A Theoretical Investigation on the Hydrodesulfurization Mechanism of Hydrogenated Thiophene Over Cu-mo Modified Fau Zeolite

Suyang Li
Shanghai Institute of Technology

Yingxin Sun (sunyingxin0312@sit.edu.cn)
Shanghai Institute of Technology https://orcid.org/0000-0001-8607-5078

Sheng Han
Shanghai Institute of Technology

Qianggen Li
Sichuan Normal University

Research Article

Keywords: Hydrogenated thiophene, Hydrogenolysis desulfurization, Ring-opening, C-S bond cleavage, Hydrogen transfer

DOI: https://doi.org/10.21203/rs.3.rs-785978/v1

License: This work is licensed under a Creative Commons Attribution 4.0 International License. Read Full License
A theoretical investigation on the hydrodesulfurization mechanism of hydrogenated thiophene over Cu-Mo modified FAU zeolite

Suyang Li†, Yingxin Sun*, Sheng Han*, Qianggen Li††

†School of Chemical and Environmental Engineering, Shanghai Institute of Technology, Shanghai 201418, China

‡‡College of Chemistry and Material Science, Sichuan Normal University, Chengdu 610068, China

*Corresponding authors: Yingxin Sun, Sheng Han, Qianggen Li

Tel: +86-21-6087-7214, +86-28-8476-0802

E-mail: sunyingxin0312@sit.edu.cn, hansheng654321@sina.com, liqgen@sicnu.edu.cn
Abstract

We have carried out a two-layer our own $n$-layered integrated molecular orbital and molecular mechanics (ONIOM) study on the hydrodesulfurization (HDS) mechanism of three hydrogenated thiophene derivatives over Cu-Mo modified FAU zeolite. The thiophene is hydrogenated relatively easily to 2,3-dihydrothiophene (2,3-DHT), 2,5-dihydrothiophene (2,5-DHT) and tetrahydrothiophene (THT) due to low free energy barriers. Hydrogenolysis desulfurization (HYD) and direct desulfurization (DDS) are discussed. Ring-opening, hydrogen transfer and C–S bond cleavage steps of thiophene derivatives are involved in the HYD process. The rate-determining steps are the hydrogen transfer step for 2,5-DHT and C–S bond cracking step for 2,3-DHT and THT. The concerted DDS pathway is probably more favorable than the HYD pathway in the desulfurization of 2,5-DHT. The hydrogenation of thiophene to 2,5-DHT, 2,3-DHT and THT and their HDS process are entropy-decreased; the formation of sulfur vacancy is entropy-increased. The difference charge density (DCD) analysis reveals that for the ring-opening process, the electrons are migrated from the organic chain to the Cu-Mo catalytic center. The reduced density gradient (RDG) plots indicate that both a steric hindrance and a weak van der Waals attractive interaction exist between organic fragment and catalytic center for all transition states (TSs). The localized orbital locator (LOL) maps for all TSs suggest that there are strong covalent interactions between the atoms in the forming chemical bonds and weak van der Waals interactions between the atoms in the breaking chemical bonds.

Keywords Hydrogenated thiophene · Hydrogenolysis desulfurization · Ring-opening · C-S bond cleavage · Hydrogen transfer
Introduction

Organic sulfides in fossil fuels are mainly thiophene, benzothiophene (BT), dibenzothiophene (DBT) and 4,6-dimethyl dibenzothiophene (4,6-DMDBT), which are harmful to the environment [1]. The combustion of these sulfides promotes the generation of SO\textsubscript{x} gas and acid rain. Some organic sulfides lead to the deactivation of catalysts and corrode refining equipment and internal combustion engine compressors [2]. Therefore, the control of sulfur content in fuel is becoming more strict. Some desulfurization technologies have been used such as hydrodesulfurization (HDS), oxidative desulfurization (ODS), and adsorption desulfurization [2–4]. As the demand for ultra-low sulfur fuels increases, the HDS techniques require larger reactors and higher operating pressures. The ODS easily oxidizes the sulfide in the fuel into advanced sulfur composition but the cost is too high and the technology still needs to be improved. Although adsorption desulfurization avoids the above-mentioned drawbacks, the low adsorption capacity and selectivity of the materials limit its application [5].

