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ARTICLE *in* CHINESE JOURNAL OF CHEMISTRY · OCTOBER 2012

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# Adsorption and Decomposition Mechanism of 1,1-Diamino-2,2-dinitroethylene on Al(111) Surface by Periodic DFT Calculations

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The adsorption of 1,1-diamino-2,2-dinitroethylene (FOX-7) molecule on the Al(111) surface was investigated by the generalized gradient approximation (GGA) of density functional theory (DFT). The calculations employ a supercell ( $4 \times 4 \times 2$ ) slab model and three-dimensional periodic boundary conditions. The strong attractive forces between oxygen and aluminum atoms induce the N—O bond breaking of the FOX-7. Subsequently, the dissociated oxygen atoms and radical fragment of FOX-7 oxidize the Al surface. The largest adsorption energy is  $-940.5$  kJ/mol. Most of charge transfer is  $3.31e$  from the Al surface to the fragment of FOX-7 molecule. We also investigated the adsorption and decomposition mechanism of FOX-7 molecule on the Al(111) surface. The activation energy for the dissociation steps of **P2** configuration is as large as  $428.8$  kJ/mol, while activation energies of other configurations are much smaller, in range of  $2.4$  to  $147.7$  kJ/mol.

**Keywords** 1,1-diamino-2,2-dinitroethylene (FOX-7), Al(111) surface, adsorption and dissociation, density functional theory

## Introduction

Powderized aluminum (Al) is the most commonly used metallic additive in rocket propellant formulations to improve the performance of high energetic ingredients. Al is known to increase the combustion exothermicity and regression rate of solid propellant grains and enhance the blast effect of explosives as well as their underwater performance.<sup>[1]</sup> The efficiency of such processes depends on the size of the Al particles. Because of its large surface area, Al nanopowder can produce significant improvement in the performance of some energetic materials.

1,1-Diamino-2,2-dinitroethylene (FOX-7), is a novel high energetic ingredient with high thermal stability (decomposes only above  $220^\circ\text{C}$ ) and low sensitivity to impact and friction.<sup>[2]</sup> Over the past decades (first synthesized in 1998),<sup>[2,3]</sup> FOX-7 received much attention and was deemed to be one of the most important preferred components of propellants in the future. So far, there have been several theoretical and experimental studies on FOX-7 and its derivatives.<sup>[4–12]</sup> For example, Sorescu has performed classical and quantum-me-

chanical investigation on crystalline FOX-7.<sup>[4]</sup> Ju *et al.* have investigated theoretically the intermolecular interaction in the dimer and the bulk state of FOX-7, as well as molecule structure at the DFT-B3LYP/6-311++G\*\* level.<sup>[5]</sup> Zhang has used quantum chemistry, molecular mechanics and Monte Carlo methods to calculate the heats of detonation, detonation velocities and pressures of FOX-7 and other high energy density materials.<sup>[6]</sup> Evers *et al.* also have studied the  $\alpha$ - $\beta$  phase transition in FOX-7 by single-crystal X-ray investigations at five different temperatures at  $200$ – $393$  K.<sup>[7]</sup> Additionally, Cheng *et al.* have provided some calculations about FOX-7 to provide a reference (including preferred reaction routes and reagents) for the synthesis of FOX-7.<sup>[8]</sup> As Al nanopowder is the most commonly used in solid propellants, it is important to understand its reaction with FOX-7 molecules. Up to now, some researches have carried out studies of the behaviors of FOX-7 on metal surface. Sorescu *et al.* used first-principles method to calculate the adsorption of FOX-7 molecules on the  $\alpha$ - $\text{Al}_2\text{O}_3(0001)$  surface.<sup>[4,13]</sup> They also studied five adsorption configurations of FOX-7 on Al(111) surface, discussed the geometries and energies.<sup>[14]</sup> Al-

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Received May 15, 2012; accepted June 24, 2012; published online August 14, 2012.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/cjoc.201200470> or from the author.

though there are many reports about FOX-7, the decomposition mechanism of FOX-7 on Al surface is not clearly elucidated. Our work focuses on the detailed atomic-level description of the interactions between the energetic compound of FOX-7 and the Al(111) surface. In this paper, we reported ten adsorption configurations of FOX-7 on Al(111) surface, among which four configurations are similar to Sorescu's results. In addition to studying the geometries and energies of adsorptions, we investigated the charge transfer analysis and the density of states. In view of the fact that the DFT calculations were employed to investigate the chemisorptions and dissociation pathways of NO on the Rh surfaces<sup>[15]</sup> as well as H<sub>2</sub>S on the closed packed surfaces of a number of important noble metals and transition metals,<sup>[16,17]</sup> we also studied the decomposition mechanism of FOX-7 molecule on the Al(111) surface.

### Computational Method

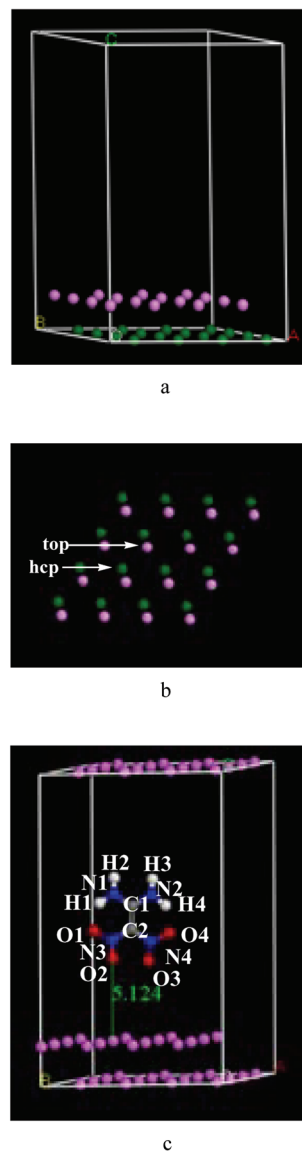
The calculations performed in this study were done using the CASTEP package<sup>[18]</sup> with Vanderbilt-type ultrasoft pseudopotentials<sup>[19]</sup> and a plane-wave expansion of the wave functions. Exchange and correlation were treated with the generalized gradient approximation (GGA), using the functional form of Perdew, Burke, and Enzerh of PBE.<sup>[20]</sup> The electronic wave functions were obtained by a density-mixing scheme<sup>[21]</sup> and the structures were relaxed using the Broyden, Fletcher, Goldfarb, and Shannon (BFGS) method.<sup>[22]</sup> In this study, the cutoff energy of plane waves was set to 300.0 eV. Brillouin zone sampling was performed using the Monkhost-Pack scheme. The values of the kinetic energy cutoff and the k-point grid were determined to ensure the convergence of total energies.

