# Ab initio effective potential calculation on $\gamma$-Mo$_2$N–thiophene systems

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## Abstract

The Mo$_2$N–thiophene model systems have been studied using ab initio effective potential calculation. The fundamental properties of Mo$_2$N have been examined by model cluster calculation. For the system of the optimized adsorptive geometry the population as well as the bond order analysis are used to examine the adsorptive bonding and extent of activation of the adsorbate. In the (100) surface the four Mo atoms located at the corners of a square without N at its center may be considered as some kind of favorable center for adsorption from the adsorptive bonding and activation extent examination. Interaction between adsorbed H and adsorbed thiophene is also studied, and the enhancement of the activation by the interaction of H at different locations is examined, and some important points involving steps of the reaction mechanism may be inferred from this examination. © 1997 Elsevier Science B.V.

## 1. Introduction

In recent years the study of molybdenum nitride has attracted much attention because of its commercial potential. Much work has been done in this field concerning the preparation, characterization, and reactivities [1–5]. Yet fundamental studies are comparatively less. Theoretical band calculations for transition metal nitrides have been discussed in a recent review article [6], but quantum chemical calculation on the adsorption systems of $\gamma$-Mo$_2$N has not been published to our knowledge.

Mo$_2$N has been reported to exhibit excellent activity for hydrodesulfurization (HDS). In order to study the activation and bonding of thiophene upon adsorption on Mo$_2$N as well as the related mechanism concerning HDS, the Mo$_2$N–thiophene model systems have been studied using ab initio effective potential calculation. The effect of adsorbed hydrogen to the bonding and activation of adsorbed thiophene is also studied for elucidating the related mechanism of HDS for the Mo$_2$N–thiophene system.

For the optimized adsorptive geometry, population analysis is used to examine the adsorption bonding and activation of the adsorbed thiophene. The interaction of adsorbed H and the adsorbed thiophene would enhance the activation and thus facilitate the cleavage of the C–S

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bond. From the interaction of adsorbed H with S and $C^{\alpha}$ of thiophene and the enhancement of the extent of activation for adsorbed thiophene, important points about the steps of HDS mechanism may be inferred.

## 2. Calculation method and models

The method used for this calculation is the ab initio effective potential method. In this method the valence orbitals are represented by truncated basis sets and the operators of the core valence
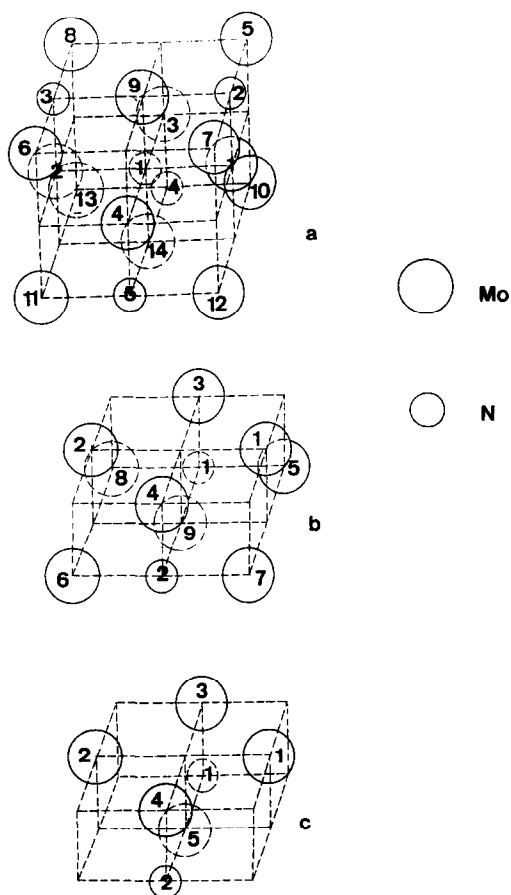
Fig. 2. A sketch of the $Mo_5N_2$–thiophene systems, The dashed lines are used to locate the relative position for the atoms in the figure. The numbers in the circles are the sequential number of the same kind atoms. Atom with this sequential number as superscript would represent that atom throughout the text.

interaction are replaced by simple effective potentials. The total potentials are represented as

$$U(r) = U_L(r) + \sum_l \left[ U_l(r) - U_L(r) \right] P_l$$

and these numerical potentials are fitted analytically by Gaussian functions in the form

$$r^2 \left[ U_l(r) - U_L(r) \right], \quad l = 0, 1, \ldots, L - 1$$

$$r_2 \left[ U_L(r) - N_c/r \right], \quad l = L$$

since

$$U_l(r) \sim 1/r^2 \quad \text{as } r \to 0$$

$$U_l(r) \sim N_c/r \quad \text{as } r \to \infty$$

Fig. 1. A sketch of the model clusters for $Mo_2N$: (a) $Mo_{14}N_5$; (b) $Mo_9N_2$; (c) $Mo_5N_2$. The dashed lines are used to locate the relative position for the atoms in the figure. The numbers in the circles are the sequential number of the same kind atoms. Atom with this sequential number as superscript would represent that atom throughout the text.
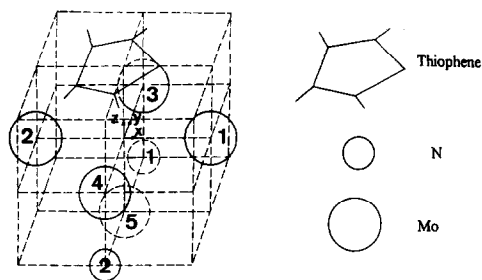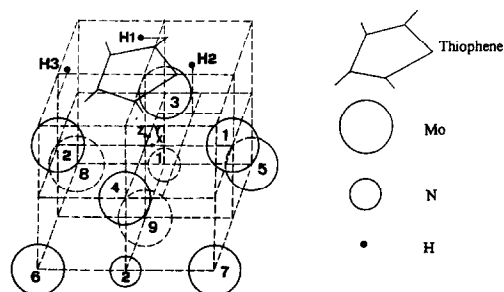
Fig. 3. A sketch of the $Mo_9N_2$–thiophene systems, The dashed lines are used to locate the relative position for the atoms in the figure. The numbers in the circles are the sequential number of atoms of the same kind. Atom with this sequential number as superscript would represent that atom throughout the text. There are three positions H1, H2 and H3 for the coadsorbed H atom or atoms in several cases.

