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Density functional theory studies on adsorption and decomposition mechanism of FOX-7 on Al_{13} clusters

Cai-Chao Ye, Feng-Qi Zhao, Si-Yu Xu, and Xue-Hai Ju

Abstract: The adsorption and decomposition of the FOX-7 molecule on Al_{13} clusters were investigated by generalized gradient approximation of the density functional theory. The strong attractive forces between the FOX-7 molecule and aluminum atoms induce the N–O bond breaking of FOX-7. Subsequently, the dissociated oxygen atoms and radical fragment of FOX-7 oxidize the aluminum clusters. The largest adsorption energy is -1020.4 kJ/mol. We also investigated three adsorption reaction paths of the FOX-7 molecule on the Al_{13} clusters in the A configuration. The activation energy for the adsorption steps are 0.2, 11.4, and 10.2 kJ/mol, respectively, and Al_{13} is more active than the Al(111) surface and the Al_{13} cluster performs better in decreasing the adsorption barrier of FOX-7 on the aluminum surface as well. The rate constants of three adsorption paths increase as temperature increases over the temperature range 275–500 K.

Key words: Al_{13} cluster, 1,1-diamino-2,2-dinitroethylene (FOX-7), adsorption and dissociation, density functional theory.

Résumé : En appliquant l'approximation du gradient généralisé de la théorie de la fonctionnelle de la densité, on a étudié l'adsorption et la décomposition de la molécule de FOX-7 sur des agrégats Al_{13} . Les grandes forces d'attraction entre la molécule de FOX-7 et les atomes d'aluminium induisent la rupture de la liaison N–O du FOX-7. Ensuite, les atomes d'oxygène dissociés et les fragments radicalaires du FOX-7 oxydent les agrégats d'aluminium. L'énergie d'adsorption la plus élevée est égale à $-1020,4$ kJ/mol. Nous avons également étudié trois chemins de réaction d'adsorption de la molécule de FOX-7 sur les agrégats Al_{13} en configuration A. Les énergies d'activation pour les étapes d'adsorption sont de 0,2, 11,4 et 10,2 kJ/mol, respectivement. En outre, Al_{13} est plus actif que la surface Al(111) et l'agrégat Al_{13} réduit mieux la barrière d'adsorption du FOX-7 sur la surface aluminium. Les constantes de vitesse des trois chemins d'adsorption augmentent quand la température augmente dans la plage de 275 à 500 K. [Traduit par la Rédaction]

Mots-clés : agrégat Al_{13} , 1,1-diamino-2,2-dinitroéthylène (FOX-7), adsorption et dissociation, théorie de la fonctionnelle de la densité.

Introduction

Powderized aluminum is the most commonly used metallic additive in rocket propellant formulations to improve the performance of high energetic ingredients. Aluminum powder 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.¹ The efficiency of such processes depends on the size of the aluminum particles. Because the burn rates of aluminum powders can be accelerated by reducing the size of the aluminum particles,² aluminum clusters can produce dramatic improvements in the performance of some energetic ingredients because of their large surface area.³ Among aluminum clusters, Al_{13} is a well-known magic cluster and its geometric structure is remarkably stable.⁴

1,1-Diamino-2,2-dinitroethylene (FOX-7) is a novel high energetic ingredient with high thermal stability (decomposes only above 220 °C) and low sensitivity to impact and friction.⁵ Over the past decades (first synthesized in 1998),^{5,6} 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.⁷ For example, Sorescu has performed classical and quantum-mechanical investigation on crystalline FOX-7.^{7a} Ju et al.

have investigated theoretically the intermolecular interaction in the dimer and the bulk state of FOX-7 as well as the molecule structure at the DFT-B3LYP/6-311++G** level.^{7b} Evers et al. have also studied the α - β phase transition in FOX-7 by single-crystal X-ray investigations at five different temperatures (200–393 K).^{7c} 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.^{7d} As aluminum clusters are the most commonly used in solid propellants, it is important to understand their reaction with the FOX-7 molecule. Up to now, some researchers have carried out studies of the behaviors of FOX-7 on metal surfaces. Sorescu et al. used the first-principles method to calculate the adsorption of FOX-7 molecules on the α - Al_2O_3 (0001) surface.^{7a,8} They also studied five adsorption configurations of FOX-7 on the Al(111) surface and discussed the geometries and energies.⁹ Recently, we also studied the adsorption and decomposition of FOX-7, RDX, and nitroamine molecules on the Al(111) surface by density functional theory (DFT).¹⁰ Oxidation of the aluminum surface readily occurs by partial or complete dissociation of the oxygen atoms from the NO_2 groups in FOX-7 and nitroamine. In the case of dissociative chemisorption, abstraction of one or both oxygen atoms of a nitro group by aluminum surface atoms was the dominant mechanism.

