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Decomposition mechanism of dihydroxylammonium 5,5'-bis(tetrazole)-1,1'-diolate on Al(111) surface by periodic DFT calculation

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Abstract: The generalized gradient approximation (GGA) of density functional theory (DFT) methods are employed to investigate the decomposition of TKX-50 molecule on the Al(111) surface. The calculation employs an Al supercell slab model and periodic boundary conditions. Five kinds of adsorption configurations for TKX-50 on Al surface are studied. The TKX-50 is adsorbed on Al surface to form the N-Al, O-Al and OH-Al bonds. The adsorption energies are in range of −113.15 to −1334.40 kJ/mol. The activation energies of all configurations are in range of 100.34−354.10 kJ/mol. The N1-N2 ruptures in V1 and N2-N3 ruptures in V2 are easy to occur. The activation energies (100.34, 108.06 kJ/mol) of these two bonds rupture are less than that of pure TKX-50 (161.58, 215.99 kJ/mol). Al atoms promote the breaking of the tetrazole ring of TKX-50. The quantities of electron transfer from Al atoms to TKX-50 are in range of 1.42−4.90 e.

Keywords: TKX-50; adsorption; transient states; activation energy; charge transfer.

INTRODUCTION

Powderized aluminum (Al) as a kind of active metal is widely used in the energetic materials (EMs) because of its excellent combustion performance. In the development and application of propellants, adding appropriate amount of aluminum powder to the propellant may efficiently improve its exothermic property of combustion, burning rate and impact effect.¹⁻³ The effects mentioned above depend on the size of Al particles. The smaller the Al particles, the more obvious the improvement of explosive performance. Some researchers indicated that the Al nanopowder with high surface area can obviously enhance the performance of EMs.⁴

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TKX-50, chemical name of dihydroxylammonium 5,5'-bis(tetrazole)-1,1'-diolate, is a newly synthesized nitrogen-rich energetic salt.\(^5\) TKX-50 possesses broad application prospects in EMs on account of its outstanding performance: high energy storage, low impact, sensitivity and low toxicity.\(^6\) Hence, TKX-50 may substitute some traditional explosives in propellants. The thermal decompositions of gaseous and solid-phase TKX-50 have been investigated experimentally and theoretically. For instance, Qi An et al. found that the initial thermal decomposition of TKX-50 involves ring breaking to release nitrogen based on the quantum calculations.\(^7\) Bing Y. et al. concluded that nitrogen products are released by the opening of the tetrazole of TKX-50 in its excited state.\(^8\) Wang et al. first time proved that diammonium 5,5'-bistetrazole-1,1'-diolate is the primary decomposition product of TKX-50\(^9\). However, the decomposition of TKX-50 on Al surface has not comprehensive. The Al(111) surface is known as easily exposed and easily oxidized.\(^10-11\) Hence, we studied the interaction mechanism between the energetic compound of TKX-50 and the Al(111) surface theoretically. Five kinds of adsorption and decomposition configurations of TKX-50 on Al(111) surface were investigated. The stable geometries and energies in the adsorption and decomposition process, the electron transfer was analyzed.

**COMPUTATIONAL METHODS**

The CASTEP module of Materials Studio 7.0 was employed to perform all calculations.\(^12\) The density functional theory methods are used widely to calculate the surface interaction.\(^13-15\) The DFT methods are suitable way to study the adsorption behavior of molecule on surface.\(^16-20\) The wave function of calculation is based on the Vanderbilt-type ultrasoft pseudopotentials and a plane-wave expansion.\(^21\) Exchange and correlation were treated with the generalized gradient approximation (GGA). Compared with local density approximation (LDA), GGA can take into account the non-uniformity of electron density in the real system. But LDA uses a uniform electron gas model. It can be used to describe a system in which the electron density does not change very much in space. Hence, The calculation results of LDA exist serious errors for systems with fewer electrons such as the transition state in a chemical reaction and the calculation of binding energy. However, GGA can describe appropriately this system above since it consider the gradient of density. The functional form of Perdew, Burke, and Ernzerh (PBE) and a density-mixing scheme are used to obtain the electronic wave functions.\(^22-23\) The Broyden, Fletcher, Goldfarb, and Shannon (BFGS) methods were used to relax the structures.\(^24\) The cutoff energy of plane waves was set to be 340 eV. The Monkhost-Pack scheme is used to perform Brillouin zone sampling. The grid parameters of k-point are set as \(3\times3\times3\). The value of kinetic energy cutoff and the k-point grid ensure the convergence of total energies.