Table 1
Comparison of the total energy and atomic populations for thiophene with the results reported in the literature

|  |  | Ab initio, 4-31G | Ab initio effective potential | Clark and Armstrong [17] | Palmer et al. [15,16] | Gelius et al. [18] |
|---|---|---|---|---|---|---|
| Total energy (hartrees) |  | − 550.5977 |  | − 550.4154 | − 550.1914 |  |
| Atomic population |  |  |  |  |  |  |
| S | 3s | 1.813 | 1.739 | 1.716 |  |  |
|  | 3p$\sigma$ | 2.065 | 2.229 | 2.219 |  |  |
|  | 3p$\pi$ | 1.708 | 1.647 | 1.680 |  |  |
|  | total p | 3.773 | 3.876 | 3.899 |  |  |
|  | $\Sigma$ | 15.586 | (15.615) | 15.616 | 15.856 | 15.518 |
| C$^\alpha$ | 2s | 1.333 | 1.358 | 1.179 |  |  |
|  | 2p$\sigma$ | 2.076 | 2.062 | 2.111 | 2.039 |  |
|  | 2p$\pi$ | 1.118 | 1.150 | 1.106 | 1.094 |  |
|  | total p | 3.194 | 3.212 | 3.217 | 3.133 |  |
|  | $\Sigma$ | 6.527 | (6.570) | 6.396 | 6.239 | 6.568 |
| C$^\beta$ | 2s | 1.171 | 1.212 | 1.096 |  |  |
|  | 2p$\sigma$ | 1.915 | 2.015 | 2.099 | 2.075 |  |
|  | 2p$\pi$ | 1.028 | 1.054 | 1.054 | 1.037 |  |
|  | total p | 2.943 | 3.069 | 3.153 | 3.112 |  |
|  | $\Sigma$ | 6.114 | (6.281) | 6.249 | 6.165 | 6.177 |
| H$^\alpha$ |  | 0.768 | 0.728 | 0.769 | 0.827 | 0.733 |
| H$^\beta$ |  | 0.797 | 0.740 | 0.778 | 0.840 | 0.764 |

where $N_c$ is the number of core electrons. The Gaussian functions take the form

$$\sum_k d_k r^{nk} \exp\left[ -\zeta_k r^2 \right]$$

where $nk = 0$, 1 or 2.

The method for generating pseudopotentials or effective potentials is described in literature [7–11]. Barthelat et al. [7] have reported non-empirical pseudopotentials for Li to Kr. Hay and Wadt [8] have reported effective potentials for elements Sc to Hg, Na to Bi and K to Au.

Table 2
Valence orbital energies (hartrees) calculated using ab initio and ab initio effective potential calculation

| Ab initio method with 4-31G | 31G valence orbitals and Barthelat's potentials | Difference in energies of column 1 and 2 | Basis sets and potentials taken from Pacios [9,10] | Shift all the energies up (+0.038) | Difference in energies of column 1 and 5 |
|---|---|---|---|---|---|
| − 1.18412 | − 1.18335 | −0.00077 | − 1.19657 | − 1.15857 | −0.02555 |
| −0.99021 | −0.98302 | −0.00719 | − 1.01435 | −0.97635 | −0.01386 |
| −0.98473 | −0.97411 | −0.01062 | − 1.01379 | −0.97579 | −0.00894 |
| −0.76289 | −0.75937 | −0.00352 | −0.79186 | −0.75386 | −0.00903 |
| −0.74845 | −0.74440 | −0.00405 | −0.78109 | −0.74309 | −0.00536 |
| −0.69936 | −0.70389 | 0.00453 | −0.73494 | −0.69694 | −0.00242 |
| −0.57776 | −0.58347 | 0.00571 | −0.62869 | −0.59069 | 0.01293 |
| −0.54829 | −0.55491 | 0.00662 | −0.59606 | −0.55806 | 0.00977 |
| −0.52339 | −0.52672 | 0.00333 | −0.57718 | −0.53918 | 0.01579 |
| −0.51917 | −0.52011 | 0.00094 | −0.55871 | −0.52071 | 0.00154 |
| −0.46491 | −0.46941 | 0.00000 | −0.49480 | −0.45680 | −0.00811 |
| −0.34536 | −0.34795 | 0.00259 | −0.39380 | −0.35580 | 0.01044 |
| −0.32611 | −0.33132 | 0.00521 | −0.39014 | −0.35214 | 0.02603 |

Pacios and Christiansen [9,10] have reported effective potentials for elements Li to Xe. Bachelet et al. [11] have reported pseudopotentials for all the elements from H through Pu. In this work the necessary data for the effective potentials and the valence basis set are taken from those of Pacios and Christiansen [9,10]. All calculations are performed with the Hondo program. Within the same program either ab initio or ab initio effective potential calculations may be performed.

It is known that in $\gamma$-$Mo_2N$ the metal atoms form a fcc crystal and nitrogen atoms occupy the largest interstitial octahedral sites, the crystal parameter is 4.164 Å. For the calculation of the fundamental properties of molybdenum nitride, $Mo_{14}N_5$, $Mo_9N_2$ and $Mo_5N_2$ are chosen as the model clusters which are depicted in Fig. 1. For the adsorption of thiophene we choose $Mo_5N_2$–thiophene as the model system which is represented in Fig. 2, in this model cluster, thiophene is adsorbed parallelly to the surface (100) plane of molybdenum nitride. The adsorptive geometry is optimized by total energy calculation. Calculation with a larger model system of $Mo_9N_2$–thiophene is also accomplished with the same adsorptive geometry, i.e., the relative position of thiophene to the surface plane atoms
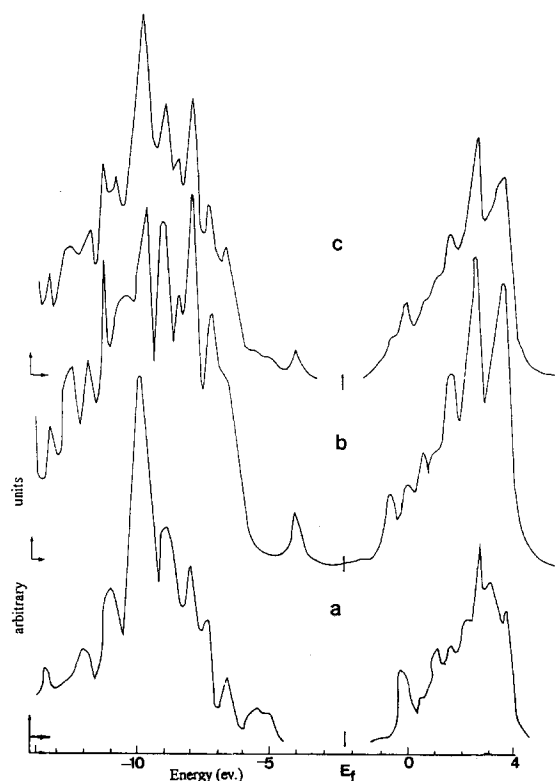