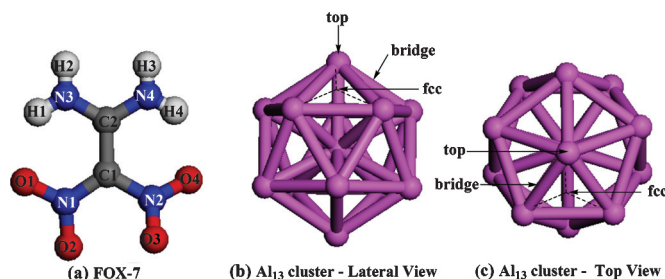
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C.-C. Ye and X.-H. Ju. Key Laboratory of Soft Chemistry and Functional Materials of MOE, School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, P.R. China.

F.-Q. Zhao and S.-Y. Xu. Science and Technology on Combustion and Explosion Laboratory, Xi'an Modern Chemistry Research Institute, Xi'an 710065, P.R. China.

Corresponding author: Xue-Hai Ju (e-mail: xhju@mail.njust.edu.cn).

Fig. 1. (a) FOX-7 molecule; (b) lateral view of the cluster model of Al_{13} ; (c) top view of Al_{13} . Surface sites are depicted.



What is the difference when the $\text{Al}(111)$ surface is replaced by nano-sized aluminum particles? To answer this question, we investigated the interactions between FOX-7 and the Al_{13} cluster. Here, the Al_{13} cluster was used as a model of nano-sized aluminum particles. We reported nine adsorption configurations of FOX-7 and the Al_{13} cluster. In addition to studying the geometries and energies of adsorptions, we investigated the density of states.

Computational procedures

In view of the fact that the DFT calculations were well employed to investigate the chemisorption and dissociation pathways of NO on the Rh surfaces¹¹ as well as H_2S on the closed packed surfaces of a number of important noble metals and transition metals,¹² we studied the decomposition mechanism between the FOX-7 molecule and the Al_{13} cluster by the DFT method. Standard DFT calculations were performed using the *DMol3*¹³ module. All geometries and energies were calculated with generalized gradient approximation using the functional PW91¹⁴ in combination with the double numerical polarized basis set. The computationally economical double numerical polarized basis set was comparable in size with the Gaussian-type 6-31G(d,p) basis set and has been found to give similar performance for aluminum cluster geometries and binding energies.¹⁵

The molecule structure of FOX-7 and the Al_{13} cluster are shown in Fig. 1, and the adsorption sites (top, bridge, and fcc) are cited in Fig. 1 as well. In all *DMol3* calculations, all of the equilibrium geometries were optimized in a large cell of $10 \text{ \AA} \times 10 \text{ \AA} \times 25 \text{ \AA}$. All atomic positions in Al_{13} clusters and adsorption geometries were relaxed in three directions of space based on the geometry optimization criterion (RMS force of $0.002 \text{ au/\AA}$ and RMS displacement of $0.005 \text{ \AA}$). The calculation of total energy and electronic structure was followed by geometry optimization with an SCF tolerance of $1 \times 10^{-5} \text{ au}$. A Fermi smearing of 0.005 Ha and the real-space global orbital cutoff of $4.9 \text{ \AA}$ were used to improve the computational performance. The quality mesh size for numerical integration was chosen. The unrestricted approach was applied for the low-spin state, that is, singlet for systems with even-number electrons and doublet for systems with odd-number electrons. These low-spin states are in general energetically preferable.

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

$$(1) \quad E_{\text{ads}} = E_{(\text{FOX-7} + \text{Al}_{13})} - (E_{\text{FOX-7}} + E_{\text{Al}_{13}})$$

where $E_{(\text{FOX-7} + \text{Al}_{13})}$ is the total energy of the adsorbate/ Al_{13} system after the FOX-7 molecule is absorbed by Al_{13} and $E_{\text{FOX-7}}$ and $E_{\text{Al}_{13}}$ are the single-point energy of the FOX-7 molecule and Al_{13} , respectively.