The Al surface was represented by a slab model with periodic boundary conditions. The energy convergence with respect to the number of layers has been tested to ensure the reliability and representative of the selected model. The surface energy ( $E_{\text{surf}}$ ) is calculated by equation,

$$E_{\text{surf}} = \frac{E_{\text{slab}} - nE_{\text{bulk}}}{2A} \quad (1)$$

here  $E_{\text{slab}}$  is total energy of the selected slab supercell,  $E_{\text{bulk}}$  is the primitive cell energy of the bulk,  $n$  is the number of atoms for the selected supercell, and  $A$  is the area of the slab. The surface energies of 1, 2 and 3 layers are 0.40 eV, 0.35 eV and 0.35 eV, respectively. In addition, we tested the adsorption cases in which the C—N bond of the nitro group is initially vertical to the Al surface and the O atom of nitro group at a hexagonal closely packed (hcp) surface site for 2 and 3 layers Al(111). The same N—O bonds of both configurations decompose and they form 4 Al—O bonds. The adsorption energies for 2 and 3 layers are −378.1 and −387.8 kJ/mol, respectively. Their difference is small. Therefore, considering the balance of both computational efficiency and accuracy, a 4×4 supercell with

two layers containing 32 Al atoms was used to study the adsorption of the molecular systems (see Figure 1). The slabs were separated by 17 Å of vacuum along the c-axis direction with a FOX-7 molecule on the top of the slab. The cell size with a rhombic box of  $a \times b \times c$  is 11.45 Å × 11.45 Å × 19.34 Å.



**Figure 1** (a) Lateral view of the slab model of Al(111). Atoms in different layers are colored differently for easy identification. (b) Top view of the surface. Surface sites are depicted in the panel. (c) FOX-7 molecule on the Al surface with no interactions.

Several tests have been performed to verify the accuracy of the method when applied to bulk aluminum and to the isolated FOX-7 molecules, such as the optimum cutoff energy for calculations. For bulk aluminum, we have tested for convergence, using the  $k$ -point sampling density and the kinetic energy cutoff. In these calculations, a Monkhost-Pack scheme with mesh parameters of 12×12×12 has been used, leading to 56  $k$ -points in the irreducible Brillouin zone. To determine the equilibrium bulk parameters of aluminum, we uni-

formly scaled the lattice vectors and performed energy calculations as a function of the unit-cell volume. The calculated lattice constants are the same values of 4.050 Å at  $E_{\text{cut}}=300$  eV and  $E_{\text{cut}}=400$  eV. It can be concluded that, at  $E_{\text{cut}}=300$  eV, the bulk structure is well converged, with respect to the cutoff energy. The calculated lattice constant of 4.050 Å is also identical to the experimental value,<sup>[23]</sup> indicating that the present set of pseudo-potentials is able to provide a very good representation of the structural properties of bulk aluminum.

An equally good representation has been observed for the geometric parameters of the isolated FOX-7 molecules. On the basis of optimizations of the isolated FOX-7 molecule in a rhombic box with dimensions of 11.45 Å × 11.45 Å × 19.34 Å, we obtained the following values: equilibrium bond lengths of  $r(\text{C—C})$  of the FOX-7 molecule = 1.430 Å,  $r(\text{N—O})=1.251\text{—}1.283$  Å,  $r(\text{C—N})$  of the bond between C atom and amino group = 1.345—1.346 Å,  $r(\text{C—N})$  of the bond between C atom and nitro group = 1.428 Å, and  $r(\text{N—H})=1.019\text{—}1.036$  Å, and bond angles of  $\theta(\text{O—N—O})=122^\circ$ ,  $\theta(\text{H—N—H})=123^\circ$ ,  $\theta(\text{N—C—N})=117^\circ$  and  $119^\circ$ ,  $\theta(\text{N—C—C})=120^\circ\text{—}122^\circ$ , and  $\theta(\text{O—N—C})=118^\circ\text{—}120^\circ$ , at  $E_{\text{cut}}=300$  eV. The increase of the cutoff energy to 400 eV leads to the following values:  $r(\text{C—C})=1.431$  Å,  $r(\text{N—O})=1.250\text{—}1.283$  Å,  $r(\text{C—N})$  of the bond between C atom and amino group = 1.344—1.345 Å,  $r(\text{C—N})$  of the bond between C atom and nitro group = 1.424—1.426 Å, and  $r(\text{N—H})=1.019\text{—}1.038$  Å, and bond angles of  $\theta(\text{O—N—O})=122^\circ$ ,  $\theta(\text{H—N—H})=124^\circ$ ,  $\theta(\text{N—C—N})=117^\circ$  and  $119^\circ$ ,  $\theta(\text{N—C—C})=120^\circ\text{—}121^\circ$ , and  $\theta(\text{O—N—C})=118^\circ\text{—}120^\circ$ . We noticed that there are no significant differences between the values obtained at the two cutoff energies, indicating the convergence of the results even at  $E_{\text{cut}}=300$  eV. These values are also very close to the experimental data for crystal FOX-7 at 298 K (C—C: 1.485 Å, N—O: 1.235—1.250 Å, C—NH<sub>2</sub>: 1.308—1.316 Å, C—NO<sub>2</sub>: 1.388—1.417 Å, N—H: 0.850—0.930, and O—N—O: 120°—122°, H—N—H: 118°—121°, N—C—N: 116°—118°, N—C—C: 119°—124°, O—N—C: 118°—121°).<sup>[7]</sup> The good agreement between our calculated properties of aluminum bulk and the isolated FOX-7 molecule and those of the experiment suggests that the performed computational method is proper to the adsorption system of FOX-7 molecule on the Al(111) surface, which qualifies us for investigation of adsorption of FOX-7 on the Al(111) surface.