Fig. 4. Partial density of states for d orbitals of $Mo_{14}N_5$: (a) spinup density of states; (b) spindown density of state; (c) average of (a) and (b).

of the substrate is the same as that optimized for $Mo_5N_2$–thiophene. We will return to discuss the choice of models after the discussion of
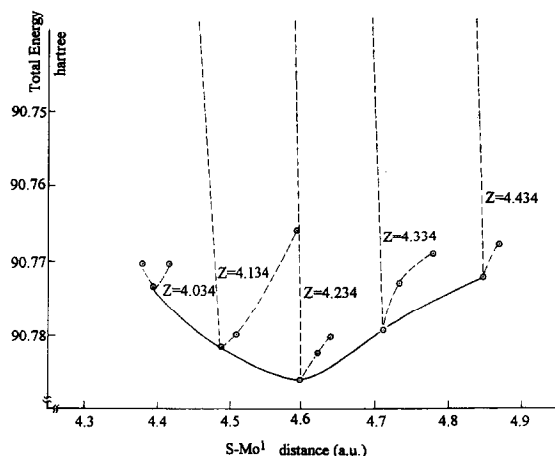
Table 3
MO [a] population for free thiophene

| Orbital | Energy (eV) | B.O. [b] for $S-C^{\alpha 1}$ | B.O. for $C^{\alpha 1}-C^{\beta 1}$ |
|---|---|---|---|
| 1,$\sigma$ | $-32.56$ | 0.183 | 0.157 |
| 2,$\sigma$ | $-27.60$ | 0.172 | 0.018 |
| 3,$\sigma$ | $-27.59$ | 0.054 | 0.351 |
| 4,$\sigma$ | $-21.55$ | $-0.056$ | 0.090 |
| 5,$\sigma$ | $-21.25$ | 0.113 | 0.038 |
| 6,$\sigma$ | $-19.99$ | 0.008 | 0.037 |
| 7,$\sigma$ | $-17.21$ | $-0.001$ | 0.211 |
| 8,$\sigma$ | $-16.22$ | $-0.001$ | $-0.050$ |
| 9,$\pi$ | $-15.71$ | 0.133 | 0.138 |
| 10,$\sigma$ | $-15.20$ | 0.176 | $-0.055$ |
| 11,$\sigma$ | $-13.46$ | $-0.010$ | $-0.021$ |
| 12,$\pi$ | $-10.72$ | / | 0.270 |
| 13,$\pi$ | $-10.62$ | 0.005 | $-0.004$ |

[a] MO stands for molecular orbital.
[b] B.O. stands for bond order.



Fig. 5. Diagram for total energy vs. distance between S–Mo[1] for $Mo_9N_2$–thiophene system, the curves drawn are used to find the total energy minimum for that system.

some results in the followings paragraph. In order to examine the effect of adsorbed H atoms to the adsorbed thiophene some H atoms are added to the $Mo_9N_2$–thiophene system. And these model clusters are depicted in Fig. 3 in which there are three positions labelled H1, H2, and H3 respectively for accommodating H atoms in different cases. For all the model clusters sketched in the figures, the numbers in the circles represent the sequential number for the same kind of atom, and atoms with this sequen-

tial number as superscript are used throughout the text. The geometry of $Mo_2N$ is thought to be the same as that in the crystal, the crystal parameter is 7.8688 a.u..

## 3. Calculated results

Particular partial density of states $D_j(E)$ is constructed by weighing each molecular energy level $E_n$ by the corresponding population for