A transition state (TS) search was conducted using a combination of the linear synchronous transit and quadratic synchronous transit methods.¹⁶ Vibrational frequency analysis was performed

to characterize all stationary points reported here as true minima or transition structures. TS optimization and TS confirmation calculations were performed to confirm that all transition structures were truly linked to the corresponding reactant and products.

The activation energy is defined as following:

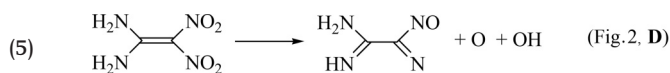
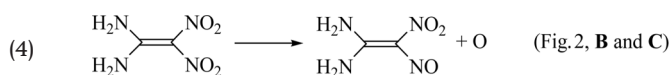
$$(2) \quad E_a = E_{\text{TS}} - E_r$$

where E_{TS} is the energy of transition state and E_r is the sum of the energies of reactants.

Results and discussion

There exist both physical and chemical adsorptions, and the latter result in the decomposition of the FOX-7 molecule on the Al_{13} cluster. There are three cases (eqs. 3–5):

(3) The FOX-7 molecule is nondissociative (Fig. 2, A and E)



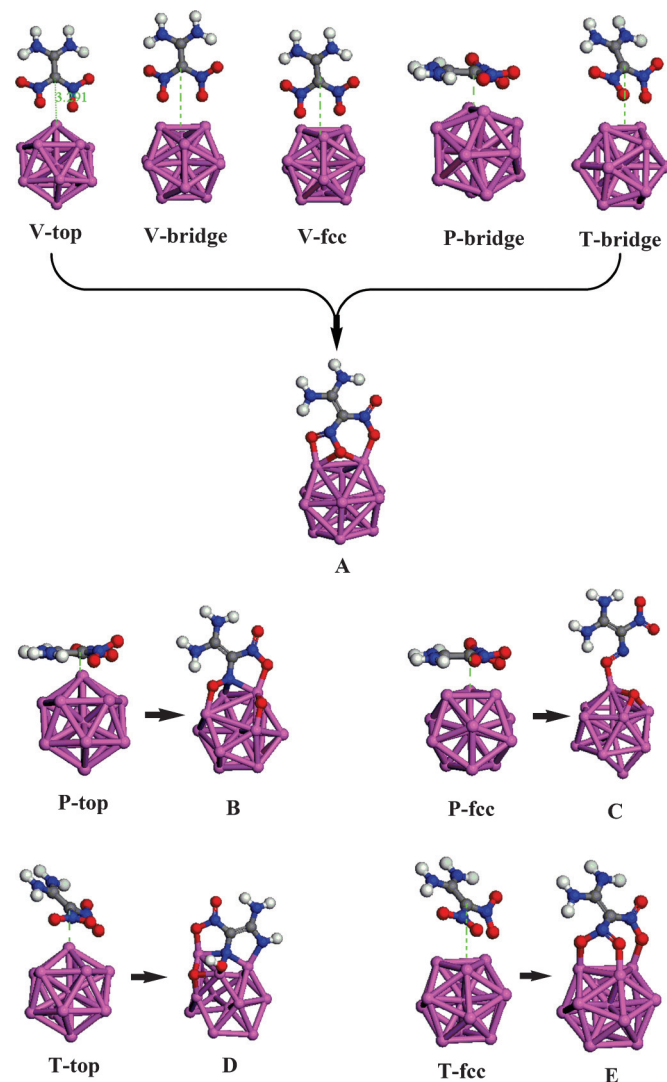
According to the orientation of the plane of FOX-7 molecule relative to the Al_{13} cluster, V, P, and T denote vertical, parallel, and tilted adsorptions of FOX-7, respectively. The lateral views of the optimized adsorption configurations after full relaxation of the atomic positions are shown in Fig. 2.