For the case of chemical adsorption configurations, the corresponding adsorption energy ( $E_{\text{ads}}$ ) was calculated according to the expression

$$E_{\text{ads}} = E_{(\text{adsorbate}+\text{slab})} - E_{(\text{molecule}+\text{slab})} \quad (2)$$

where  $E_{(\text{adsorbate}+\text{slab})}$  is the total energy of the adsorbate/slab system after the FOX-7 molecule being absorbed by Al slab and  $E_{(\text{molecule}+\text{slab})}$  is the single-point energy of the FOX-7/slab system as a whole but without interactions between FOX-7 molecule and the Al slab

(FOX-7 molecule is as far as 5.1 Å away from Al surface).

The  $E_{(\text{adsorbate}+\text{slab})}$  and  $E_{(\text{molecule}+\text{slab})}$  were calculated with the same periodic boundary conditions and the same Brillouin-zone sampling. A negative  $E_{\text{ads}}$  value corresponds to a stable adsorbate/slab system. Figure 1 shows the Al slab model, the absorbed surface sites and the configuration of FOX-7 molecule on the Al surface atoms with no interactions of adsorbate/Al.

Transition states (TS) were located by using the complete LST/QST method.<sup>[24]</sup> Firstly, the linear synchronous transit (LST) maximization was performed, followed by an energy minimization in directions conjugated to the reaction pathway. The TS approximation obtained in that way was used to perform quadratic synchronous transit (QST) maximization. From that point, another conjugate gradient minimization was performed. The cycle was repeated until a stationary point was located. The convergence criterion for transition state calculations was set to 0.25 eV/Å for the root-mean-square forces. The activation energy is defined as  $E_{\text{a}} = E_{\text{TS}} - E_{\text{R}}$ , where  $E_{\text{TS}}$  is the energy of transition state, and  $E_{\text{R}}$  is the sum of the energies of reactants.

## Results and Discussion

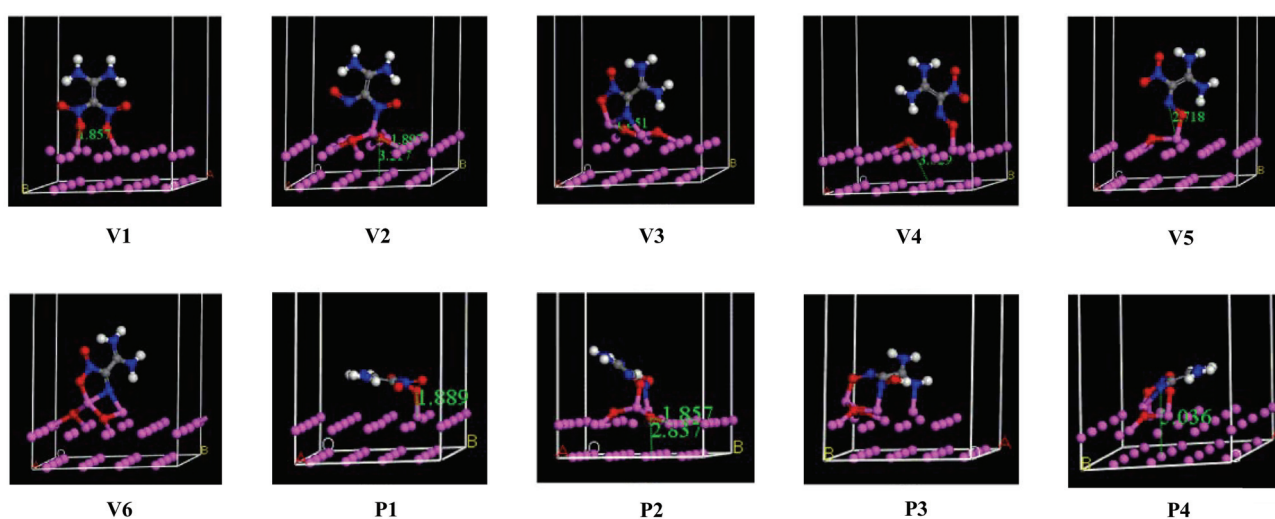
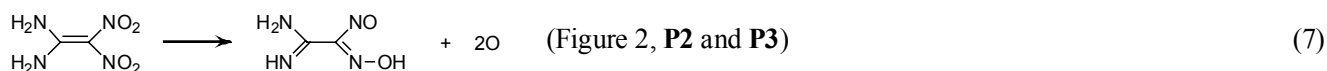
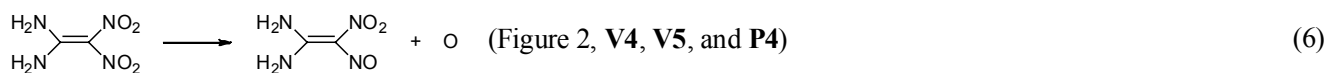
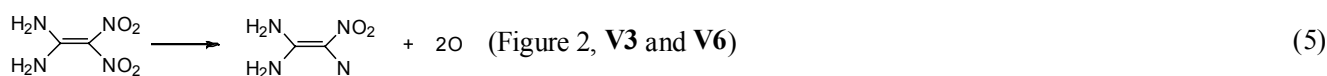
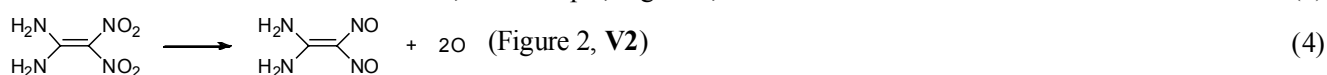
The adsorption and decomposition of FOX-7 molecule on the Al(111) surface are very complicated. There exist both physical and chemical adsorptions, and the latter result in the decomposition of the FOX-7 molecule on the Al surface. There are five cases as formula (3) to (7).

According to the orientation of the plane of FOX-7 molecule relative to the Al(111) surface, **V** and **P** denote vertical and parallel adsorptions of FOX-7, respectively. The lateral views of the optimized adsorption configurations after full relaxation of the atomic positions were shown in Figure 2.