Table 4
Calculated fundamental properties for model clusters of $Mo_2N$

| Clusters | Total energy (and $E_f$ [a]) (hartrees) | Bond order for Mo–N | | Bond order for Mo–Mo | | Charge | |
|---|---|---|---|---|---|---|---|
| $Mo_{14}N_5$ | $-157.0844$ | N with 6 n.n. [b] Mo | | $Mo^1$–$Mo^{10}$, $Mo^2$–$Mo^{11}$ | 0.254 | $Mo^{1,2}$ | 0.236 |
| | | $N^1$–$Mo^{1,2}$ | 0.346 | $Mo^1$–$Mo^{12}$, $Mo^2$–$Mo^{13}$ | 0.452 | $Mo^{3,4}$ | 0.423 |
| | | $N^1$–$Mo^{3,4}$ | 0.450 | $Mo^{1,2}$–$Mo^{14}$ | 0.022 | $Mo^{5,6}$ | 0.197 |
| | | $N^1$–$Mo^9$ | 0.224 | $Mo^3$–$Mo^5$, $Mo^4$–$Mo^6$ | 0.164 | $Mo^{7,8}$ | 0.285 |
| | | $N^1$–$Mo^{14}$ | 0.262 | $Mo^3$–$Mo^8$, $Mo^4$–$Mo^7$ | 0.096 | $Mo^9$ | 0.761 |
| | | av. | 0.346 | $Mo^3$–$Mo^{10}$, $Mo^4$–$Mo^{11}$ | 0.024 | $Mo^{10,11}$ | 0.123 |
| | | N with 4 n.n. [b] Mo | | $Mo^5$–$Mo^8$, $Mo^6$–$Mo^7$ | 0.080 | $Mo^{12,13}$ | 0.096 |
| | | $N^2$–$Mo^1$, $N^3$–$Mo^2$ | 0.271 | $Mo^5$–$Mo^{10}$, $Mo^6$–$Mo^{11}$ | 0.172 | $Mo^{14}$ | 0.583 |
| | | $N^2$–$Mo^5$, $N^3$–$Mo^6$ | 0.552 | $Mo^{7,8}$–$Mo^9$ | 0.030 | av. | 0.290 |
| | | $N^2$–$Mo^7$, $N^3$–$Mo^8$ | 0.664 | $Mo^7$–$Mo^{12}$, $Mo^8$–$Mo^{13}$ | 0.128 | $N^1$ | $-0.902$ |
| | | $N^2$–$Mo^9$, $N^3$–$Mo^9$ | 0.392 | $Mo^{10}$–$Mo^{12}$, $Mo^{11}$–$Mo^{13}$ $Mo^{13}$ | 0.112 | $N^{2,3}$ | $-0.789$ |
| | | $N^4$–$Mo^3$, $N^5$$Mo^4$ | 0.352 | $Mo^{10,11}$–$Mo^{14}$ | 0.036 | $N^{4,5}$ | $-0.791$ |
| | | $N^4$–$Mo^{10}$, $N^5$–$Mo^{11}$ $Mo^{11}$ | 0.574 | $Mo^{12,13}$–$Mo^{14}$ | 0.056 | av. | $-0.812$ |
| | | $N^4$–$Mo^{13}$, $N^5$–$Mo^{12}$ $Mo^{12}$ | 0.582 | av. | 0.125 | | |
| | | $N^{4,5}$–$Mo^{15}$ | 0.368 | | | | |
| | | av. | 0.470 | | | | |
| $Mo_9N_2$ | $-88.4580 \, (-0.0923)$ | N with 4 n.n. [b] Mo | | $Mo^1$–$Mo^7$, $Mo^2$–$Mo^8$ | 0.318 | $Mo^{1,2}$ | $-0.029$ |
| | | $N^1$–$Mo^3$, $N^2$–$Mo^4$ | 0.430 | $Mo^1$–$Mo^5$, $Mo^2$–$Mo^6$ | 0.524 | $Mo^{3,4}$ | 0.122 |
| | | $N^1$–$Mo^5$, $N^2$–$Mo^6$ | 0.562 | $Mo^1$–$Mo^3$, $Mo^2$–$Mo^4$ | 0.458 | $Mo^{5,6}$ | 0.193 |
| | | $N^1$–$Mo^8$, $N^2$–$Mo^7$ | 0.522 | $Mo^1$–$Mo^4$, $Mo^2$–$Mo^3$ | 0.490 | $Mo^{7,8}$ | 0.139 |
| | | $N^1$–$Mo^9$, $N^2$–$Mo^9$ | 0.346 | $Mo^1$–$Mo^7$, $Mo^2$–$Mo^8$ | 0.594 | $Mo^9$ | 0.703 |
| | | av. | 0.465 | $Mo^1$–$Mo^9$, $Mo^2$–$Mo^9$ | 0.228 | av. | 0.251 |
| | | | | $Mo^3$–$Mo^5$, $Mo^4$–$Mo^6$ | 0.202 | $N^{1,2}$ | $-0.777$ |
| | | | | $Mo^5$–$Mo^7$, $Mo^6$–$Mo^8$ | 0.170 | | |
| | | | | $Mo^7$–$Mo^9$, $Mo^8$–$Mo^9$ | 0.074 | | |
| | | | | av. | 0.342 | | |
| $Mo_5N_2$ | $-57.2840 \, (-0.1364)$ | N with 2 n.n. [b] Mo | | $Mo^3$–$Mo^1$, $Mo^4$–$Mo^1$, | 0.452 | $Mo^{1,2}$ | 0.195 |
| | | | | $Mo^3$–$Mo^2$, $Mo^4$–$Mo^2$ | 0.452 | $Mo^{3,4}$ | 0.300 |
| | | $N^1$–$Mo^3$, $N^2$–$Mo^4$ | 0.808 | $Mo^5$–$Mo^1$, $Mo^5$–$Mo^2$ | 0.362 | $Mo^5$ | 0.032 |
| | | $N^1$–$Mo^5$, $N^2$–$Mo^5$ | 0.572 | av. | 0.422 | av. | 0.204 |
| | | av. | 0.690 | | | $N^{1,2}$ | $-0.512$ |

[a] $E_f$ denotes Fermi energy.
[b] n.n. stands for nearest neighbors.

that level $f_j(n)$ and after which summation follows

$$D_j(E) = \pi/s \sum f_j(n)/\left[(E - E_n)^2 + s^2\right]$$

Here each level is broadened into a Lorentzian of width $s = 0.006$ hartrees. Total normalized density of states is expressed as [12].

$$D(E) = \Sigma Dj = \sum (\pi/s)f_j/\left[(E - E_n)^2 + s^2\right]$$

The bond orders are calculated as [13,14]:

$$\sum_i \sum_{\mu \neq \nu} f_i C_{\mu i} C_{\nu i}\langle f_\mu | f_\nu\rangle$$

Where $f_\mu$ and $f_\nu$ are atomic orbitals centered on different atoms respectively, $C_{\mu i}$, $C_{\nu i}$ are their corresponding coefficients in the occupied molecular orbitals $i$, and $f_i$ is the occupancy of the molecular orbital $i$. If the calculation is carried out for a single molecular orbital (not summed over $i$) then it is the molecular orbital (MO) bond order.

Table 6
Several typical MO [a] bond order values for part of atom pairs in the optimized adsorption system

| MO | | $Mo^1$–S | | $Mo^3$–$C^{\alpha 1}$ | | S–$C^{\alpha 1}$ | | $C^{\alpha 1}$–$C^{\beta 1}$ |
|----|----|----------|----|-----------------------|----|------------------|----|------------------------------|
| 33 | $\sigma$ | −0.059 | $\sigma$ | −0.027 | $\sigma$ | 0.000 | $\sigma$ | 0.005 |
|    | $\pi$ | 0.130 | $\pi$ | 0.121 | $\pi$ | −0.164 | $\pi$ | −0.164 |
|    | $\Sigma$ | 0.071 | $\Sigma$ | 0.094 | $\Sigma$ | −0.164 | $\Sigma$ | −0.159 |
| 15 | $\sigma$ | −0.035 | $\sigma$ | −0.001 | $\sigma$ | 0.001 | $\sigma$ | 0.000 |
|    | $\pi$ | 0.165 | $\pi$ | 0.011 | $\pi$ | −0.061 | $\pi$ | 0.057 |
|    | $\Sigma$ | 0.130 | $\Sigma$ | 0.010 | $\Sigma$ | −0.060 | $\Sigma$ | 0.057 |
| 13 | $\sigma$ | 0.258 | $\sigma$ | 0.004 | $\sigma$ | 0.050 | $\sigma$ | −0.016 |
|    | $\pi$ | 0.022 | $\pi$ | 0.001 | $\pi$ | −0.003 | $\pi$ | 0.003 |
|    | $\Sigma$ | 0.280 | $\Sigma$ | 0.005 | $\Sigma$ | 0.047 | $\Sigma$ | −0.013 |

[a] MO stands for molecular orbitals and the number in this column indicates the sequential number of valence orbital.