In recent years, transition metal modified zeolite catalysts are widely used in the industrial desulfurization of thiophene. The metal modified zeolites can be employed in both adsorptive desulfurization and HDS of thiophene. For the adsorptive desulfurization, the metal zeolites can enhance the adsorption ability for the thiophene through the π-complexation between metal atoms and thiophene molecules. The acidic zeolites have low adsorption abilities because of the weak interaction between acidic protons and thiophene. For the HDS process, metal zeolites are more suitable because the acidic zeolites often lead to various by-products through hydrocarbon conversion reactions and thus decrease the octane number of gasoline. Many transition metal modified zeolites such as Cu-Na-Y [6], Cu(I)-Y [7], AgY [8], nickel(II)-Y [9], Ni-Mo-MCM-41 [10], CuCeY [11] are widely used for the adsorption desulfurization and HDS process. The metal atoms Cu, Ag, Ni, Mo, and Ce are effective desulfurization sites for thiophene, BT, DBT and 4,6-DMDBT.

Although much experimental work has been done on HDS process on transition
metal supported zeolites, a detailed mechanism on the HDS over metal supported zeolites remains unclear from a theoretical standpoint due to the complexity of HDS reaction system. Many related theoretical work has been reported. Jayaraman pointed out that the presence of organic nitrogen compounds and polycyclic aromatic hydrocarbons on Cu(I)Y zeolite could not remove dibenzothiophene well through π-complexation [12]. In the work of Wang et al., the Cu(I)-Y had the best adsorption capacity on cation-exchanged Y zeolites among the thiophene and BT [13]. Bian et al. investigated the oxidative desulfurization mechanism of aromatic sulfides on Ti-MWW zeolite and found that thiophene had the highest oxidation activation energy than BT, DBT, and 4,6-DMDBT [14]. If the Ce atoms are added into the Cu-Y zeolite, the CuCeIVY zeolite has a higher sulfur adsorption capacity and high selectivity for sulfur compounds such as BT, similar to CeIVY, as reported by Song et al. [15]. Jiao et al. investigated the HDS mechanism of BT on Mo3S9 cluster catalyst. Liu et al. used the DFT method to study the mechanism of thiophene HDS on a sulfide Co-Mo catalyst supported zeolite L [17]. In the work of Jiao and Liu et al., the desulfurization mechanisms of BT and thiophene are similar but the energy barriers are different in the Mo3S9 cluster and Co-Mo-L zeolite.

FAU zeolite is a typical industrial catalyst and widely used in HDS of thiophene. In this work, the thiophene HDS mechanism catalyzed by Cu-Mo-supported FAU zeolite will be studied through a two-layer ONIOM method to understand the nano-confinement effect of the zeolite channel and the nature of the transition states. The Cu and Mo atoms were chosen because of their good performance in experimental HDS process. The following two interesting theoretical questions will be considered. (1) What is the rate-determining step for the HDS process over the Cu-Mo-supported FAU zeolite? (2) What is the relationship between the characteristic of thiophene desulfurization and the topological structure of zeolite? It is expected that the theoretical results will provide useful insights into the experimental design of more efficient desulfurization catalysts.
Computational methods

We constructed a 156T FAU nanocluster from the original crystal structure [18]. The FAU model covers the region of two supercages interconnected by a 12-membered ring (12MR) window. A silicon (Si) atom is replaced by an aluminum (Al) atom. A molybdenum (Mo) atom connects with the Al atom through two bridging oxygen (O) atoms. A copper (Cu) atom connects with the Mo atom through two bridging sulfur (S) atoms. The Co and Mo atoms with two bridging S atoms are placed around the \([(≡SiO)_3Al(OSi≡)]\) cluster in the Cu-Mo-supported FAU zeolite model. The corresponding zeolite model is displayed in Fig. 1.

We carried out a two-layer ONIOM study. In the ONIOM scheme, the total energy of the entire system is calculated according to the following equation [19]:

\[
E_{\text{ONIOM}} = E_{\text{MM(real)}} - E_{\text{MM(inner)}} + E_{\text{QM(inner)}}
\]  

(1)

Herein, the real region contains an inner region and a larger outer region. Both quantum mechanics (QM) and molecular mechanics (MM) calculations are needed for the inner region (reactants) and only MM calculations are needed for the real region (zeolite framework). The MM energy term is used to treat the van der Waals (VDW) and classical electrostatic interactions. The MM electrostatic interaction energy is obtained from the Coulomb's law, that is, the classic charge-charge interaction.

We used the DFT method with the M06 hybrid function and the universal force field (UFF) to describe the inner and outer regions respectively [20,21]. It is well-known that the B3LYP function often underestimates the activation barrier height of the transition state and is not accurate enough to treat the medium-range VDW interactions [22]. The M06 functional developed by Zhao et al. exhibits remarkable accuracy for predicting the main group thermochemistry, kinetics, non-covalent interaction, electronic excitation energy and aromatic-aromatic stacking interaction [23-25]. In particular, M06 functional can be used to deal with the problem of multi-reference rearrangement involving reactions in which both organic and transition metal bonds are formed or broken.