Geometries and energies

The adsorption energies were calculated with eq. 1 and are given in Table 1. As Fig. 2 shows, the V-top, V-bridge, V-fcc, P-bridge, and T-bridge configurations obtain the same product A after adsorption and lead to the formation of four Al–O bonds with lengths of 1.848 to 2.005 $\text{\AA}$. The distortion of the FOX-7 molecule is small, and all of the bond angles and lengths change slightly except that the lengths of two N–O bonds (N1–O1 and N1–O2) change from 1.266/1.228 $\text{\AA}$ to 1.448/1.432 $\text{\AA}$. As the formation of four Al–O bonds, these two N–O bonds significantly increase. As Fig. 2 shows, the P-top configuration obtains the product B after adsorption, in the B configuration, and one oxygen atom of the nitro group is dissociated. The FOX-7 fragment and dissociated O2 atoms interact strongly with the Al_{13} cluster, which leads to the formation of four Al–O bonds and two Al–N bonds. Product C comes from the P-fcc configuration, and the adsorptions lead to dissociation of one of the nitro oxygen atoms. The oxygen atoms from the ruptured radicals ($\text{RNO} + \text{O}$) interact strongly with neighboring aluminum atoms to form four Al–O bonds in lengths of 1.834–1.922 $\text{\AA}$. The next configuration, D, gives the case as formula 5 in which the adsorption of FOX-7 leads to the formation of a total of four Al–O bonds, four Al–N bonds, and one O–H bond. Finally, in E, our study indicated that the FOX-7 molecule rotates to maximize the interaction with the Al_{13} cluster during the optimization. As a result, the FOX-7 molecule is nondissociative, as shown in formula 3. Configuration E illustrates that the FOX-7 molecule tilted adsorbed on the Al_{13} , and each oxygen atom forms an Al–O bond with an aluminum atom underneath (bond lengths are in the range of 1.819–1.858 $\text{\AA}$), except the O4 atom.

As can be seen from Table 1 and Fig. 2, the E_{ads} value of -228.3 kJ/mol for E is the smallest, since only three Al–O bonds formed and the FOX-7 molecule in E does not dissociate. A is similar to E: the E_{ads} value of -266.5 kJ/mol for A is the second smallest, since four Al–O bonds formed and the FOX-7 molecule does not dissociate either. Otherwise, when one nitro oxygen atom of the FOX-7 molecule is dissociated, the corresponding adsorption energies are larger. The

Fig. 2. Five adsorption configurations of FOX-7 on the Al_{13} clusters. V, P, and T denote vertical, parallel, and tilted adsorptions of FOX-7, respectively.



adsorption energies of **B** and **C** are -362.2 and -594.5 kJ/mol, respectively. Although the decomposition products of **B** and **C** are similar, the corresponding adsorption energies are different, since there are two additional Al–N bonds in **B** as compared with **C** (E_{ads} is almost 232.3 kJ/mol larger). The largest adsorption energy is -1020.4 kJ/mol for the **D** configuration, as shown in Fig. 2.

As a whole, when the decomposition products of the FOX-7 molecule in the **D** configuration are three radical species, their adsorption energies are much larger than those of two radical species and nondissociative configurations. Herein, these radical species readily oxidize the aluminum and form strong Al–O and Al–N bonds. In a word, for all of the abovementioned configurations of FOX-7 except **A** and **E**, the FOX-7 molecule is decomposed to different products when initially positioned on different 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 nitro nitrogen atoms with the aluminum atoms. The fact that the dissociation of the nitro group on the Al_{13} cluster was observed in simple energy minimizations suggests that the uncoated aluminum surface is very active to the electron acceptors, as further discussed below.

Density of state (DOS)

The electronic structures are 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 aluminum surface initiates from the rupture of N–O bonds and results in the formation of Al–O and Al–N bonds. Therefore, the knowledge of their electronic properties appears to be useful for further understanding the behaviors of the FOX-7 molecule on the aluminum cluster. Figure 3 displays the calculated partial DOS (PDOS) from -0.6 to 0.2 Ha for all adsorption configurations. For comparison, the PDOS of the free FOX-7 molecule and Al_{13} are also shown in Fig. 3. The electronic structures vary with adsorption configurations due to the differently dissociated products of the FOX-7 molecule.