The calculated results for free thiophene are tabulated in Tables 1–3. The fundamental properties of molybdenum nitride are listed in Table 4, and the density of states for the d band of $Mo_{14}N_5$ are sketched in Fig. 4. The data for the optimization of the adsorption geometry for the $Mo_5N_2$–thiophene system are listed in Table 5 and sketched in Fig. 5. Several typical MO bond

Table 5
Data for the optimization of the adsorption geometry for $Mo_5N_2$–thiophene

| Distances between $Mo^1$–S (a.u.) | | | Total energy | Bond order | |
|------|------|---------|--------------|------------|------|
| Dz [a] | Dx [a] | $Mo^1$–S | (hartrees) | S–$C^\alpha$ | S–$Mo^1$ |
| 4.0344 | 1.7000 | 4.3779 | −90.7704 | | |
|        | 1.7500 | 4.3976 | −90.7735 | 0.656 | 0.386 |
|        | 1.8000 | 4.4177 | −90.7704 | 0.652 | 0.386 |
| 4.1344 | 1.7000 | 4.4703 | −90.7299 | | |
|        | 1.7500 | 4.4895 | −90.7813 | 0.654 | 0.388 |
|        | 1.8000 | 4.5093 | −90.7799 | | |
|        | 2.0000 | 4.5927 | −90.7657 | | |
| 4.2344 | 1.7500 | 4.5818 | −90.7245 | | |
|        | 1.8000 | 4.6011 | −90.7858 | 0.656 | 0.386 |
|        | 1.8500 | 4.6209 | −90.7834 | | |
|        | 1.9000 | 4.6411 | −90.7802 | | |
|        | 2.0000 | 4.6830 | −90.7670 | | |
| 4.3344 | 1.8000 | 4.6933 | −90.7279 | | |
|        | 1.8500 | 4.7127 | −90.7791 | 0.672 | 0.346 |
|        | 1.9000 | 4.7326 | −90.7728 | | |
|        | 2.0000 | 4.7736 | −90.7689 | | |
| 4.4344 | 1.9000 | 4.8243 | −90.7358 | | |

[a] Dz, Dx and Dy are the $z$, $x$ and $y$ components of the $Mo^1$–S distance respectively; in which Dy is taken to be zero and Dz is also the distance between thiophenic ring and the surface plane.

  
Table 7
Influence of the size of substrate cluster on the bonding and activation of adsorbate

| Model | Total energy (hartrees) | Bond order values | | | |
|---|---|---|---|---|---|
| | | $S-C^{\alpha 1}$ | $C^{\alpha 1}-C^{\beta 1}$ | $S-Mo^1$ | $C^{\alpha 1}-Mo^3$ |
| Free thiophene | −33.4756 | 0.766 | 1.180 | | |
| $Mo_5N_2$–thiophene | −90.7858 | 0.656 | 1.018 | 0.378 | 0.116 |
| $Mo_9N_2$–thiophene | −121.9553 | 0.660 | 1.010 | 0.318 | 0.164 |

Table 8
Total energy and bond order values for $Mo_9N_2$–thiophene with adsorbed H atoms at various positions

| Model [a] | Total energy (hartrees) | Bond Order Value | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $S-C^{\alpha 1}$ | $C^{\alpha 1}-C^{\beta 1}$ | $C^{\beta 1}-C^{\beta 2}$ | $S-Mo^1$ | $C^{\alpha 1}-Mo^3$ | $H^{ad}-Mo^1$ | $H^{ad}-Mo^3$ | $H^{ad}-S$ | $H^{ad}-C^{\alpha 1}$ |
| C1 | −121.9552 | 0.660 | 1.012 | 1.174 | 0.318 | 0.164 | | | | |
| C2 | −122.7842 | 0.578 | 0.846 | 1.176 | 0.354 | | H1 | 0.296 | | 0.412 |
| C3 | −122.9183 | 0.324 | 0.940 | 1.128 | 0.208 | | H2.024 | 0.180 | 0.296 | 0.218 |
| C4 | −123.5564 | 0.324 | 0.860 | 0.928 | 0.184 | | H1 | 0.368 | 0.026 | 0.308 |
| | | | | | | | H2.130 | 0.274 | 0.156 | 0.154 |
| | | | | | | | H3 [b] | 0.194 [b] | | 0.572 [b] |

[a] The models C1, C2, C3 and C4 denote the $Mo_9N_2$–thiophene system, C1 + H1, C1 + H2 and C1 + H1 + H2 + H3 respectively.
[b] 0.97 and 0.286 are bond order values for $H3-Mo^2$ and $H3-C^{\beta 1}$ respectively.

order values for some atom pairs for the optimized adsorptive geometry are listed in Table 6. Data for the comparison of the bonding and activation of thiophene for the $Mo_5N_2$–thiophene system and the $Mo_9N_2$–thiophene system are listed in Table 7. The data for the effect of adsorbed H atoms to the adsorbed thiophene is represented in Table 8. Now we would like to discuss some problems about the bonding and electronic properties of molybdenum nitride, bonding and activation of adsorbed thiophene, interaction between adsorbed H atoms and adsorbed thiophene and the related mechanism of hydrogenation of the cyclic ring and the cleavage of the C–S bond for thiophene.

## 4. Discussions

### 4.1. About the method

Firstly ab initio all electron calculations for thiophene are performed with the 4-31G basis set, as can be seen from Table 1 the total energy obtained in this work is lower than that of Palmer et al. [15,16] and that of Clark and Amstrong [17]. This is not surprising since the 4-31G basis set chosen by us is more suitable. From Table 1 it can be seen that our results for orbital population are comparable with that of published ab initio results [17,15,16,18]. Secondly ab initio effective potential calculation for thiophene with Barthelat potentials and 31G valence basis sets are performed. Upon comparing the results with that of ab initio all electron calculations for thiophene, it is found from Table 2 that the valence molecular orbital energies differ about several thousands of hartrees, a negligibly small difference. The population data are comparable, this indicates that the results of ab initio effective potential are reliable. In the effective potential calculation of this work, for the compatibility of the effective potentials and the valence basis sets, all the data are taken from Pacios et al. [9,10], therefore calculations for thiophene with Pacios data are also performed, and the results are listed in column 4 of Table 2. Since the ab initio calculation for the valence basis sets are the 31G Gaussians, which

are different from that of Pacios, the values for valence orbital energies are different. It is reasonable to compare the energy spacing to see their difference. For this purpose we shift all the valence orbital energies of the effective potential calculation with Pacios data by a small amount and then compare them with that of the ab initio results. The energy spacings differ about several thousandth of hartrees to 2 hundreds of hartrees, a fairly acceptable results, the population data are comparable in these two cases.