### Geometries and energies

The adsorption energies were calculated by Eq (2) and given in Table 1. As can be seen in Figure 2, configurations **V1** and **V2** show that the N—O bond of the nitro group is initially vertical to the Al surface and above an on-top site and hcp site of the Al surface, respectively. Adsorption at **V1** site leads to the formation of two Al—O bonds with length of 1.822 Å and 1.857 Å, respectively. The distortion of the FOX-7 molecule is small, and all the bond angles and lengths change slightly except that the lengths of two N—O bonds (N3—O2 and N4—O3) change from 1.253/1.253 Å to 1.375/1.358 Å. As the formation of two Al—O bonds, these two N—O bonds (N3—O2 and N4—O3) significantly increase. These results of geometric parameters are similar to Sorescu's results,<sup>[14]</sup> which verifies the reliability of the method used in this research. In the configuration **V2**, one oxygen atom of each nitro group is dissociated. The N4 and dissociated O atoms interact

The FOX-7 molecule is nondissociative, for example, Figure 2, **V1** and **P1**. (3)



**Figure 2** Adsorption configurations of FOX-7 on the Al(111) surface. V and P denote vertical and parallel adsorptions of FOX-7, respectively.

**Table 1** Adsorption energies ( $E_{\text{ads}}$ ), activation energies ( $E_{\text{a}}$ ) and adsorption sites of FOX-7 on the Al(111) surface

Relation of plane of FOX-7 molecule with the Al slab	Configurations	Adsorption sites	$E_{\text{ads}}/(\text{kJ}\cdot\text{mol}^{-1})$	$E_{\text{a}}/(\text{kJ}\cdot\text{mol}^{-1})$
vertical	<b>V1</b>	top	−106.8	—
	<b>V2</b>	hcp	−723.3	—
	<b>V3</b>	top	−910.6	—
	<b>V4</b>	hcp	−378.1	49.6
	<b>V5</b>	top	−380.7	67.0
	<b>V6</b>	hcp	−940.5	71.7
parallel	<b>P1</b>	top	−48.0	2.4
	<b>P2</b>	hcp	−805.5	428.8
	<b>P3</b>	top	−857.6	147.7
	<b>P4</b>	hcp	−522.1	—

strongly with the surface Al, which leads to the formation of six Al—O bonds and one Al—N bond. Another four cases in which the C—N bond of the nitro group is initially vertical to the Al surface also have been investigated: the O atom of nitro group above an on-top site of an Al surface atom (**V3**), above an hcp site (**V4**), the

N atom of nitro group above an on-top site of an Al surface atom (**V5**), and above an hcp site (**V6**). The structures of **V3** is also similar to Sorescu's results, in this case, the adsorption leads to a complete dissociation of both O atoms of the N4 nitro group. The N4 and two dissociated O atoms are adsorbed on the Al surface,



resulting in a total seven Al—O bonds and two Al—N bonds. The Al—O and Al—N bond lengths are in range of 1.829—1.901 Å and 1.867—1.913 Å, respectively. Configurations **V4** and **V5** are similar, the adsorptions lead to dissociation of one of nitro O atoms. The dissociated and undissociated O atoms interact strongly with neighboring Al atoms to form four Al—O bonds in lengths of 1.834—1.871 Å. For **V6**, the adsorption leads to a complete dissociation of both O atoms of the N4 nitro group, which is similar to **V3**. The N4 and two dissociated O atoms are adsorbed on the Al surface, resulting in a total seven Al—O bonds and two Al—N bonds. The Al—O and Al—N bond lengths are in range of 1.773—1.902 and 1.879—1.903 Å, respectively.

In addition to the vertical adsorption configurations previously described, we have also tested the case in which the amino group of FOX-7 initially oriented toward the Al surface. Chemisorption does not occur because the amino group does not strongly interact with the surface Al atoms. Therefore, such configurations do not lead to stable chemisorptions but local minimum of physical adsorption, so they are not discussed further.

Besides the vertical adsorption configurations, we also studied the cases in which the FOX-7 molecule was initially parallel to the Al surface. Four cases have been investigated: the O atom of nitro group above an on-top site of an Al surface atom (**P1**), above an hcp site (**P2**), the N atom of nitro group above an on-top site of an Al surface atom (**P3**), and above an hcp site (**P4**). Our study indicated that the FOX-7 molecule rotates to maximize the interaction with the Al surface during the optimization. As a result, the FOX-7 molecule is dissociated in two ways, as reaction formula (6) and (7). The configuration **P1** illustrates that the adsorption of FOX-7 leads to the formation of one Al—O bond with length of 1.889 Å. The distortion of the FOX-7 molecule is small. The configuration **P2**, which is also similar to a configuration discussed in ref. [14], leads to dissociation of two O atoms (O1 and O3) of the nitro group. The products of the dissociated FOX-7 molecule are similar to **V3** and **V6**. However the dissociated two O atoms in **P2** come from two different nitro groups, instead of from one nitro group in **V3** and **V6**. Obviously, the product is different from other configurations discussed above, an H atom dissociated from amino group of FOX-7 combines with a nitro O atom to form an O—H bond (O4—H4) by length of 1.058 Å. The next configuration **P3** gives the case in which the adsorption of FOX-7 leads to the formation of a total seven Al—O bonds, two Al—N bonds and one O—H bond. The dissociated product of the FOX-7 molecule in **P3** is much similar to **P2**, except one more Al—N bond formed between the N2 atom and an Al atom with the bond length of 2.309 Å. Finally, in **P4**, one of nitro O atoms dissociates, which is similar to **V4** and **V5**. The dissociated O atom (O3 atom) and undissociated O atoms (O2 and O4 atoms) interact strongly with neighboring Al atoms to form six Al—O bonds in lengths of