As can be seen from Fig. 3, compared with the free FOX-7 molecule and original Al_{13} cluster, the PDOS peak changes greatly in the **A** to **E** configurations. The values of the peaks become much smaller, while the number of peaks increases, which indicates that the stability of FOX-7 and Al_{13} declines greatly and the activity increases. For the **A** configuration, after adsorption, the highest PDOS peaks of oxygen atoms become smaller and shift down -0.10 Ha, and the peaks become smoother, whereas the number of PDOS peaks becomes more in the range of -0.4 to 0 Ha. Compared with the free FOX-7 molecule, the distortion of the adsorbed FOX-7 is very small (see Fig. 2) and the highest PDOS peaks of oxygen atoms overlap the peaks of aluminum atoms at -0.15 to -0.10 Ha completely. Hence, the shift of energy can be attributed to the formation of the four Al–O bonds. For **B**, the highest peaks of oxygen atoms shift to -0.15 Ha and become lower and wider. For nitrogen atoms, because of two Al–N bonds formed, the PDOS peaks overlap most peaks of aluminum atoms in range of -0.35 to -0.10 Ha. The PDOS of oxygen atoms in the **C** configuration is similar to that in **A**; this is because there are four Al–O bonds formed in these two configurations. In the **D** configuration, with three Al–N bonds formed, three PDOS peaks for nitrogen atoms overlap the corresponding peaks of aluminum atoms in the range of -0.35 to -0.10 Ha. Finally, for the **E** configuration, the highest PDOS peak of O atoms shifts down -0.10 Ha and splits into two peaks. As Fig. 3 shows, the highest peak of aluminum atoms at Fermi energy (0 Ha) and the peak of **E** are the highest compared with the other four configurations (**A**–**D**), while the E_{ads} value of **E** (-228.3 kJ/mol) is the smallest in the five configurations.

From the above analysis, we can conclude that when bonding interactions between the adsorbates and the aluminum cluster are strengthened, the PDOS shifts and becomes smoother with respect to those of the isolated FOX-7 molecule. These explain the dissociation of N–O bonds and the formation of strong Al–O and Al–N bonds. In addition, the lower the PDOS peak value of aluminum atoms, the more active and greater the E_{ads} value of the adsorbate/ Al_{13} system.

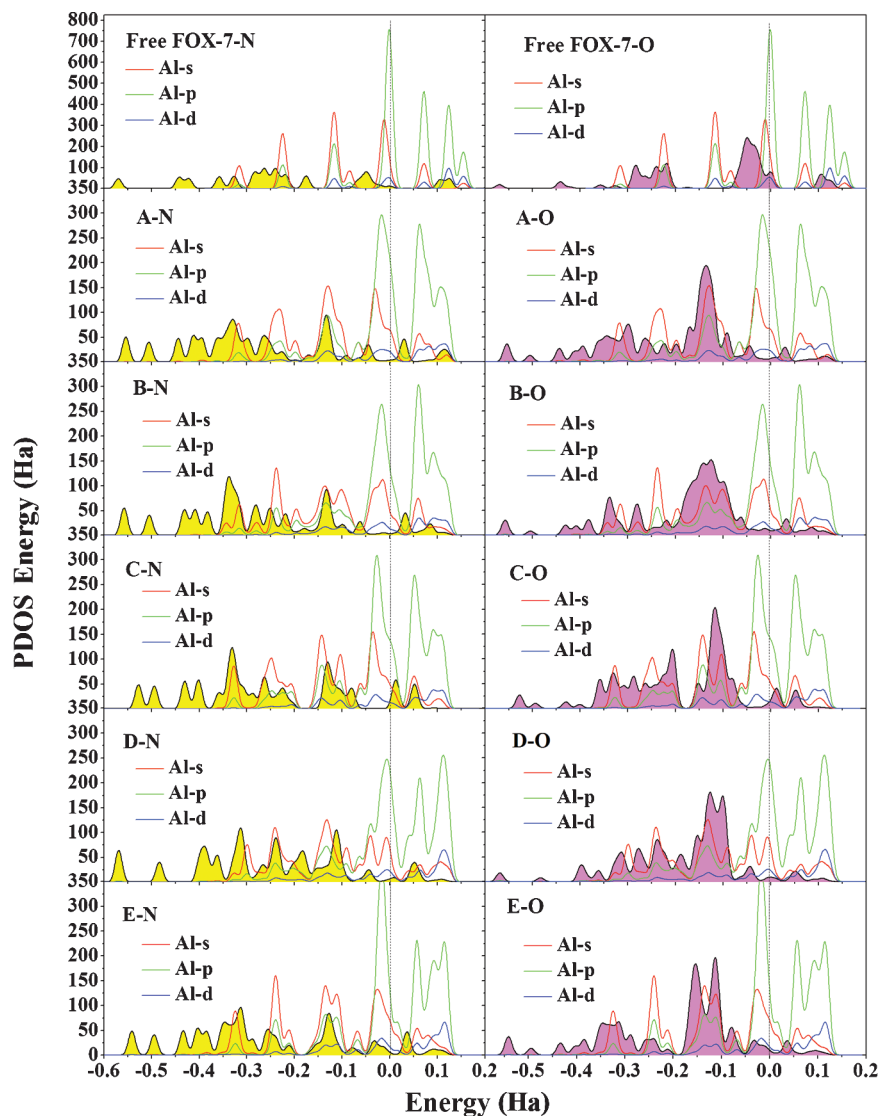
Mechanism of dissociation

The reactants, transition state, and products of three paths for the adsorption reaction of the **A** configuration are depicted in Fig. 4 on which the reactants and transition state are denoted with **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 are tabulated in Table 1 and shown in Fig. 4.