A zeolite model called ONIOM (M06 (qm1 (6-31G (d,p)): qm2 (3-21G)): UFF)
is employed in order to save computational time. The inner QM region can be divided into two parts: qm1 and qm2 subregions. The active centers of zeolite and reactants are included in the qm1 subregion and calculated by the 6-31G (d,p) basis set; the qm2 subregion includes the rest of inner QM region and treated by the 3-21G basis set. We employed the 6-31G (d,p) basis set for Si, Al, O, C, S and H atoms and the LANL2DZ effective core potential for Mo and Cu atoms. The use of the mixed basis sets can be found in many published works [26-29]. For FAU, the qm1 and qm2 subregions contains 12T and 6T atoms respectively. From the previous theoretical works, the 18T QM size is reliable enough in the ONIOM model for studying the desulfurization reaction network in the bulk catalytic system [30].

The atoms in the catalytic center Cu-S-Mo cluster and reactant molecules were relaxed and zeolite framework was rigid in the geometry optimization. The intrinsic reaction coordinates (IRC) were calculated to verify the transition states [31]. The typical experimental temperature of 673.15 K is used for energy thermal corrections. In order to obtain more accurate energies, we carried out single-point energy calculations for QM region at M06 (qm1(6-311+G(2df,2p)):qm2(6-31G(d,p))) level.

The classical electrostatic interaction energy in the force field calculations is calculated by the Coulomb's law, that is, the classic charge-charge interaction:

$$E_{el} = \sum_{i<j} \frac{q_i q_j}{r_{ij}}$$  \hspace{1cm} (2)

where the $q_i$ is the force field atomic charge of atom $i$. The van der Waals (VDW) energy in the UFF force field is obtained according to the Lennard-Jones 12-6 type expression [21]:

$$E_{vdw} = \sum_{i<j} \varepsilon_{ij} \left( \left( \frac{\sigma_{ij}^0}{r_{ij}} \right)^{12} - 2 \left( \frac{\sigma_{ij}^0}{r_{ij}} \right)^6 \right)$$  \hspace{1cm} (3)

where $\varepsilon_{ij}$ is the well depth and $r_{ij}^0$ is the VDW bond length. The $\varepsilon_{ij}$ and $r_{ij}^0$ are calculated from a geometric mean combination rule:

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \times \varepsilon_j}$$  \hspace{1cm} (4)
\[ r_{ij}^0 = \sqrt{|r_i^0 \times r_j^0|} \]  

(5)

The \( \varepsilon_i \) and \( r_i^0 \) parameters for atom \( i \) can be taken from the UFF force field.

The difference charge densities (DCDs) was employed to describe the migration of electrons [32,33] in a transition state structure as the following equation:

\[ \Delta \rho = \rho_{\text{zeolite–organic fragment}} - \rho_{\text{zeolite}} - \rho_{\text{organic fragment}} \]  

(6)

where \( \rho_{\text{zeolite–organic fragment}}, \rho_{\text{organic fragment}} \) and \( \rho_{\text{zeolite}} \) are the electron densities of the TS, organic fragment and isolated zeolite in the TS, respectively.

The isosurface plots of reduced density gradient (RDG) and \( \Omega \) function are employed to distinguish and visualize different types of interactions of important intermediates and transition states in the zeolite system [34]. These two functions are given as follows:

\[ RDG(r) = \frac{1}{2(3\pi^2)^{1/3}} \left| \nabla \rho(r) \right| \rho(r)^{4/3} \]  

(7)

\[ \Omega(r) = \text{Sign} \left( \lambda_2(r) \right) \rho(r) \]  

(8)

where \( \rho(r) \) is the total electron density, and \( \lambda_2 \) is the second largest eigenvalue of the Hessian matrix of electron density.

The electron density is further analyzed by the local orbital locator (LOL). The LOL is defined as the following equation [35]:

\[ t_{\sigma} = \frac{\tau_{\sigma}^{\text{LSDA}}}{\tau_{\sigma}^{\text{exact}}} \]  

(9)

\[ \nu_{\sigma} = \frac{t_{\sigma}}{1+t_{\sigma}} \quad (0 \leq \nu_{\sigma} \leq 1) \]  

(10)

\[ \tau_{\sigma}^{\text{LSDA}} = \frac{3}{5} \left( 6\pi^2 \right)^{2/3} \rho_{\sigma}^{5/3} \]  

(11)

\[ \tau_{\sigma}^{\text{exact}} = \sum_i |\nabla \psi_{i\sigma}|^2 \]  

(12)

where \( \tau_{\sigma}^{\text{LSDA}}, \tau_{\sigma}^{\text{exact}} \) and \( \nu_{\sigma} \) are the LOL function, non-interacting Kohn–Sham kinetic energy density and local spin density approximation (LSDA), respectively.