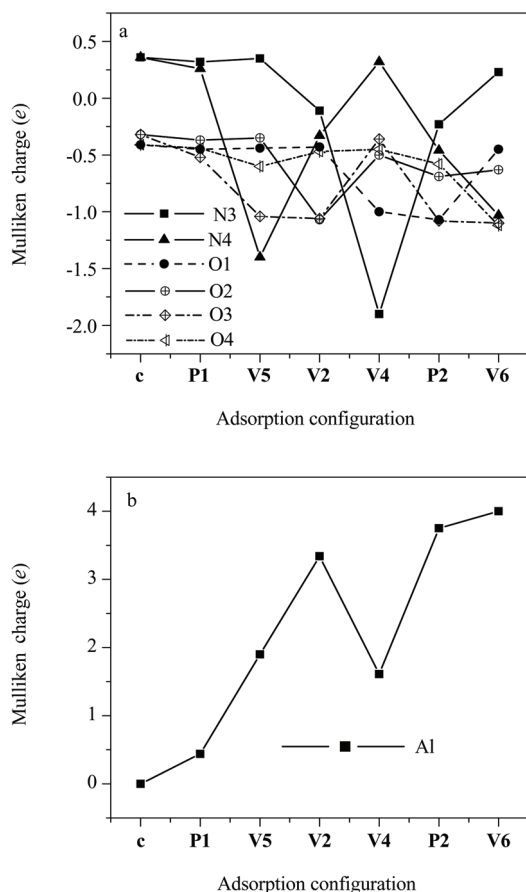
1.800—2.058 Å.

As can be seen from Table 1 and Figure 2, when the FOX-7 molecule does not dissociate, the corresponding adsorption energy is small, which is  $-48.0$  and  $-106.8$  kJ/mol (**P1** and **V1**), the  $E_{\text{ads}}$  of **V1** is two times larger than the  $E_{\text{ads}}$  of **P1**, since there are two Al—O bonds in **V1** but only one Al—O bond in **P1**. When the FOX-7 molecule is dissociated, the corresponding adsorption energies are very large. The adsorption energy with two N—O bonds dissociated in **V2** is  $-723.3$  kJ/mol, which is almost two times the adsorption energies of **V4** or **V5** ( $-378.1$  and  $-380.7$  kJ/mol, respectively). Although the decomposition products of **P4** are the same as those of **V4** and **V5**, the corresponding adsorption energies are much larger than those of **V4** and **V5** (almost 143.0 kJ/mol larger), because there is an additional Al—N bond and two more Al—O bonds in **P4** as compared to **V4** and **V5**. The largest adsorption energy is  $-940.5$  kJ/mol when the C—N bond of the nitro group is initially vertical to the Al surface and the N atom of nitro group at an hcp surface site, that is, **V6** in Figure 2.

As a whole, when the decomposition products of the FOX-7 molecule in **V2**, **V3**, **V6**, **P2** and **P3** configurations are of three radical species, their adsorption energies are much larger than those of two radical species. Herein, these radical species readily oxidize the Al and form strong Al—O and Al—N bonds. In a word, for all the above mentioned configurations of FOX-7 except **V1** and **P1**, the FOX-7 molecule is decomposed to different products when initially being placed on different surface sites, resulting in strong chemical adsorptions. In addition to the formation of strong Al—O bonds, the Al—N bonds are also formed through the strong interaction of N atoms in either the nitro group or the amino group with the surface Al atoms. The fact that the dissociation of the nitro group on the Al(111) surface was observed in simple energy minimizations suggests that the uncoated Al surface is very active to the electron acceptors as further discussed below.

### Charge transfer

The Mulliken population analysis method is a useful tool to provide a quantitative measure of charge transfer,<sup>[25,26]</sup> in which the electronic charge is distributed among the individual atoms. Figure 3 shows Mulliken charges on the individual N, O, and Al atoms of the FOX-7 molecule on the Al(111) surface. The obtained charges indicate that a significant charge transfer occurs as a result of adsorption. For a non-dissociative adsorption configuration, such as **V1** and **P1** in Figure 2, the charges of  $0.85e$  and  $0.42e$  are transferred from the surface Al atoms to the FOX-7 molecule, respectively, as compared to the **c** configuration (Figure 1). The charges of N and O atoms of nitro group decrease, while those of surface Al atoms increase. For N—O bond-dissociated with three Al—O bonds formed adsorption configurations of **V4** and **V5**, the charges of  $3.02e$  and



**Figure 3** Mulliken charges on each individual atom of FOX-7 (a) and on the top layer of Al (b), **c** refers to the non-adsorption configuration.

2.66 $e$  are transferred from Al atoms to the adsorbate, respectively. Similarly, for the results of two N—O bond-dissociated with six Al—O bonds and one Al—N bond formed adsorption configuration in **V2**, the transfer charge is 2.69 $e$ . At last, for the configurations **V3**, **V6**, **P2** and **P3** of two N—O bond-dissociated with seven Al—O bonds formed adsorption, the transfer charges are 3.15 $e$ , 3.31 $e$ , 3.31 $e$  and 3.29 $e$ , respectively.

Moreover, as can be seen from Figure 3a, for one N—O bond-dissociated with three Al—O bonds formed adsorption configurations in **V4** and **V5**, the charge on the N atom (on dissociated nitro) decreases dramatically in comparison with **c**. From **c** to **P1**, because there is no N—O bond-dissociated, the charges of N and O atoms almost do not change. However the charge on the Al atom bonding with O atom increases slightly. For **V2**, because of the dissociation of N3—O2 and N4—O3 bonds, the charge on the N3, N4, O2 and O3 atoms bonding with the Al atoms decreases dramatically. Similarly, for **P2**, because of the dissociation of N3—O1 and N4—O3 bonds, the charge on the N3, N4, O1 and O3 atoms bonding with the Al atoms decrease obviously. For **V6**, because of the dissociation of the N4—O3 and N4—O4 bond and the formation of two Al—N4 and seven Al—O bonds, the charge on the N4

atom decreases dramatically, whereas the charges on the O3 and O4 atoms change slightly. Figure 3b indicates that charges of the Al atoms increase with the number of the dissociated bonds on the FOX-7 molecule increasing.