## 4.2. Fundamental properties of molybdenum nitride

For the calculation of the fundamental properties of molybdenum nitride, three model clusters are used. As can be seen in Fig. 4, the density of states for the $Mo_{14}N_5$ cluster differ very much, in their patterns, from those for transition metals. For transition metals the Fermi energy passes through the top of the d band [19], while for molybdenum nitride the Fermi energy passes through the middle of the d band, and the d band goes over the vacuum levels. In order to study the bonding, bond order values for atom pairs in the model clusters are tabulated in Table 4. For the Mo–N pair, positive bond order values occur only between the nearest neighbors, and the bond order value changes with the number of the nearest neighbor Mo atoms of N, for N coordinated with 2, 4 and 6 nearest neighbor Mo atoms, the average bond order values are 0.69, 0.47 and 0.35 respectively. For Mo, the nearest pairs are the next nearest neighbor pairs for the crystal. As can be seen from the table, the bond order values for Mo–Mo pairs changes irregularly. In $Mo_{14}N_5$, the bond order value is lower (0.125), while in $Mo_9N_2$ and $Mo_5N_2$, the bond order value is higher (0.342 and 0.422 respectively). It can thus be inferred that in the bulk of the crystal the Mo–Mo bonding may be weaker than in the surface, as manifested from the data of larger cluster $Mo_{14}N_5$.

For the three clusters of $Mo_2N$, electrons are transferred from Mo to N. On the average there is 0.29 positive charge per Mo and 0.81 negative charge per N for $Mo_{14}N_5$. For $Mo_9N_2$, the positive charge per Mo and the negative charge per N are respectively 0.25 and 0.78 on the average. For $Mo_5N_2$, the positive and negative charge per atom are 0.20 and 0.51 for Mo and N respectively. These charges are obtained by Mulliken population analysis. In this analysis the overlap population is equally partitioned to each of the atom pair. The reason for this needs to be discussed. We take $Mo_{14}N_5$ as an example. The summation of the overlap population for all the Mo–N pairs is 8.700, and 4.350 electrons are obtained from the partition of overlap population for all Mo or N atoms. The total of negative charges for all N atoms is 4.063, their difference is 0.287. That is to say, in forming the covalent bond for the $Mo_{14}N_5$ cluster, if all the N atoms contribute more than 0.29 electrons which consist of only 3.3% of the total overlap population 8.700, then the electrons contributed by all N in excess of 0.29 would be the electron transferred from all the Mo atoms to all the N atoms irrespective of the partition details involved in population analysis. Similarly for $Mo_9N_2$ and $Mo_5N_2$, in both cases the necessary percentages to determine the transfer of electron from Mo to N are 5.8. Evidently contribution of the electrons for each kind of atom of the bonding pair in forming covalent bonds would exceed such a small percentage. Thus from our calculated results it is most probable that electrons are transferred from Mo to N in molybdenum nitride. This is in consistency with the results of band calculation [6].

## 4.3. Adsorption of thiophene on $Mo_2N$

### 4.3.1. Adsorption geometry

As can be seen from Fig. 3, thiophene is adsorbed with its ring parallel to the (100) surface and the whole adsorption system pos-

sesses a $C_s$ symmetry. In determining the adsorption geometry, the distance between the S of thiophene and $Mo^1$ is changed while keeping $C_s$ symmetry of the whole system, until the minimum total energy of the adsorption system is obtained. In reality, in the whole calculation the $y$ component of the $Mo^1$–S distance is taken to be zero and the $y$ coordinates of all the atoms in the adsorbed thiophene are kept unchanged. Varying the $x$ coordinate of all the atoms of thiophene synchronously, and keeping the $z$ coordinates as a first constant, we get an energy minimum $M1$, similarly for a second constant of $z$ coordinate, the $x$ coordinate of the ring is also varied, and a second minimum $M2$ is obtained. Continuing this process we get $M3$, ... until the obtained minima $M1$, $M2$, $M3$, ... are sufficient in number. The data for this process are listed in Table 5 and sketched in Fig. 5 to find the energy minimum. As can be seen, for the optimized adsorption geometry the S–$Mo^1$ distance is 4.60 a.u., it is slightly larger than the Mo–S distance (4.45 a.u.) in the $MoS_2$ crystal. This is a reasonable result. For this optimized adsorption geometry, the total energy for the adsorption system is −90.7858 hartrees, which is lower than the sum of the total energy for $Mo_5N_2$ (−57.2840 hartrees) and the total energy for thiophene (−33.4756 hartrees), it is also reasonable.

### 4.3.2. Bonding and activation of thiophene on $Mo_2N$

For the above optimized adsorption geometry of $Mo_5N_2$–thiophene system, the bond order values for S–$Mo^1$, $C^\alpha$–$Mo^{3,4}$ are 0.378 and 0.116 respectively, as can be seen from Table 7, that is to say, thiophene is bonding with the surface by using the S and the $C^\alpha$ atoms. At the same time the $C^\alpha$–S bonding is decreased from 0.766 for free thiophene to 0.656 for the adsorbed thiophene (Table 7), i.e., it is activated to some extent. We would like to discuss this in detail by MO population analysis. As a convention, for atom pairs of both the free and adsorbed thiophene we call the bonding in the plane of the cyclic ring $\sigma$ bonding, and the corresponding orbitals $\sigma$ orbitals. We call the bonding in the planes perpendicular to the plane of the cyclic ring $\pi$ bonding, and the corresponding orbitals $\pi$ orbitals. Similarly, for the bond order between the atoms of the thiophenic ring and that of the substrate we divide them into $\sigma$ and $\pi$ parts, where $\sigma$ and $\pi$ represent the orbitals of the constituting atoms of thiophenic ring which are of $\sigma$ and $\pi$ character.