For these three reaction paths, the FOX-7 molecule does not decompose. As compared with the local minimum of physical adsorption, the FOX-7 molecule moves down towards the aluminum cluster and interacts with two-edged aluminum atoms of Al_{13} . As a result, the FOX-7 molecule aslope moves to the Al_{13} cluster. Compared with the initial state, the closest distance between oxygen atoms and aluminum atoms decreases greatly

Table 1. Adsorption energies (E_{ads}), activation energies (E_a), and adsorption sites of FOX-7 on the Al_{13} cluster.

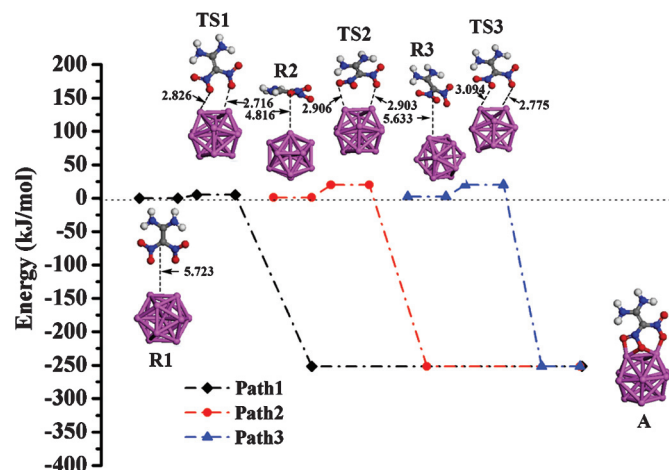
Relation of the C–C bond with the Al_{13} cluster	Initial configuration	Final configuration	Adsorption site	E_{ads} (kJ/mol)	E_a (kJ/mol)
Vertical	V-top	A	top	–266.4	0.2
	V-bridge	A	bridge	–266.6	
	V-fcc	A	fcc	–266.5	
Parallel	P-top	B	top	–594.5	11.4
	P-bridge	A	bridge	–266.6	
	P-fcc	C	fcc	–362.2	
Tilted	T-top	D	top	–1020.4	10.2
	T-bridge	A	bridge	–266.5	
	T-fcc	E	fcc	–228.3	

Fig. 3. PDOS for the FOX-7 molecule and the absorbed aluminum atoms. The area filled with yellow color represents the PDOS of nitrogen atoms and the area filled with pink color represents the PDOS of oxygen atoms (color in the online version only). The Fermi energy is set to zero.

(2.716 Å in TS1, 2.903 Å in TS2, and 2.775 Å in TS3). As the reaction goes on, the oxygen atoms oxidize the Al_{13} cluster. Four Al–O bonds are generated and product A comes into being. As can be seen from Table 1 and Fig. 4, the activation energies are 0.2 kJ/mol (path 1), 11.4 kJ/mol (path 2), and 10.2 kJ/mol (path 3). This indicates that all three processes are very easy to take place, and when the

FOX-7 molecule is initially vertical to the Al_{13} cluster, the adsorption reaction is slightly easier to occur than parallel or tilted configurations. Compared with the activation energies of the FOX-7/ $\text{Al}(111)$ system (in the range of 49.6–428.8 kJ/mol),^{10a} the activation energy of the FOX-7/ Al_{13} system is lower. Therefore, it can be concluded that the interacting of the FOX-7 molecule and Al_{13} cluster

Fig. 4. Relative energy profile for three paths of FOX-7 adsorption on the Al_{13} clusters in the A configuration and lateral views of the FOX-7/ Al_{13} system, R and TS denote the reactant and transition state, respectively.



is much easier to occur than for the FOX-7/ $\text{Al}(111)$ system. The nano-sized aluminum particle (Al_{13}) is more active than the $\text{Al}(111)$ surface and the Al_{13} cluster performs better in decreasing the adsorption barrier of FOX-7 on the aluminum surface as well.

