/0.00	-1.03
	(10)	10.574	2.81	0.00/0.00/0.00	-1.03

week, then we optimize the structure again to get the configuration of oxidized cluster. By taking a large number of initial adsorption sites and comparing the total energies of these optimized clusters, we can obtain the most stable state for the final reacted products. Here, we report ten different initial adsorption configurations and the corresponding final products for O_2 adsorption on Ba_5 cluster. For the reaction of O_2 with Ba_2 dimer, we only present the final product with the lowest energy.

III. RESULTS AND DISCUSSIONS

A. The reaction of O_2 with Ba_2

For the reaction of O_2 with Ba_2 dimer, the following reaction is obtained: $\text{Ba}_2 + \text{O}_2 \rightarrow \text{BaO} + \text{BaO}$, $\Delta E = 6.639$ eV, which is in good agreement with the experimental result.¹⁹ In this reaction process, O_2 is chemisorbed and dissociated onto Ba_2 molecule, and finally two BaO molecules are produced. We did not observe any energy barrier for dissociation of O_2 and oxidization of Ba in our calculations. In the final product, the Ba-O bond length is about 2.06 Å, which is almost equal to that of the isolated BaO molecule. This result implies that the interaction between the two BaO molecules is quite weak.

In the reaction, the Ba_2 dimer is easily dissociated into two Ba atoms when O_2 is approached, which is easily to be understood as the weak van der Waals binding in Ba_2 . Local electronic structure analysis has been made for the reaction products, and the obtained results are shown in Table I. One can get that the final product BaO is spin singlet, and the bonding of the BaO shows ionic character with about 0.8e transferred from the Ba atom, which is supported by Voronoi deformation density³⁶ (VDD) charges analysis performed by ADF.³⁷

B. The reaction of O_2 with Ba_5

1. Initial reaction configurations and final products structures

As to the reaction of O_2 with Ba_5 clusters, we find that the structures of Ba_5O_2 are dependent on the initial configu-

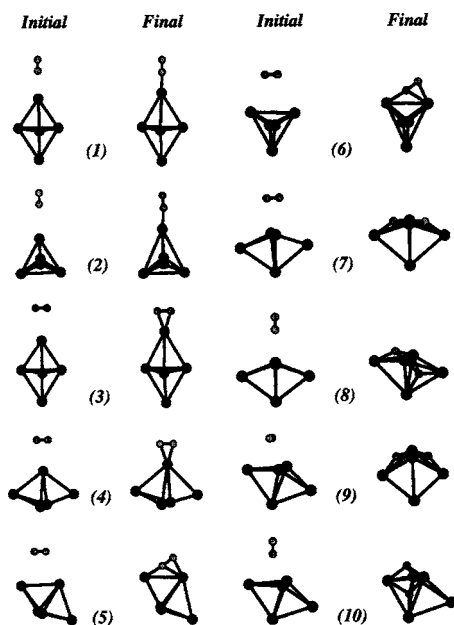


FIG. 1. Different atomic configurations for the initial reactants (initial) and the final stable products (final). The bigger black and smaller gray spheres denote Ba and O atoms, respectively.

rations. Ten final structures with different initial adsorption sites are shown in Fig. 1. These final structures can be divided into three groups: The first group is for O₂ molecularly chemisorbed on Ba₅ cluster (Figs. 1.1–1.4). In the second group, as presented in Figs. 1.7–1.10, O₂ dissociatively chemisorbs on Ba₅ cluster, and the third group presents the intermediate states between molecular adsorption and dissociative adsorption, as shown in Figs. 1.5 and 1.6.

O₂ can only molecularly adsorb on Ba₅ if O₂ is on the top of the Ba atom. In the cases of Figs. 1.1 and 1.2, O₂ are molecularly adsorbed with the O–O bond distances of 1.36 Å, slightly larger than that in the ground state. The adsorption energies vary from 1.6 to 2.1 eV. In the cases of Figs. 1.3 and 1.4, O₂ are molecularly adsorbed with the O–O bond lengths of 1.45–1.47 Å, about 0.2 Å larger than that of the ground state. The adsorption energies are about 2.5–2.9 eV.

O₂ can readily dissociate on the Ba₅ cluster if the O₂ is initially located above one of the faces of Ba₅ cluster, or the O–O axis is perpendicular to the Ba–Ba bonds, as shown in Figs. 1.7–1.10. In these cases, the O–O bonds have been broken, with more than 10.0 eV adsorption energies. The most stable structure is one of the cases of dissociative chemisorption, which is shown in Fig. 1.8. The most stable structure obtained here is just almost the same as that of the ground state of Ba₅O₂ cluster found in the work of Chen *et al.*²⁵

By using nudged elastic band (NEB) theory,^{38,39} only about 0.05 eV energy barrier has been found in the minimum energy path (MEP) from the structure of the product in Fig. 1.7 to that presented in Fig. 1.8, with one oxygen atom penetrating into the interstice of the Ba₅ cluster, as presented in Fig. 2. These results indicate that the ground state of the final product Ba₅O₂ cluster may be obtained with the initial adsorption sites in both Figs. 1.7 and 1.8, considering the temperature effect.