Examining the data obtained it is found that the bonding for S–$Mo^1$ and $C^\alpha$–$Mo^{3,4}$ especially for the former occurs mainly in the three MO's 13, 15 and 33, therefore the MO bond order values for the atomic pairs S–$Mo^1$, $C^{\alpha 1}$–$Mo^3$ ($C^{\alpha 2}$–$Mo^4$ is the same due to symmetry of the model) of this three MO's are listed in Table 6. At the same time the bond order values for the atomic pairs S–$C^{\alpha 1}$ and $C^{\alpha 1}$–$C^{\beta 1}$ are also listed in order to examine the activation extent of these bondings. From the data in Table 6 it is found that for the S–$Mo^1$ and $C^{\alpha 1}$–$Mo^3$ pairs in the MO 33, the $\sigma$ bond order values are negative while the $\pi$ bond order values are positive, i.e., thiophene is $\pi$ bonded with the $\pi$ orbitals to Mo atoms of the substrate. At the same time the $\sigma$ bond order values for S–$C^{\alpha 1}$ and $C^{\alpha 1}$–$C^{\beta 1}$ are very small, and the $\pi$ bond order values are negative and large, i.e., S–$C^{\alpha 1}$ and $C^{\alpha 1}$–$C^{\beta 1}$ are antibonding for this MO. For the case of MO 15, the situation is almost the same except that $C^{\alpha 1}$–$C^{\beta 1}$ is bonding. The sum of $\pi$ bond order value of S–$C^{\alpha 1}$ for this two MO's is −0.225, the absolute value of which exceeds the $\pi$ bonding for S–$C^{\alpha 1}$ (0.138, see Table 3) in the free thiophene. The $\pi$ bond order value of $C^{\alpha 1}$–$C^{\beta 1}$ for MO 15 is −0.164, the absolute value of which approaches 41% of $\pi$ bonding for $C^{\alpha 1}$–$C^{\beta 1}$ (0.404, see Table 3) in the free thiophene. That is to say, the adsorbed thiophene bonds to the substrate by its $\pi$ orbitals and the $\pi$ bonding of S–$C^\alpha$ and $C^\alpha$–$C^\beta$ in the molecule is activated. As for MO 13, S is $\sigma$ bonded with $Mo^1$, and the total $\sigma$ bond order value is 0.280, while $C^{\alpha 1}$ is almost nonbonding

with $Mo^3$. For $S-C^{\alpha 1}$ pair, the $\pi$ and $\sigma$ bond order values are $-0.003$ and $0.050$ respectively. For the $C^{\alpha 1}-C^{\beta 1}$ pair, the $\sigma$ and $\pi$ bond order values are $-0.016$ and $0.003$ respectively. From the energy consideration it is probable that this MO 13 ($-14.08$ eV) may be formed by the interaction of MO 11 for free thiophene ($-13.46$ eV) with the substrate, and the bond order value for MO 11 of free thiophene is $-0.010$. If this analysis is correct, then when S is $\sigma$ bonded with $Mo^1$, the $\sigma$ bonding of $S-C^{\alpha 1}$ is strengthened to a certain extent.

From the above discussion, it may be concluded that: (1) In the (100) surface the four Mo atoms located at the corners of a square without N at its center (Fig. 2) may be a favorable center of adsorption (2) With the optimized adsorption geometry, thiophene is moderately bonding with S to $Mo^1$ and $C^\alpha$ to $Mo^{3,4}$ of the surface and the $\pi$ bondings of $C^\alpha-S$ and $C^\alpha-C^\beta$ are activated, thus the bond order of C–S and $C^\alpha-C^\beta$ decrease to 0.85 and 0.92 of that for the free thiophene respectively.

### 4.3.3. About the model of the adsorption system

In order to compare the above results for the $Mo_5N_2$–thiophene system with that obtained from larger substrate clusters we perform calculation for the $Mo_9N_2$–thiophene systems. The adsorption geometry for the latter case is not optimized but taken the same as the former case, i.e., the relative position for the thiophenic ring to the first plane atoms for these two cases is the same. As can be seen from Table 7 the difference of the bond order values for $Mo^1$–S, $C^{\alpha 1}-Mo^3$, $C^{\alpha 1}-S$, $C^{\alpha 1}-C^{\beta 1}$ for $Mo_5N_2$–thiophene and $Mo_9N_2$–thiophene systems is small. It can be said that the bonding of thiophene to the substrate may be slightly weaker for the latter case while the activation of the adsorbate is almost the same for these two cases. Therefore we choose $Mo_5N_2$ as the substrate model in optimizing the adsorptive geometry for the sake of saving computer time and without any adverse effect on the discussions and conclusions.

### 4.3.4. Interaction of adsorbed H atom with the adsorbed thiophene

In order to see the interaction of the adsorbed H atom and the adsorbed thiophene, model clusters of coadsorbed H and thiophene are used. The calculated total energies and related bond order values are tabulated in Table 8. As can be seen in Fig. 3, the adsorbed H may be located at three positions separately or simultaneously, and they are labelled as H1, H2 and H3 respectively. The distances between $H1-Mo^3$, $H1-C^{\alpha 1}$, $H2-Mo^1$, $H2-Mo^3$, $H2-S$, $H2-C^{\alpha 1}$, $H3-Mo^2$ and $H3-C^{\beta 1}$ are 3.44, 2.14, 3.83, 3.76, 2.50, 2.55, 3.44 and 2.13 a.u. respectively, in which the $H2-S$ distance is just the same as that in $H_2S$, $H1-C^{\alpha 1}$ and $H3-C^{\beta 1}$ distances are almost the same as that of a single C–H bond. For the C2 model in Table 8, one H atom is located at position H1 in that figure. This H1 atom interacts with $C^{\alpha 1}$ and the bond order value for $H^1-C^{\alpha 1}$ approaches 0.178. At the same time, the activations of $C^{\alpha 1}-S$ and $C^{\alpha 1}-C^{\beta 1}$ are enhanced, since the bond order value for $S-C^{\alpha 1}$ and $C^{\alpha 1}-C^{\alpha 2}$ decreased from 0.660 and 1.012 for the adsorbed thiophene to 0.578 and 0.846 respectively for this model C2, as can be seen from the data in the table. Similarly For the C3 model, one H atom is located at position H2. Not only the bond order for $S-C^{\alpha 1}$ decreases from 0.660 to 0.324, but also the bond order for $C^{\alpha 1}-C^{\beta 1}$ decreases from 1.012 to 0.940. Since $Mo^1$ and $Mo^3$ are bonded with S and $C^{\alpha 1}$ respectively, of course this H2 would be adsorbed by both $Mo^1$ and $Mo^3$. This H atom also interacts with both S and $C^{\alpha 1}$, as can be seen from the bond order for $H2-S$ and $H2-C^{\alpha 1}$. All these facts are determined by the adsorption geometry. In the final C4 case three H atoms are located at positions labeled H1–H3 simultaneously, in which H1 interacts with $C^{\alpha 1}$, H2 interacts with S and $C^{\alpha 1}$, H3 interacts with $C^{\beta 1}$, the bond order value for $S-C^{\alpha 1}$, $C^{\alpha 1}-C^{\beta 1}$ and $C^{\beta 1}-C^{\beta 2}$ decreased from 0.660, 1.012 and 1.174 for the adsorbed thiophene without adsorbed H to 0.324, 0.860 and 0.928 respectively for the discussed case. In all the three cases the

total energy is lower than that for the sum of the $Mo_9N_2$–thiophene system and the H atom or atoms. That is to say, in going from the thiophene only adsorptive system to the hydrogen interacting adsorptive system, the latter is favored from the total energy consideration.