A slab model with periodic boundary conditions represents the Al surface (Fig 1). In view of the balance of both computational efficiency and precision, a \(4\times5\) supercell with three layers containing 60 Al atoms was constructed to study the decomposition process of TKX-50 molecular on the Al(111) surface. The slabs were separated by 16 Å of vacuum along the c-axis direction with a TKX-50 molecular on the top of the slab. The lattice parameters of \(a\times b\times c\) are 11.43×14.29×20.67 Å.
In order to confirm the accuracy of the calculation method, the functionals form of Perdew–Burke–Ernzerhof (PBE), Perdew–Wang 91 (PW91), revised Perdew–Burke–Ernzerhof (RPBE), Wu–Cohen (WC) are use to optimize the isolated TKX-50 molecule in a box with dimensions of 11.43×14.29×20.67 Å and Al cell. There in, The Al original cell is obtained from COD database. The equilibrium structure parameters calculated by these four functionals are compared with the experiment datas. TABLE SI and TABLE SII of supplementary file present the equilibrium structure parameters of TKX-50 and Al cell, respectively. It can be observed that the structure parameters calculated by PBE functional are closest to the experimental data. For instance, the calculation results show that the crystal cell parameters optimized is 4.058×4.058×4.058 Å. The computational lattice constants are close to the experimental value (4.050×4.050×4.050 Å), indicating that the present method can simulate the structural properties of bulk aluminum properly. These tests also verify the accuracy of the calculation method for the adsorption between TKX-50 molecular and Al (111) surface, such as the optimum cutoff energy and k-points for calculations. The good agreement between simulation results of aluminum and the TKX-50 molecule with the experiment suggest that the computation method is suitable for the simulation of TKX-50 molecular adsorption and decomposition behavior on the Al(111) surface.

For the adsorption configurations, the adsorption energy ($E_{ad}$) was calculated according to the equation:

$$E_{ad} = E_{(adsorbate + slab)} - E_{(molecule + slab)}$$

where $E_{(adsorbate + slab)}$ is the total energy of the adsorbate/Al-slab system after TKX-50 molecular absorbed onto the Al-slab; $E_{(molecule + slab)}$ is the single-point energy of the TKX-50/Al-slab system but without interactions between TKX-50 molecule and the Al-slab surface.

The LST/QST method was used to search the transition states (TS). Firstly, the linear synchronous transit (LST) maximization was performed, then the energy along the reaction pathway was minimized. The quadratic synchronous transit (QST) maximization was performed by the TS approximation obtained in that way. Another conjugate gradient minimization was performed from the point. The cycle was repeated until a stationary point was located. The convergence criterion of the transition state calculations was set to 0.25 eV/Å for the root mean-square force. The activation energy is defined as:

$$E_a = E_{TS} - E_R$$

where $E_{TS}$ is the energy of transition state, $E_R$ is the sum of energies of reactants.
RESULTS AND DISCUSSION

Decomposition configuration and adsorption energy

On the basis of the initial orientation of tetrazole ring of TKX-50 relative to the Al(111) surface, five kinds of configurations (P, T1, T2, V1, V2) are defined. P is a parallel to the Al(111) surface, T1 and T2 are tilt, V1 and V2 are vertical. The structure of TKX-50 and its atomic number are given in Fig 2. The adsorption configurations of decomposed TKX-50 molecule are shown in Fig 3. Table I presents the adsorption energies calculated by Eq (1).

![Fig 2. Molecular structure of TKX−50](image)

![Fig 3. Reactants, transition states and products of TKX−50 decomposition process on Al(111) surface (bond lengths are in Å)](image)
The adsorption energy ($E_{ad}$) and amount of charge transfer ($\Delta Q$) from Al surface to TKX-50 in the decomposition process.

<table>
<thead>
<tr>
<th>Configurations</th>
<th>$E_t$ / kJ·mol$^{-1}$</th>
<th>$E_{ad}$ / kJ·mol$^{-1}$</th>
<th>$\Delta Q_{\text{Muliken}} / e$</th>
<th>$\Delta Q_{\text{Hartree-Fock}} / e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>145.69</td>
<td>-239.01</td>
<td>1.70</td>
<td>0.31</td>
</tr>
<tr>
<td>T2</td>
<td>287.52</td>
<td>-383.39</td>
<td>2.15</td>
<td>0.55</td>
</tr>
<tr>
<td>V1</td>
<td>100.34</td>
<td>-113.15</td>
<td>1.42</td>
<td>0.28</td>
</tr>
<tr>
<td>V2</td>
<td>108.06</td>
<td>-222.96</td>
<td>1.81</td>
<td>0.31</td>
</tr>
<tr>
<td>P</td>
<td>354.10</td>
<td>-1334.40</td>
<td>4.90</td>
<td>1.35</td>
</tr>
</tbody>
</table>

$^a$: Tilt, V: Vertical, P: Parallel.