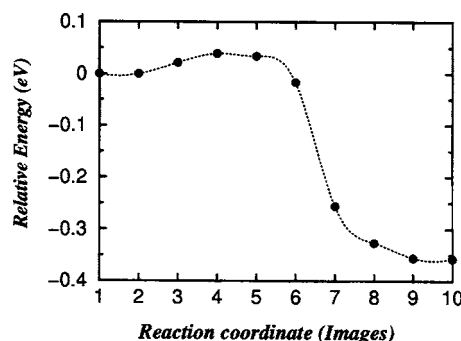


FIG. 2. Potential energy along the minimum energy path (MEP) obtained with nudged elastic band (NEB) theory from the structure of the product in Fig. 1.7 (the starting point) to that of in Fig. 1.8 (the ending point). Energy barrier of about 0.05 eV is obtained.

When O₂ is adsorbed on Ba₅ cluster with initial adsorption sites presented in Figs. 1.5 and 1.6, in which the axis of the O₂ is parallel to one Ba–Ba bond (we simply call it PB site latter), the intermediate states (IS) are obtained. There is about 38° angle between the O–O and its nearest Ba–Ba bond, with about 1.45 Å O–O bond length and about 4.5 eV adsorption energy. The local electronic structure analysis shows that about 0.5*e* have transferred from Ba cluster to per oxygen atom.

It is interesting that the charge transfers in the intermediate states have intermediate values between that of in the molecular adsorption products and that of in the dissociative adsorption products (see Table I). And the final structures become more and more stable from molecular absorptions to dissociative absorptions of O₂, with the O–O distances in the final products increasing, which can be easily understood from the point of view of electrostatic repulsive interaction, as the oxygen atoms have been charged negative electrons. These results also indicate that the charge transfer from Ba cluster to oxygen may play an important role in the dissociative adsorption.

2. Charge transfer and orbital hybridization

To make clear what makes the O₂ dissociate in some sites but not in other cases, we do local electronic structure analysis for the products during the reaction process. For all these ten cases as presented in Fig. 1, in the initial states, the charge transfers are not more than 0.1*e*. In the final products with molecular adsorption, each oxygen atom is charged about 0.3–0.4*e*. Correspondingly, each oxygen atom is charged about one negative electron in the dissociative adsorption products. Though there may be some uncertainty for the charge transfer analysis, these results still strongly imply that the charge transfer may be very important in the dissociation of O₂.

To make further clear whether the charge transfer is the sole reason for the dissociation of O₂, we also investigated the charge transfer for some intermediate states, where the bond lengths of O₂ vary from 1.5 to 1.6 Å corresponding to the onset of the dissociation of O₂. It is found that only about 0.4–0.5*e* are transferred from Ba₅ cluster to each oxygen atom. Here, the charged electrons will occupy the π^* orbital of O₂ and weaken the O–O bond. The quantity of such

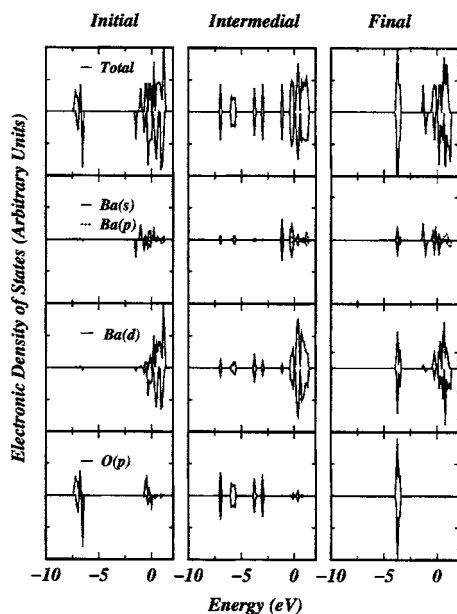


FIG. 3. Electronic density of states for the initial state, the intermediate state, and the final product corresponding to the reaction in Fig. 1.7. The Fermi level has been shifted to zero point.

charge transfer found here is in good agreement with the result for O_2 adsorption on Al_6 cluster.²⁰ However, it seems that such small charge transfer may be not enough to break the O–O bond. As we have also obtained the bond length of an isolated O_2^- has just been weakened to about 1.33 Å by the charge, which illustrates that charge transfer may not be the only reason for the dissociation of O_2 adsorbed on Ba_5 cluster.