### 4.4. About the cleavage of $S$–$C^{\alpha 1}$ bond and the related mechanism

From the above discussions it is obvious that the $S$–$C^{\alpha 1}$ bonding of thiophene decreases to 86% after adsorption (model C1), interaction of H1 with $C^{\alpha 1}$ makes it decrease further to 75% (model C2), and interaction of H2 with S and $C^{\alpha 1}$ makes it decrease further to 42% (model C3). While interaction of three H atoms with $C^{\alpha 1}$, S and $C^{\beta 1}$ simultaneously makes $S$–$C^{\alpha 1}$ also decrease to 42% (model C4). Evidently, in the case of C1 and C2, cleavage of $S$–$C^{\alpha 1}$ is very difficult for its small and insufficient activation extent. Only for the case of C3 and C4 where the activation extent is large, cleavage of $S$–$C^{\alpha 1}$ is possible. That is to say, for the cleavage of $S$–$C^{\alpha 1}$, adsorbed H atoms would play an important role. At first sight, the probability for cleavage of $S$–$C^{\alpha 1}$ would be equal because of the equality of the bond order values in these two cases. However, the important point is that the hydrogenation of thiophene is a successive process. For the C3 model, the bond order values for $H2$–$Mo^1$, $H2$–$Mo^3$, $H2$–S and $H2$–$C^{\alpha 1}$ are 0.024, 0.180, 0.296 and 0.218 respectively, i.e., $H2$–$Mo^1$ bonding is negligibly small that we could say that $H2$–$Mo^3$ bonding is fairly strong. At the same time, H2 interacts with S and $C^{\alpha 1}$ with comparable strength. If $S$–$C^{\alpha 1}$ cleavage occurs under this condition, due to the fairly strong $S$–$Mo^1$ bonding (bond order value 0.208), it would be strengthened after cleavage. At the same time H2 would attach to $C^{\alpha 1}$ and $Mo^3$, thus a methylene group is formed at $C^{\alpha 1}$ for this case. This process is called process 1. While for the C4 model, H1 is bonded to $Mo^3$ and interacts with $C^{\alpha 1}$, bonding

of H2 with $Mo^1$ (0.130) is also weaker than that with $Mo^3$ (0.274). At the same time H2 interacts with S and $C^{\alpha 1}$ with almost the same strength (bond order values are 0.156 and 0.154 respectively). If $S$–$C^{\alpha 1}$ is cleaved under such a condition, H2 may attach to $C^{\alpha 1}$ or S, since the bond order values for $S$–$Mo^1$, $H2$–$Mo^1$, $H2$–$Mo^3$, $H2$–S and $H2$–$C^{\alpha 1}$ are almost of the same magnitude, as can be seen in Table 8, therefore there is no preference for the position for H2. Thus a methyl group is formed at $C^{\alpha 1}$ when H2 attaches to $C^{\alpha 1}$ and a methylene group is formed when H2 attaches to S. The process in which H2 is attached to S is called process 2 while the process in which H2 is attached to $C^{\alpha 1}$ is called process 3. If process 1 occurs for both $C^{\alpha 1}$ and $C^{\alpha 2}$, butadiene is the final product from HDS of thiophene, If process 3 occurs for both $C^{\alpha 1}$ and $C^{\alpha 2}$, then butane is the final product from the reaction. If process 1 or 3 does not occur simultaneously for both $C^{\alpha 1}$ and $C^{\alpha 2}$, then the final product would be butenes. If the probability of occurrence for the process 1, 2 and 3 is equal, then the probability for the same process occurring for both $C^{\alpha 1}$ and $C^{\alpha 2}$ is 1/9, i.e., as a final product, butadiene and butane would be in small content, while butenes would be the predominant products. This deduced result is in good accord with the experimental findings [4]: at small conversion of thiophene, butenes were the predominant desulfurization products and a small amount of tetrahydrothiophene were detected in the products. In fact, the reaction for HDS of thiophene over molybdenum nitride is expected to be much more complicated than that described above. However, the main points about the products distribution would remain unchanged irrespective of the complication of the reaction mechanism. From the above discussion, it is plausible to say that hydrogenation of the thiophenic ring is favorable to the activation of the $S$–$C^{\alpha 1}$ and cleavage of $S$–$C^{\alpha 1}$ bond before hydrogenation of the ring is much less likely than that after hydrogenation.

# 5. Conclusions

(1) The fundamental properties for molybdenum nitride have been calculated. The Fermi energy passes through the middle of the d band, and the d band goes over the vacuum levels. For N coordinated with 2, 4 and 6 nearest neighbor Mo atoms, the average bond order values are 0.69, 0.47 and 0.39 respectively which are larger than that for Mo–Mo (0.12–0.42). It is most probable that electrons are transferred from Mo to N in molybdenum nitride.

(2) In the (100) surface the four Mo atoms located at the corners of a square without N at its center may be one of the favorable centers of adsorption.

(3) With the optimized adsorption geometry, thiophene is bonding with S to the $Mo^1$ and $C^\alpha$ to $Mo^{3,4}$ of the surface and the $S-C^\alpha$ and $C^\alpha-C^\beta$ bondings are activated, the bond orders of $S-C^\alpha$ and $C^\alpha-C^\beta$ decrease to 0.86 and 0.92 of that for free thiophene respectively. The adsorbed thiophene bonds with the substrate by its $\pi$ orbitals and the $\pi$ bonding of $S-C^\alpha$ and $C^\alpha-C^\beta$ is activated. When S is $\sigma$ bonded with $Mo^1$, the $\sigma$ bonding of $S-C^{\alpha1}$ may be somewhat strengthened.

(4) The cleavage of $S-C^\alpha$ bonding of adsorbed thiophene is very difficult because of its small and insufficient activation extent. Adsorbed H in the vicinity of S interacts strongly with $C^{\alpha1}$ in addition to its interaction with S. Although single H in the vicinity of S would enhance the activation of $S-C^{\alpha1}$ to the largest extent, due to the strong interaction of this H and $C^{\alpha1}$ the cleavage of $S-C^{\alpha1}$ bond before hydrogenation of the ring is less likely than that after hydrogenation.

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