Rate constants of the adsorption process

The energies and molecular parameters obtained from the DFT calculations can be applied to the rate constant calculation. The rate constants of the initial adsorption process of the FOX-7/ Al_{13} system was predicted according to the transition state theory of Eyring as follows:

$$(6) \quad k = \frac{k_B T}{h} \left(\frac{p^\circ}{RT} \right)^{1-n} \exp \left[\frac{\Delta_r^\ddagger S_m^\circ(p^\circ)}{R} \right] \exp \left[-\frac{\Delta_r^\ddagger H_m^\circ(p^\circ)}{RT} \right]$$

where k_B is the Boltzmann constant, h is Planck's constant, $\Delta_r^\ddagger S_m^\circ(p^\circ)$ and $\Delta_r^\ddagger H_m^\circ(p^\circ)$ are the standard molar entropy and standard molar enthalpy of activation at the condition of $p^\circ = 100$ kPa, respectively, and n is the sum of computation coefficients for all reactants. For the initial decomposition reaction, $n = 2$.

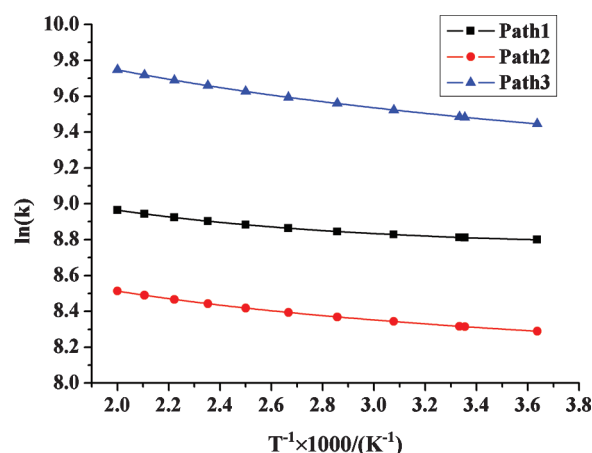
Figure 5 shows the rate constants over the temperature range 275–500 K. As seen in Fig. 5, there is no crossover among the three lines at 275–500 K. The rate constant of path 3 is larger than the rate constants of other two paths, and the rate constants of the three paths are more than 3981.6/s. This indicates that the three reactions occur rapidly. As the temperature increases, the rate constants of the three paths increase. Meanwhile, the absolute value of the slope increases with the temperature increasing as well. Therefore, it can be concluded that the value of $\Delta_r^\ddagger H_m^\circ(p^\circ)$ becomes larger as the temperature increases.

Conclusions

Based on the investigation of the FOX-7 molecule on the Al_{13} cluster, the major findings can be summarized as follows.

- (1) There exist chemical adsorptions when the FOX-7 molecule approaches the Al_{13} cluster. The Al_{13} is readily oxidized by the oxygen-rich nitro group of the dissociatively adsorbed FOX-7. Dissociations of the N–O bonds of the nitro group result in the formations of strong Al–O and Al–N bonds. As the number of formations of Al–O and Al–N bonds increases, the corresponding adsorption energy increases greatly.

Fig. 5. Rate constants of three adsorption reactions: path 1, path 2, and path 3.



- (2) The PDOS projections on the nitrogen and oxygen atoms for the dissociated N–O bond adsorptions occur with an obvious shift of peaks, which infers that energy bands become broad and the interactions of chemical bonds are strengthened. In addition, the lower the PDOS peaks of aluminum atoms, the larger the adsorption energies and more active for the FOX-7/ Al_{13} system.
- (3) The adsorption processes on the Al_{13} cluster are predicted to be exothermic. The activation energy for studied three paths of the A configuration are 0.2, 11.4, and 10.2 kJ/mol, respectively, and when the FOX-7 molecule is initially vertical to the Al_{13} cluster, the adsorption reaction is slightly easier to occur than parallel or tilted configurations. As compared with previous work,^{10a} it can be concluded that Al_{13} is more active than the $\text{Al}(111)$ surface and performs better in decreasing the adsorption barrier of FOX-7 on the aluminum surface as well.
- (4) The rate constant of path 3 is larger than the rate constants of the other two paths at 275–500 K. The rate constants increase as temperature increases. Therefore, it can be concluded that the value of $\Delta_r^\ddagger H_m^\circ(p^\circ)$ becomes larger as the temperature increases.

Acknowledgements

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