In the catalytic reactions, the organic fragments in transition states in the zeolite channel are cationic and zeolitic framework is anionic in nature. It is important to
describe accurately the electrostatic interaction between the cationic transition state and the anionic framework of zeolite. In present study, the QM atomic charges were obtained from the DFT calculations and the MM charges were taken from our previous work [36]. Gaussian 09 and Multiwfn software packages were employed for the ONIOM calculations and the analysis of DCDs, RDGs and LOLs functions respectively [37,38].

Results and discussion

Generally speaking, the sulfur vacancies on the sulfided Cu-Mo catalyst serve as the active center for the HDS reaction of thiophene and its derivatives. As a promoter, Cu atoms promote the activation of molecular hydrogen and the formation of sulfur vacancies between Mo and Cu atoms [39,40]. The main hydrogenated species of thiophene are 2,3-dihydrothiophene (2,3-DHT), 2,5-dihydrothiophene (2,5-DHT) and tetrahydrothiophene (THT) [41,42]. According to the previous work [17], hydrogenolysis desulfurization (HYD) and direct desulfurization (DDS) will be discussed (Schemes 1–5). In the HYD pathway, hydrogenation of C=C bond occurs before the C–S bond is broken. In this work, the HDS means HYD and H\textsubscript{2} molecules participate in the desulfurization process. In the DDS pathway, the concerted desulfurization of hydrogenated thiophene is investigated and the H\textsubscript{2} molecules do not participate in the desulfurization process. All transition states (TSs) and intermediates are identified in the elementary steps. All important information of TSs is shown in the Figs. 1–12 and Figs. S1–S11. The free energy barriers of TSs are given in Tables 1–5. Schemes 1–5 display the HYD and DDS pathways. In the following sections, when we use the word "FAU", it represents the Cu-Mo-FAU zeolite.

The Formation of Sulfur Vacancies

Scheme 1 shows the pathway for the formation of sulfur vacancy on the FAU zeolite. The free energy profile is given in Fig. S1. Firstly, one H\textsubscript{2} molecule is adsorbed on the zeolite through a Cu–H\textsubscript{2} interaction (complex-1). The H–H bond in the H\textsubscript{2} fragment in complex-1 is 0.77 Å and the Cu–H bond is about 1.86 Å. Subsequently, the H–H bond is broken and a new S–H bond is formed through the transition state TS-1 (Fig.
3) with an activation free energy barrier of 178.62 kJ mol\(^{-1}\) (Table 1). Weber et al. reported an activation barrier of 71.13 kJ mol\(^{-1}\) for the dissociation of one H\(_2\) molecule on a NiMoS cluster catalyst [43].

After TS-1, intermediate INT-1 is formed. The hydrogen transfer from INT-1 (TS-2) leads to the formation of H\(_2\)S molecule and the generation of a sulfur vacancy (complex-2). In TS-2, a new S–H bond is forming and the Cu–H bond is breaking; the bond lengths of S–H and Cu–H are 1.44 and 2.46 Å (Fig. 3). This step needs to overcome an activation barrier of 113.62 kJ mol\(^{-1}\) (Table 1) and the subsequent desulfurization of hydrogenated thiophene is occurred on the sulfur vacancy. Liu et al. reported that the TS-2 needed to overcome higher activation barrier than that in TS-1 in zeolite L [17]. In present study, the calculated results show that the H–H bond cracking step (TS-1) is more difficult to occur than the formation of H\(_2\)S (TS-2) due to the higher activation barrier over Cu-Mo-FAU zeolite.

The rate-determining step is very important for understanding the difficulty of occurrence of a reaction pathway. According to the Murdoch's work [44], we displayed the energy profile of the formation of sulfur vacancy in Fig. S1. When the whole reaction pathway is divided into several different sections, we calculated the energy difference \(\Delta E_i\) between the TS with the highest energy and the initial intermediate in each section \(i\). The maximum (\(\Delta E_i\)) corresponds to the rate-determining step. A effective method on how to divide the reaction pathway is that we first choose a intermediate INT\((i)\) and then select another intermediate INT\((j)\) with lower energy than the INT\((i)\) and the same number of atoms as the INT\((i)\). This method is often used several times throughout the whole reaction pathway to obtain several different reaction sections; for the simple pathways, we probably divide the reaction pathway only once. In Fig. S1, one section is involved: complex-1 to complex-2. The largest energy difference is obtained for TS-2 with the free energy barrier of 178.64 kJ mol\(^{-1}\), showing that the rate-determining step is the formation of H\(_2\)S. The free energy barrier of 178.64 kJ mol\(^{-1}\) is obtained from energy difference between TS-2 and complex-1. In addition, one can see that from the Fig. S1, the formation of sulfur vacancy is thermodynamically endothermic reaction and thus high
reaction temperature is needed to produce enough sulfur vacancies.