As shown in Fig. 3, N$_1$-N$_2$ bond has broken in T1 configuration, N$_1$ and N$_2$ atoms interact with Al atoms to form six Al-N bonds in length of 1.962-1.990 Å. The O$_1$ atom forms an Al-O bond with Al atom, its bond length is 1.993 Å. The H atom of hydroxylammonium transferred to the N$_4$ atom to form N-H bond. In T2 configuration, the O$_1$ atom is detached from the tetrazole ring and adsorbed on the Al(111) surface. O$_1$ atom interacts with neighbouring Al atoms to form three Al-O bonds in lengths of 1.832-1.868 Å. Moreover, N$_1$-N$_2$ bond ruptures, N$_1$ and N$_2$ atoms interact with Al atoms to form four Al-N bonds totally, among these Al-N bonds, N$_1$ atom interacts with Al atom to form one Al-N bond with length of 1.798 Å, N$_2$ atom interacts with Al atoms to form three Al-N bonds in length of 1.945-1.958 Å. In V1 configuration, the N$_1$-N$_2$ bond ruptures. N$_1$, N$_2$ and N$_3$ atoms interact with Al atoms to form four Al-N bonds in length of 1.883-1.952 Å. N$_2$-N$_3$ bond ruptures in the V2 configuration. O$_1$, N$_2$ and N$_3$ atoms interact with Al atoms to form seven Al-X (X is O or N atom) bonds. These bonds include an Al-O bond with length of 1.993 Å and six Al-N bonds in length of 1.962-1.989 Å. In P configuration, O$_1$ and O'$_1$ atoms dissociate from tetrazole ring and adsorb on the Al(111) surface to form six Al-O bonds in length of 1.843-1.866 Å. Meanwhile, OH- also dissociated from the hydroxy-/ammonium and interacts with Al atom to form an OH-Al bond with length of 1.748 Å. The N1-N2 bond ruptures, then N$_1$ and N$_2$ atoms interact with Al atoms to form six Al-N bonds in lengths of 1.926-2.019 Å. The N$_1'$ atom also interacts with Al atoms to form Al-N bond with length of 1.963 Å. In all absorption configurations, due to bonding with the dissociated atoms of TKX-50, the Al atoms on the Al(111) surface deviate significantly from the original position.

As can be seen from Table I, the $E_{ad}$ value of V1 (−113.75 kJ/mol) is the smallest in all adsorption configurations, since there are only four Al-N bonds in V1 configuration. The quantities of bonding are the minimum in all adsorption configurations. Although the atom bonding types and quantities of V2 and T1 are the same, the $E_{ad}$ value of T1 configuration (−239.01 kJ/mol) is slightly larger than V2 (−222.96 kJ/mol) since the bond ruptures type of T1 is difference with V2 configurations. Comparing T1 and T2 configurations, although the number of Al-N bonds of T2 is less than that of T1, the number of Al-O bonds is more than
that of T1. Consequently, the $E_{ad}$ of T2 ($-383.39$ kJ/mol) is larger than that of T1. The $E_{ad}$ value of P is the largest ($-1334.4$ kJ/mol) among all configurations, since P includes the maximum number of Al-N and Al-O bonds.

As a whole, the tetrazole ring of TKX-50 molecule can rupture in the adsorption process. The O atoms can dissociate from tetrazole ring due to the attraction of Al atoms. Subsequently, O and N atoms of TKX-50 molecule interact with Al atoms to form Al-N and Al-O bonds. With the number of Al-X bond increases, the absolute values of adsorption energies increase.

**Reaction mechanism**

The reactants (R), transition state (TS) and products for the surface reaction of TKX-50 molecule on the Al(111) were depicted in Fig 3. The detailed energy profile for dissociation of TKX-50 on the Al(111) surface were presented in Fig 4. The activation energies were tabulated in Table I.