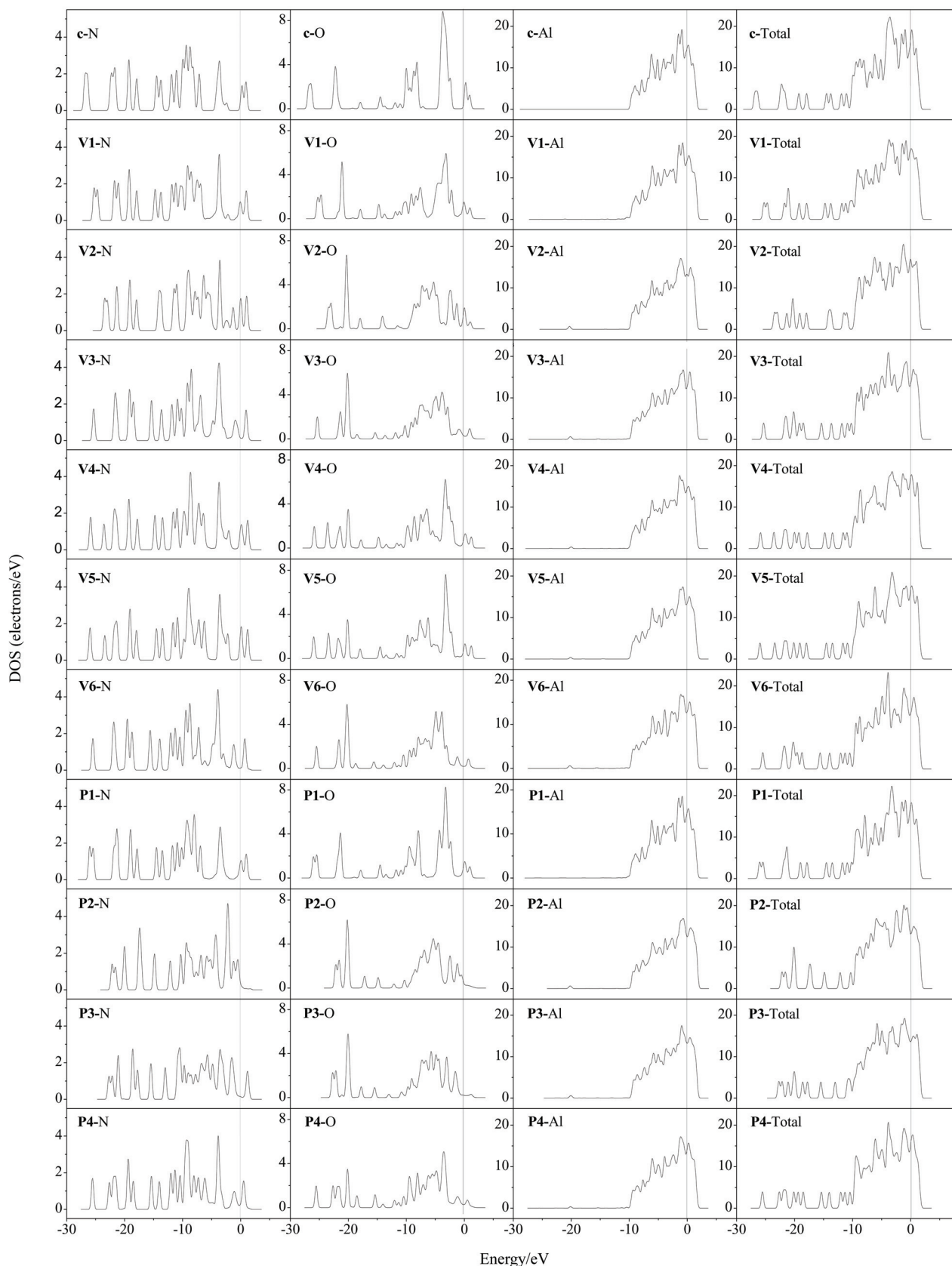
In a word, the charges on the nitro N3 and N4 atoms of those are similar because the number on the dissociated bonds of **V4** and **V5** are equal, and the O1 atom with three nearby surface Al atoms forms three almost identical Al—O bonds, as well as the O3 atom of another nitro with three nearby surface Al atoms forms three almost identical Al—O bonds. The charges on two nitro O1 and O3 atoms of **P2** and two nitro O3 and O4 atoms of **V6** are identical because each O atom combines with nearby surface Al atoms and forms seven almost identical Al—O bonds. As a general trend, the charges on N and O atoms decrease dramatically when the number of the dissociated N—O bonds on FOX-7 molecule and the formed Al—O bonds increases.

### Density of state (DOS)

The electronic structure is intimately related to their fundamental physical and chemical properties. Moreover, the electronic structures and properties are related to the adsorptions and decompositions for the adsorbates. The discussion above suggests that the decomposition of the FOX-7 molecule on the Al surface initiates from the rupture of N—O bond and results in the formation of Al—O and Al—N bonds. Therefore, the knowledge of their electronic and properties appears to be useful for further understanding the behaviors of the FOX-7 molecule on the Al surface. Figure 4 displays the calculated total DOS and their projection on the N, O, and Al atoms for all adsorption configurations. Clearly, the total DOS equals the sum of its projections on N, O, and Al atoms for adsorption configurations. The electronic structures vary with adsorption configurations due to the differently dissociated products of the FOX-7 molecule.

As can be seen from Figure 4, for N and O atoms of **P1**, the DOS of the N is almost the same with that of **c**, while the highest peak value of DOS for O atoms becomes smaller than those of **c** (there is only a Al—O bond formed between the non-dissociative FOX-7 molecule and Al surface), whereas the number of DOS peaks almost unchanged, as compared to **c**. Similarly, for **V1**, the highest peak values of DOS for N and O atoms become smaller than those of **c** in the range of  $-10$  to  $0$  eV, whereas the number of DOS peaks becomes more than those of **c** in the range of  $-30$  to  $-5$  eV (there are two Al—O bonds formed between the non-dissociative FOX-7 molecule and Al surface). However, the DOS of surface Al atoms appears almost unchanged, as compared to **c**. This indicates the weak interaction of the FOX-7 molecule with the surface Al atoms.

For **V4** and **V5**, for O atoms, the highest peak value of DOS atoms becomes smaller, the number of DOS peaks becomes much more in the range of  $-30$  to



**Figure 4** Total DOS and their projections on the N, O, and Al atoms for all adsorption configurations. **c** is a non-adsorption configuration.