Decomposing the ONIOM total energy barriers into QM and MM contributions is an important way to investigate the effect of zeolite framework on the reaction mechanisms. According to eq 1, the total ONIOM free-energy barrier for a given reaction step from INT to TS can be calculated from the following equation [45]:

\[
\Delta E_{\text{free-energy-barrier}} = E_{\text{ONIOM}}(TS) - E_{\text{ONIOM}}(INT) = \Delta E_{\text{QM}} + \Delta \Delta E_{\text{MM}}
\]

\[
\Delta \Delta E_{\text{MM}} = \Delta E_{\text{MM}}(TS) - \Delta E_{\text{MM}}(INT)
\]

\[
\Delta E_{\text{MM}} = E_{\text{MM(\text{real})}} - E_{\text{MM(\text{inner})}}
\]

(13)

The \( \Delta \Delta E_{\text{MM}} \) value is called MM energy contribution to the total ONIOM free energy barrier and listed in Tables 1–5. The sign of \( \Delta \Delta E_{\text{MM}} \) indicates that the zeolite framework is favorable (\( \Delta \Delta E_{\text{MM}} > 0 \)) or unfavorable (\( \Delta \Delta E_{\text{MM}} < 0 \)) for the formation of TS. In Table 1, one can see that zeolite framework is favorable for the formation of TS1 and TS2 because the \( \Delta \Delta E_{\text{MM}} \) values are negative. On the other hand, the free energy barriers are controlled by the \( \Delta E_{\text{QM}} \) values because of the small \( \Delta \Delta E_{\text{MM}} \) values.

The enthalpy barriers (\( \Delta H^\ddagger \)), entropy losses (\(-T\Delta S^\ddagger\)), free energy barriers (\( \Delta G^\ddagger \)) at 673.15 K for TS1 and TS2 are also given in Table 1. It can be seen that these reaction steps are mainly dominated by enthalpy barriers because all entropy losses are very small. The entropy losses in TS1 and TS2 are negative, which suggests that the formation of sulfur vacancy is an entropy-increased pathway.

**The desulfurization of thiophene**

According to the work of Liu et al., the HDS of thiophene (not hydrogenated thiophene) can occur through ring-opening and C–S bond cracking steps on Co-Mo-supported L zeolite [17]. We investigated carefully the HDS pathway of thiophene on Cu-Mo-supported FAU zeolite and did not find the corresponding transition states. Many experimental work has suggested that CuO/SBA-15 [46], Cu/ZrO\(_2\) [47], CuCeY [48,49], CuNaY [50] and CuY [51] can been used for adsorptive desulfurization of thiophene. We optimized adsorbed structures of
thiophene on Cu-S$_2$-Mo and Cu-S-Mo FAU zeolites. On Cu-S$_2$-Mo FAU, the C=C double bond of thiophene interacts with the Cu atom; the bond length of Cu···C=C is about 2.21 Å (Fig. S4a). The Cu···C=C structure is consistent with the reported experimental prediction for the $\eta^5$ adsorption mode of thiophene [52]. On Cu-S-Mo FAU, the sulfur atom of thiophene interacts with the Mo atom; the bond distance of S···Mo is 2.40 Å (Fig. S4b). The S···Mo adsorption model is in accord with the experimental prediction for the $\eta^1$ adsorption mode of thiophene [52]. At 0 K, the adsorption energies of thiophene on Cu-S$_2$-Mo and Cu-S-Mo FAU zeolites are -100.21 and -146.19 kJ mol$^{-1}$ respectively. At 673.15 K, the adsorption energies of thiophene on Cu-S$_2$-Mo and Cu-S-Mo FAU are -4.19 and -9.76 kJ mol$^{-1}$ respectively, indicating that even if at high temperatures, thiophene still tends to adsorb on the zeolite. Therefore, we predict that the HDS pathway of thiophene is probably adsorptive desulfurization.

**The hydrogenation of thiophene to 2,5-DHT, 2,3-DHT and THT**

In the HYD pathway, the C=C double bond of thiophene molecule is firstly hydrogenated and then the C–S bond is broken [41,52]. Zhu and Hensen et al. pointed out that the hydrogenated intermediates of thiophene are 2,5-DHT, 2,3-DHT and THT [41,42]. The investigation on hydrogenation process from thiophene to 2,5-DHT, 2,3-DHT and THT is crucial to better understand the HDS mechanism of thiophene because hydrogenation of C=C bond of thiophene is probably competitive with the HDS process. Scheme 2 gives the pathway of the hydrogenation of thiophene on the Cu-2S-Mo FAU zeolite.