![Fig 4. Relative energy profile for TKX−50 decomposition on the Al(111) surfaces](image)

As can be seen from Fig 3, N1, N2 and N3 atoms interacts with several Al atoms that deviate from the Al surface obviously in V1TS configuration. The length of N1-N2 bond increases to 1.926 Å. The activation energy ($E_a$) of this transition state is 108.06 kJ/mol, indicating that this process is relatively easy to occur. In the subsequent decomposition process, the length of N1-N2 atom continue to increase until N1-N2 bond is completely broken, N2 and N3 atoms are getting closer to the Al surface to form Al-N bonds. In V2TS, the N2-N3 bond increases to 1.936 Å since N3 and N4 atoms interact with Al atoms. Meanwhile, several Al atoms on Al(111) surface also deviate from the initial location. The activation energy ($E_a$) of V2TS is 100.34 kJ/mol, indicating that this reaction is easy to occur. The length of N3-N4 bond increases to 1.956 Å in T1TS configuration. The interaction between N3, N4 and Al atoms make several Al atoms deviate from the initial Al surface. The H1A atom moves away from N5 atom to N4 atom. In the subsequent decomposition process, the distance between
N₁ and N₄ atoms continue to increase, N₃ and N₄ atoms are getting closer to the Al surface until the Al-N bond forms. The O₁ atom also interact with Al atom to form Al-O bond. In T₂RS configuration, the O₁ atom move away from N₁ atom. The distance of O₁ and N₁ extends to 1.877 Å. Meanwhile, the length of N₁-N₂ bond increases to 1.820 Å. Subsequently, O₁ atom is getting closer to the Al surface until three Al-O bonds are generated. The N₁ and N₂ atoms also form Al-N bond with Al atoms. The activation energy (Eₐ) of T₂RS is 287.52 kJ/mol, indicating that this reaction is hard to occur. The reaction of P₃S needs the largest activation energy (Eₐ = 354.10 kJ/mol), indicating that this process is difficult to occur. In P₃S configuration, several Al atoms deviate from the Al surface obviously due to their interactions with TKX-50 molecule. The distance of O₁ and N₁ increases to 1.718 Å. The distance of O₁' and N₁' extends to 1.685 Å, the N₂-N₃ bond increases to 1.665 Å. The OH- moves away from the hydroxyl-ammonium. As the reaction goes on, O₁ and O₁' atoms separate completely from TKX-50 molecule and form Al-O bonds with Al atoms. The distance of N₁-N₂ continue to increase, N₁ and N₂ atom are getting closer to the Al surface and form Al-N bonds. OH- also interacts with Al atom and forms OH-Al bond.

By comparing with the paper on the study of TKX-50 decomposition [7], we found that the activation energy of N-N bonds rupture on the Al surface is reduced. For example, the activation energy of N₁-N₂ ruptures in pure TKX-50 molecule is 161.58 kJ/mol, but the activation energy of N₁-N₂ ruptures on the Al surface is 100.34 kJ/mol. In addition, the activation energy of N₂-N₃ ruptures on the Al surface (108.60 kJ/mol) is lower than that of pure TKX-50 molecule (215.99 kJ/mol). The results show that Al can obviously promote the breaking of the tetrazole ring of TKX-50.

Charge transfer

Muliken population and Hirshfeld population were used to analyze the charge transfer. Table I presents the total charge transferred from the aluminum surface to TKX-50 molecule. Although there are difference in the values of the both charges, the trend of charge is consistent. The result helps us to describe more accurately the relationship between reaction and charge transfer. In all adsorption configurations, the amount of charge transferred in P is largest; T₁ has the least amount of charge transferred. Table II and Table III show the Muliken atomic charges of TKX-50. By comparing the atomic charge before and after adsorption, we observed that the atomic charge varies significantly when the atom bonds with Al atom. The charges of atoms (N, O atoms) that bond to Al atom decline significantly, the charge of Al atom on the surface increase obviously. The more the number of Al-X (X is N or O atom) bonds formed in the Al surface, the more the electron transfer from Al surface to TKX-50 molecule. T₁ configuration only has four Al-N bonds, but T₂ includes one Al-O bond and six Al-N bonds. The number of charge transfer in T₂ is more than that of T₁. The
P configuration forms the largest number of Al-X bonds, so its charge transfer is the most. Although there are both N-N bond rupture and the formation of Al-N bond in V1 and V2 configurations, there is an O atom move to Al surface to form three Al-O bonds in V2 configuration, resulting the number of charge transfer in V2 is more than that of V1 configurations.