−15 eV, as well as the peaks are more smooth in the range of −10 to 0 eV, as compared to **c**. At the same

time, the peak number of DOS on N atom becomes more, and the DOS of the Al atom appears as a small



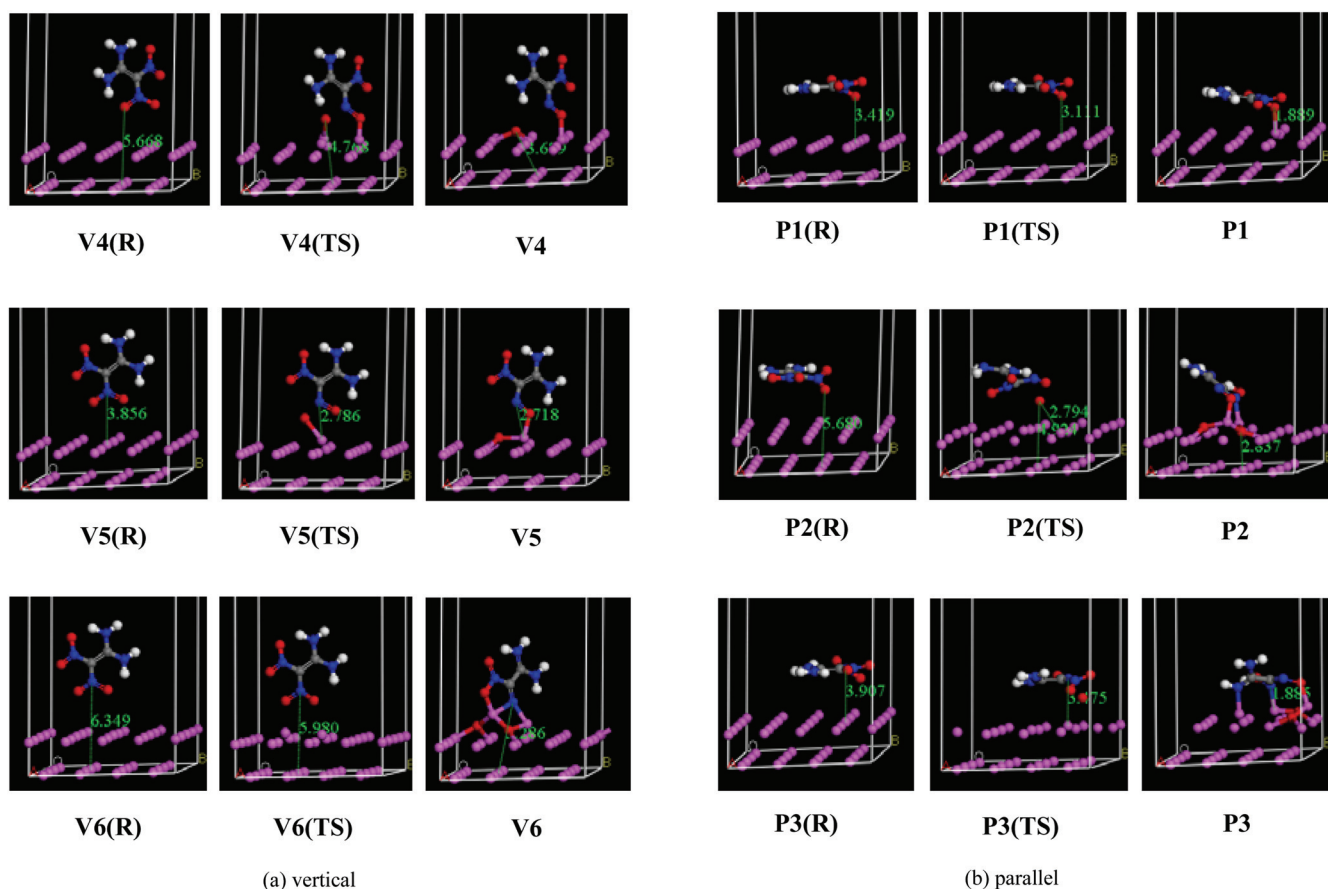
peak at the energy of 20 eV. This suggests the dissociation of one N—O bond and the formation of three strong Al—O bonds in these two adsorption configurations. For **V3** and **V6**, the changes in the DOS of N, O, and Al atoms are obviously similar to each other and the individual peaks of N and O atomic DOS are almost overlapped (two N—O bonds dissociated, seven strong Al—O bonds and two Al—N bonds formed, both in these two adsorption configurations). Similarly, the same situation occurs in between configurations **P2** and **P3** (two N—O bonds dissociated, and seven strong Al—O bonds formed). From the above analysis we can draw that when bonding interactions between the adsorbates and the Al surface are strengthened, the DOS shifts and overlaps with respect to those of **c**. These explain the dissociation of N—O bonds and the formation of strong Al—O and Al—N bonds, and the results also show the very strong interaction of the decomposition products from FOX-7 with the surface Al atoms.

### Mechanism of dissociation

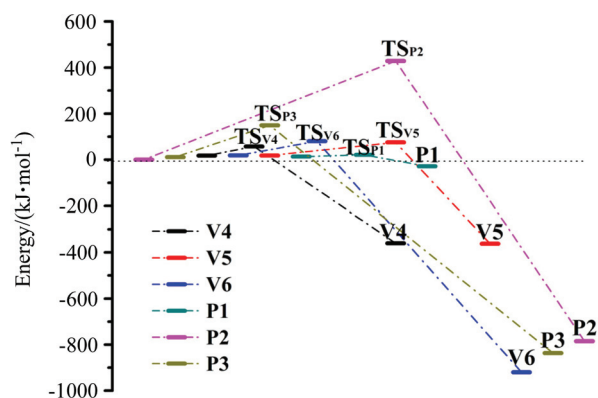
The reactants, transition state and products for the surface reaction of FOX-7 molecule on the Al(111) were depicted in Figure 5, and a detailed energy profile for six dissociation of adsorbed FOX-7 configurations were presented in Figure 6. In Figure 5, the reactants and transition state were denoted with indices **R** and **TS**,

representing the local minimum of physical adsorption and lateral views of the transition state, respectively. The activation energies and reaction energies at transition state were tabulated in Table 1 and shown in Figure 6.