The initial step is the adsorption of thiophene on the Cu-2S-Mo catalytic center with a S···Mo adsorption mode (complex-trans-1). Subsequently, the Cu–H is breaking and a new C–H bond in thiophene is forming through the transition state TS-trans-1 (Scheme 2); the bond lengths of Cu–H and C–H are 1.44 and 1.65 Å respectively (Fig. 4a). The activation free energy barrier of the hydrogen transfer step is 152.73 kJ mol$^{-1}$ (Table 2).

The complex-trans-2 undergoes two different hydrogen transfer steps through the transition states TS-trans-2 and TS-trans-4 to form complex-trans-3 and
The activation free energy barriers for TS-trans-2 are calculated to be 49.95 kJ mol\(^{-1}\). In the TS-trans-2 (Fig. 4b), the S–H bond is breaking and a new C–H bond is forming; the bond lengths of S–H and C–H are 1.62 and 1.43 Å respectively. The TS-trans-1 and TS-trans-2 lead to the formation of 2,5-DHT with free energy barriers of 152.73 and 49.95 kJ mol\(^{-1}\) respectively. Jiao et al. theoretically reported that the hydrogenation of thiophene to 2,5-DHT needed to overcome a moderate energy barrier of 93.50 kJ mol\(^{-1}\) on Mo\(_3\)S\(_9\) cluster catalyst [16].

Another hydrogen transfer step through TS-trans-4 needs an activation free energy barrier of 67.57 kJ mol\(^{-1}\) (Table 2), suggesting that these two hydrogen transfer steps (TS-trans-2 and TS-trans-4) can occur easily on FAU zeolite. In TS-trans-4 (Fig. 4d), the S–H bond is breaking (1.65 Å) and a new C–H bond is forming (1.44 Å). After TS-trans-4, 2,3-DHT is formed and adsorbed on the Cu-2S-Mo catalytic center. One H\(_2\) molecule is then chemically co-adsorbed with 2,5-DHT in complex-trans-3 to form complex-trans-4 or co-adsorbed with 2,3-DHT in complex-tran-6 to form complex-trans-7. Subsequently, THT could be produced from two different pathways. In the first pathway, the S–H and Cu–H bonds are breaking and two new C–H bonds are forming (complex-trans-5) through the transition state TS-trans-3 with a high free energy of 182.97 kJ mol\(^{-1}\). The structure of TS-trans-3 is displayed in Fig. 4c with concerted breaking of Cu–H and S–H bonds and forming of two C–H bonds. The bond lengths of Cu–H, S–H and are C–H are in the range of 1.39–2.08 Å.

The second pathway for the formation of THT is two successive hydrogen transfer steps in TS-trans-5 and TS-trans-6 from complex-trans-7 and complex-trans-9 respectively (Scheme 2). In the TS-trans-5 (Fig. 4e), the Cu–H bond is breaking and the Mo–H bond is forming and the 2,3-DHT (complex-trans-7) is converted into 2,5-DHT (complex-trans-8) with a moderate free energy of 134.47 kJ mol\(^{-1}\) (Table 2). The 2,5-DHT in complex-trans-8 is then desorbed and the 2,3-DHT is adsorbed again (complex-trans-9). The 2,3-DHT in complex-trans-9 is subsequently converted into THT with concerted breaking of Mo–H and S–H bonds (TS-trans-6) and this step needs to overcome a small free energy of 67.84 kJ mol\(^{-1}\). Therefore, the lower
activation barrier from TS-trans-6 (67.84 kJ mol⁻¹) than TS-trans-3 (182.97 kJ mol⁻¹) indicates that the formation of THT occur more easily through the hydrogenation of 2,3-DHT. Jiao et al. reported that the formation of THT from the conversion of 2,5-DHT needed an energy barrier of 109.20 kJ mol⁻¹ on Mo₃S₉ cluster catalyst [16]. The corresponding structures of TS-trans-5 and TS-trans-6 are given in Figs. 4e and 4f respectively. The bond lengths of Cu−H, S−H and C−H are in the range of 1.20–1.97 Å. In summary, the formation steps of 2,5-DHT (TS-trans-2, 49.95 kJ mol⁻¹), 2,3-DHT (TS-trans-4, 67.57 kJ mol⁻¹) and THT (TS-trans-6, 67.84 kJ mol⁻¹) are all favorable because of the low free energy barriers, showing that three hydrogenated derivatives are important intermediates involved in the HYD process.