TABLE III. Atomic charge of hydroxylammonium anion in adsorption of Al(111)

<table>
<thead>
<tr>
<th>Configuration</th>
<th>O</th>
<th>O'</th>
<th>N</th>
<th>N'</th>
<th>H'</th>
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<tbody>
<tr>
<td>Initial</td>
<td>−0.55 −0.48 0.13 0.12 −0.11 −0.11 −0.11 −0.11 −0.11 −0.28 −0.29 0.24 0.30</td>
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<tr>
<td>T1</td>
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<tr>
<td>T2</td>
<td>−1.01 −0.49 −0.77 0.11 −0.85 −0.14 −0.13 −0.13 −0.12 −0.22 −0.28 0.22 0.30</td>
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<tr>
<td>V1</td>
<td>−0.56 −0.48 −0.31 0.12 −0.83 −0.13 −0.27 −0.07 −0.27 −0.27 0.27 0.36</td>
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<tr>
<td>V2</td>
<td>−0.64 −0.49 −0.12 0.11 −0.87 −0.14 −0.79 −0.09 −0.26 −0.29 0.22 0.32</td>
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<tr>
<td>P</td>
<td>−1.01 −1.03 −0.96 −0.42 −0.86 −0.13 −0.25 −0.11 −0.32 −0.33 0.12 0.23</td>
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TABLE II. Atomic charge of TKX-50 anion in adsorption of Al(111)

<table>
<thead>
<tr>
<th>Configuration</th>
<th>O</th>
<th>O'</th>
<th>N</th>
<th>N'</th>
<th>H'</th>
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<th>H'</th>
<th>H'</th>
<th>H'</th>
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<tbody>
<tr>
<td>Initial</td>
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<tr>
<td>T1</td>
<td>−0.65 −0.58 −0.70 −0.57 0.42 0.42 0.45 0.51 0.46 0.43 0.52 0.51</td>
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<tr>
<td>T2</td>
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<tr>
<td>V1</td>
<td>−0.63 −0.63 −0.67 −0.68 0.40 0.44 0.46 0.46 0.46 0.48 0.50 0.53</td>
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<tr>
<td>V2</td>
<td>−0.58 −0.63 −0.59 −0.69 0.42 0.44 0.51 0.47 0.41 0.48 0.47 0.52</td>
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<tr>
<td>P</td>
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CONCLUSION

TKX-50 decomposes easily in the adsorption process on the Al(111) surface. The decomposition initiates with the ruptures of N-N and N-O bonds. Subsequently, The N and O atoms interact with Al atoms to form Al-N and Al-O bonds. As the number of Al-N and Al-O bonds increase, the absolute value of adsorption energy increases correspondingly. The decomposition of TKX-50 on Al surface is exothermic. The activation energies are in range of 100.34-354.10 kJ/mol. The charge transfer is obvious after adsorption. The atomic charge varies significantly when it bonds with Al atom. As the number of bonds increase, the charge transfer increase.

Acknowledgements. Y Zhao gratefully thanks the Postgraduate Innovation Project of Jiangsu Province for partial financial support.
ИЗВОД
МЕХАНИЗАМ РАЗЛАГАЊА ДИХИДРОКСИАМОНИЈУМ-5,5'-БИС(ТЕТРАЗОЛ)-1,1'-ДИОЛАТА НА Al(111) ПОВРШИНИ ПРЕМА ПЕРИОДИЧНОМ DFT ИЗРАЧУНАВАЊУ

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Методе апроксимација уопштеног градијента (GGA) из теорије функционална густине (DFT) коришћене су за истраживање разлагања ТКХ-50 молекула на Al(111) површини. За израчунање је коришћен плочаст модел Al суперрељија и периодични гранични услови. Проучавано је пет врста конфигурација адорбовања ТКХ-50 на Al површини. ТКХ-50 је адорбован на Al површини у формирање N-Al, O-Al и OH-Al веза. Енергије адорбције су у распону од 113,15 до 1334,40 kJ/mol. Активационе енергије свих конфигурација су у распону 100,34-354,10 kJ/mol. Раскидање N2H2 у V1 и раскидање N2N1 у V2 се лако дешава. Активационе енергије (100,34, 108,06 kJ/mol) ових два веза су мање него у чистом ТКХ-50 (161,58, 215,99 kJ/mol). Al атоми олакшавају раскидање тетразолског прстена у ТКХ-50. Количина преноса електрона са Al атома на ТКХ-50 је у распону од 1,42-4,90 e.

(Примљено 28. августа; ревирирано 1. новембра; прихваћено 27. новембра 2019)

REFERENCES