As can be seen from Figure 5(a), for **V5(TS)** and **V6(TS)**, the decomposition process of FOX-7 molecule on the Al surface is much similar: one nitro N—O bond for both **TS** breaks and forms an Al—O bond with a surface Al atom. In **V4(TS)**, the FOX-7 molecule on the Al surface attracts three Al atoms, resulting in the deformation of Al surface. The O1 atom moves away from N3 atom. The distance between N3 and O1 increases from 1.240 to 1.725 Å. The O1 atom tilts towards the closest Al atom, and the distance between O1 and the Al atom is 1.929 Å. While the O2 atom binds to another surface Al atom with Al—O length of 1.572 Å. In this transition state, the activation energy ( $E_a$ ) is 49.6 kJ/mol (see Table 1 and Figure 6), indicating that this process is easy to take place. In the process of decomposition, the Al—O1 bond tilts to the Al surface and another two strong Al—O bonds formed. In **V5(TS)**, the process of decomposition of FOX-7 molecule is almost similar to **V4(TS)**, the FOX-7 molecule moves towards the Al surface, and the O3 atom moves away from N4 atom. The dissociated oxygen atom attracts a nearby Al atom that deviates from the Al surface, and forms an Al—O



**Figure 5** Lateral views of FOX-7 on the Al(111) surface. The index **R** and **TS** denote the reactant and transition state, respectively.



**Figure 6** Relative energy profile for FOX-7 decomposition on the Al(111) surfaces.

bond. The corresponding activation energy ( $E_a$ ) is 67.0 kJ/mol (see Table 1 and Figure 6). After the transition state, N4—O3 bond continues to move apart, the Al—O3 bond keeps tilting to the Al surface, and three more Al—O bonds come into being (see V5). For V6(TS), the FOX-7 molecule does not decompose in this state, as compared to the local minimum of physical adsorption, the FOX-7 molecule moves down towards the Al surface and interacts with two Al atoms. As a result, these two Al atoms deviate from the Al surface obviously. Compared to the initial state, the bond length of N4—O4 bond increases from 1.242 to 1.418 Å, while the bond angle  $\theta(\text{O3-N4-O4})$  decreases from 121° to 114°. With the reaction going on, two O atoms dissociated from N4 atom. The distances between the partially dissociated O atoms and the nearest Al atoms decrease from 3.801 to 2.816 Å (O3 atom) and from 3.533 to 2.593 Å (O4 atom), respectively. The activation energy ( $E_a$ ) is 71.7 kJ/mol (Table 1 and Figure 6). After the transition state, N4—O3 bond and N4—O4 bond move apart and the dissociated moiety binds to the surface and forms seven Al—O and two Al—N interactions (see P6).

Similarly, we have also studied the transition states, of which the FOX-7 molecule was initially parallel to the Al surface beside the vertical adsorption configurations [see Figure 5(b)]. For P1(TS), the FOX-7 molecule does not decompose via this transition state. Compared to the local minimum of physical adsorption, the FOX-7 molecule moves towards the Al surface and attracts one Al atom that deviates from the Al surface obviously, and the bond length of N4—O3 bond increases from 1.242 to 1.273 Å, while the distances between the O3 atoms and the nearest Al atoms both decrease from 3.419 to 3.111 Å. The activation barrier ( $E_a$ ) of P1(TS) is 2.4 kJ/mol. Through P1(TS), the FOX-7 molecule forms an Al—O bond (see P1).

Finally, for the case of P2(TS) and P3(TS), one N—O bond for each nitro group breaks and forms two dissociated fragments  $\text{C}_2\text{H}_4\text{N}_4\text{O}_3$  and O atom. In P2(TS), the FOX-7 molecule attracts several Al atoms that deviate from the Al surface obviously. The O3 atom moves

away from N4 atom, as the distance between N4 and O3 increases from 1.242 to 1.965 Å, while the distance between N3 and O1 increases from 1.249 to 1.273 Å. The O1 atom tilts towards the closest Al atom and the distance between O1 and the Al atom is 3.003 Å, as the distance between O1 and the Al atom is 4.324 Å in the reactant. The activation energy ( $E_a$ ) of P2(TS) is as large as 428.8 kJ/mol (Table 1 and Figure 6), which means that this process is hard to occur. In the decomposition process, the O3 atom keeps moving to the Al surface, and the O1 atom also leaves the N3 atom. These two O atoms bind with the surface Al atoms and form six Al—O bonds. In addition, another Al—O bond (between O2 atom and a surface Al atom) and one Al—N bond (between N4 atom and a surface Al atom) come into being. In P3(TS), the decomposition process of FOX-7 molecule is similar to P2(TS) except that, for P3(TS), the activation energy  $E_a$  is 147.7 kJ/mol [much smaller than the  $E_a$  in P2(TS)] and one more Al—N bond forms between N2 atom and a surface Al atom, as compared to P2(TS).

## Conclusions

Based on the investigation of FOX-7 molecule on Al(111) surface, the major findings can be summarized as follows.

(1) There exist both physical and chemical adsorptions when the FOX-7 molecule approaches the Al surface. The Al surface is readily oxidized by the oxygen-rich nitro group of the dissociatively adsorbed FOX-7. Dissociations of the N—O bonds of nitro group result in the formations of strong Al—O and Al—N bonds. As the number of the formations of Al—O and Al—N bonds increases, the corresponding adsorption energy increases sharply.

(2) With the number of the dissociated bonds on the FOX-7 molecule and the formed Al—O bonds increasing, the charges on N and O atoms decrease sharply, while charges of the Al atoms increase. The most charge transfer is 3.31e from the Al surface to the FOX-7 molecule.

(3) The DOS projections on the N and O atoms for dissociated N—O bonds adsorptions occur with an obvious shift of peaks, which infers that energy bands become broad and the interactions of chemical bonds are strengthened.

(4) The decomposition processes on Al surface are predicted to be exothermic. The activation energy for P2 configuration is as large as 428.8 kJ/mol. However, the activation energies of other configurations are in range of 2.4 to 147.7 kJ/mol.

## Acknowledgement

We gratefully acknowledge the funding provided by the Laboratory of Science and Technology on Combustion and Explosion (Grant No. 9140C3501021101) for

supporting this work. C.-C.Y. thanks the Innovation Foundation from the Graduate School of NJUST for partial financial support.

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