Table 2 lists the enthalpy barriers, entropy losses, QM and MM contributions for the free energy barriers at 673.15 K for all TSs. Several interesting viewpoints can be obtained. First, all MM energy values are positive in FAU, suggesting that FAU zeolite framework is unfavorable for the hydrogenation of thiophene to 2,5-DHT, 2,3-DHT and THT. Second, positive entropy losses values for all TSs indicate that the hydrogenation process of thiophene is entropy-decreased. Third, all the free energy barriers are controlled by the QM contributions except TS-trans-6. In TS-trans-6, the entropy loss is larger than the enthalpy barrier, showing the hydrogen transfer step in TS-trans-6 is controlled by entropic effect.

The HYD pathway of 2,5-DHT

In the HYD pathway, the reactant is the hydrogenated thiophene. As mentioned above, one or two C=C bonds of thiophene can be hydrogenated into three different derivatives: 2,3-DHT, 2,5-DHT and THT. Due to the low activation barriers, the hydrogenation process occurs easily on the zeolite. Experimental observations showed that the hydrogen transfer and the cleavage of C−S bond are the main steps in the HYD pathways of the three hydrogenated species [53-55].

Scheme 3 displays the HYD pathway of 2,5-DHT on the sulfided Cu-Mo-FAU zeolite. The corresponding energy profile is given in Fig. 2. After the sulfur vacancy is formed (Scheme 1), the 2,5-DHT is firstly adsorbed on the sulfur vacancy. Then, one H₂ molecule is co-adsorbed with the 2,5-DHT through a Mo···H₂ interaction on
Cu-S-Mo cluster to form a complex-2,5DHT-2. The H–H and C–S bonds in complex-2,5DHT-2 are broken through the transition state TS-2,5DHT-1 (Fig. 5a); the Gibbs activation free energy barrier is calculated to be 52.48 kJ mol\(^{-1}\) (Table 3), which indicates that C–S bond cleavage in 2,5-DHT can occur easily on FAU zeolite. Jiao et al. theoretically reported that the activation barrier for the ring-opening step of 2,5-DHT was 138.60 kJ mol\(^{-1}\) on Mo\(_3\)S\(_9\) cluster catalyst [16]. Guo et al. studied the HDS of 2,5-DHT on Pt(111) and found that the energy barrier for the ring-opening of 2,5-DHT was 139.91 kJ mol\(^{-1}\) [41]. Weber et al. reported an activation barrier of 133.05 kJ mol\(^{-1}\) for the ring-opening of a dibenzothiophene (DBT) molecule on a NiMoS cluster catalyst [43]. Their energy barrier values are higher than our calculated result mainly because of the different catalysts.

After TS-2,5DHT-1, the INT-2,5DHT-1 is formed and then converted into 2-butene through hydrogen transfer (TS-2,5DHT-2) and C–S bond cracking steps (TS-2,5DHT-3). The INT-2,5DHT-2 is produced through the hydrogen transfer step of INT-2,5DHT-1; the corresponding transition state is TS-2,5DHT-2 and the activation free energy barrier is 141.14 kJ mol\(^{-1}\). At TS-2,5DHT-2 (Fig. 5b), the Cu–H bond is breaking and a new S–H bond is forming; the bond lengths of S–H and Cu–H are 1.52 and 2.15 Å respectively. Weber et al. reported a low activation barrier of 40.58 kJ mol\(^{-1}\) for the hydrogen transfer of a DBT molecule on a NiMoS cluster catalyst [43].

The subsequent C–S bond cracking step from the TS-2,5DHT-3 leads to the formation of 2-butene molecule and the regeneration of the catalyst (Scheme 3). This step needs to overcome a low activation free energy barrier of 38.03 kJmol\(^{-1}\) (Table 3). Weber et al. reported a low activation barrier of 130.96 kJ mol\(^{-1}\) for the same step of a DBT molecule on a NiMoS cluster catalyst [43]. Guo et al. studied the HDS of 2,5-DHT on Pt(111) and found that the energy barrier for the C–S bond cracking of 2,5-DHT was 51.14 kJ mol\(^{-1}\) [41]. Jiao et al. reported that the calculated activation barrier for the C–S bond cracking step of 2,5-DHT was 39.0 kJ mol\(^{-1}\) on Mo\(_3\)S\(_9\) cluster catalyst [16], which is nearly equal to our result.

At TS-2,5DHT-3 (Fig. 5c), we can see that C–S and S–H bond are breaking and a new C–H bond is forming; the bond lengths of C–S, S–H and C–H are in the range
of 1.58–2.78 Å. After TS-2,5DHT-3, the S atom of the –SH group replenishes the S vacancy on the zeolite, and the catalyst is regenerated (complex-2,5-DHT-3). The predicted product 2-butene was experimentally observed in situ FTIR and XANES studies for thiophene HDS on Ni2P/MCM-41 zeolite by Oyama et al. [52].