The hybridization of $2p\pi^*(2p\pi)$ of O_2 with the d orbital [highest occupied molecular orbital (HOMO)] of Ba_5 cluster may play a key role in the dissociation of O_2 . In Figs. 3 and 4, the density of states (DOS) for the reactions presented in

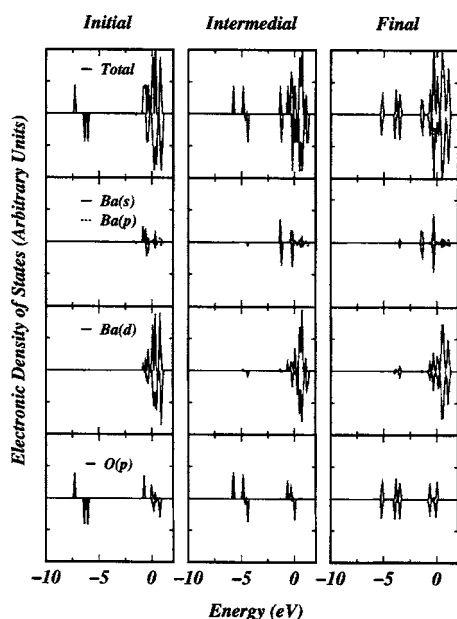


FIG. 4. Electronic density of states for the initial state, the intermediate state, and the final product corresponding to the reaction in Fig. 1.4. The Fermi level has been shifted to zero point.

Figs. 1.7 and 1.4 is shown, respectively. For the initial reacting states in both of the above two cases, one can see that there are almost not any overlaps between the p orbital of O_2 and Ba_5 states. While in the intermediate state presented in Fig. 3, there is obvious hybridization between the $2p\pi^*$ as well as the $2p\pi$ orbitals of O_2 and the d (s) states of Ba_5 cluster. And the π - π^* gap begins to decrease implying that the O–O bond has been weakened. In the final product the π and π^* orbitals are thoroughly superposed, indicating that the oxygen exists atomically and form strong Ba–O hybridization bonds. However, in Fig. 4 where O_2 can only molecularly adsorb on Ba_5 cluster, one can get that there is no obvious overlap between the states of O_2 and that of Ba_5 in both the intermediate state and the final product. These results indicate that the orbital hybridization may play a key role in O_2 dissociation.

3. Spin state and magnetic moment

We have observed that the local spin-triplet state of O_2 must be changed to spin singlet before it is dissociated in the adsorption. The ground state of O_2 is spin triplet with $2\mu_B$ paramagnetic moment; however, in the most stable product (see Table I), where O_2 is dissociated, the local magnetic moment is zero for each oxygen atom. To study the evolution of the spin degree of freedom of O_2 in the adsorption process, we investigated the magnetic moment variation during the reaction process. For all the intermediate states in the dissociative adsorption cases (see Figs. 1.6–1.10), the local magnetic moments contributed by oxygen have vanished thoroughly. On the contrary, in the final products of Figs. 1.1–1.4, where O_2 molecularly exists, there are still about 0.8–1.0 μ_B net magnetic moment contributed by oxygen, indicating that the local spin triplet-singlet state transition for O_2 (if we can still call it this way) is not finished. The changes of the local magnetic moments of O_2 in both the intermediate states and the final product states can also be seen qualitatively from the DOS as shown in Figs. 3 and 4.

The adsorption format is spin state dependent for O_2 on Ba_5 . In the IS products (see Figs. 1.5–1.6), O_2 can only molecularly adsorb on Ba_5 though there is already no net local magnetic moment contributed by oxygen. However, with spin-unpolarized calculations, O_2 will be dissociated onto Ba_5 and one oxygen will penetrate into the interstice of Ba_5 cluster with the same starting configurations as presented in Figs. 1.5 and 1.6. In our spin-polarized calculations, if we keep the triplet state for O_2 (spin conserving) adsorption on Ba_5 cluster, O_2 can only molecularly adsorb on Ba_5 cluster even with the initial adsorption sites presented in Figs. 1.7–1.10.

Above results about the changes of the spin states during the reaction may present an interesting physical picture as the follows: The ground state of O_2 in spin triplet, Ba_5 is spin singlet, and there will be an energy barrier when O_2 approaches to Ba_5 cluster accompanied with the local spin-triplet wave function of O_2 overlapping with the local spin-singlet wave function of Ba_5 . If the oxygen molecule can change from local spin triplet to spin singlet, then the energy barrier will be lowered or vanished, which benefits the dissociation. We are pleased to get that, very recently, Belher

*et al.*⁴⁰ also found the similar role of spin selection rules on the dissociation of O₂ at Al(111) surfaces. And we suppose that the spin selection may be a general rule for O₂ adsorption and oxidation.

IV. SUMMARY

We investigated the reaction of O₂ with Ba₂ molecule and Ba₅ cluster with first-principles calculations. For the reaction of Ba₂ with O₂ molecule, two BaO molecules have been produced with about 6.64 eV adsorption energy. Our calculation results show that the reaction products are adsorption-site and spin-state dependent. The hybridization between the π^* (π) orbit and the *d* state of Ba₅ cluster as well as the charge transfer from Ba atoms to O₂ may together play a key role in the dissociation adsorption.

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