A concerted direct desulfurization (DDS) pathway is proposed for the desulfurization of 2,5-DHT without H2 molecules (Scheme 3). The two alkyl C–S bonds of 2,5-DHT in the complex-2,5DHT-1 are simultaneously broken through the TS-2,5DHT-4 to form 1,3-butadiene (complex-2,5DHT-4). The activation free energy barrier is 98.54 kJ mol⁻¹. Jiao et al. studied the formation of 1,3-butadiene on Mo2S9 cluster and the calculated activation barrier was 89.6 kJ mol⁻¹, which is slightly lower than our result. The structure of TS-2,5DHT-4 is displayed in Fig. 5d; new Cu–S and Mo–S bonds are forming and two C–S bonds in 2,5-DHT are breaking. The breaking bond lengths of two C–S bonds is about 2.25 Å. The product 1,3-butadiene was experimentally observed by Oyama et al. in situ FTIR and XANES studies of thiophene HDS on Ni2P/MCM-41 [52].

In the energy profile of desulfurization of 2,5-DHT (Fig. 2), two sections are involved on FAU: complex-2,5DHT-2 to INT-2,5DHT-1 (52.48 kJ mol⁻¹, TS-2,5-DHT-1) and INT-2,5DHT-1 to complex-2,5DHT-3 (141.14 kJ mol⁻¹, TS-2,5DHT-2). The largest energy difference is obtained in the second section (from INT-2,5DHT-1 to complex-2,5DHT-3) with the free energy barrier of 141.14 kJ mol⁻¹, showing that the rate-determining step is not the ring-opening and C–S bond cracking of 2,5-DHT but the hydrogen transfer of INT-2,5DHT-1. The ring-opening and C–S bond cracking steps of 2,5-DHT are easy to occur because of the low free energy barriers (less than 53 kJ mol⁻¹). In addition, one can see that from the Fig. 2, the HYD of 2,5-DHT is thermodynamically exothermic reaction. It should be noted that the free energy barrier for the concerted DDS pathway (98.54 kJ mol⁻¹, TS-2,5DHT-4) is lower than the energy barrier (141.14 kJ mol⁻¹, TS-2,5DHT-2) for the rate-determining step in the HYD pathway. Therefore, the concerted DDS pathway is probably more favorable than the HYD pathway in the desulfurization of 2,5-DHT.

We calculated the enthalpy barriers, entropy losses, QM and MM contributions for the free energy barriers at 673.15 K for all TSs in Table 3. Several interesting
viewpoints can be obtained. First, positive entropy loss values for all TSs indicate that the HDS of 2,5-DHT is entropy-decreased. Second, most of MM energy values except TS-2,5DHT-2 are positive, suggesting that FAU zeolite framework is generally unfavorable for the formation of TSs in the HDS of 2,5-DHT. Third, all the free energy barriers are controlled by the QM contributions. Fourth, all the free energy barriers are controlled by the enthalpy barriers except TS-2,5DHT-3 and TS-2,5DHT-4; In these two TSs, the entropy losses are larger than the enthalpy barriers, showing the C–S bond cleavage step in TS-2,5DHT-3 and concerted elimination step of 2,5-DHT in TS-2,5DHT-4 are controlled by entropic effect.

**The HYD pathway of 2,3-DHT**

Scheme 4 shows the HYD pathway of 2,3-DHT on sulfided Cu-Mo-FAU zeolite. The corresponding energy profile is given in Fig. S2. Firstly, 2,3-DHT is adsorbed on the sulfur vacancy through a Mo···H$_2$ interaction (complex-2,3DHT-1). One H$_2$ molecule is co-adsorbed with 2,3-DHT to form complex-2,3DHT-2. The H–H and C–S bonds in complex-2,3DHT-2 are broken through transition state TS-2,3DHT-1 (Fig. 6a). The calculated Gibbs free energy barrier for this step is 164.72 kJ mol$^{-1}$ (Table 4), which indicates that the ring-opening of 2,3-DHT is more difficult than 2,5-DHT because of the lower activation barrier of 52.48 kJ mol$^{-1}$ (Table 3). Guo et al. studied the HDS of 2,3-DHT on Pt(111) and found that the energy barrier for the ring-opening of 2,3-DHT on Pt(111) was 103.24 kJ mol$^{-1}$ [41].

INT-2,3DHT-1 is converted to 1-butene through hydrogen transfer (TS-2,3DHT-2) and C–S bond cracking steps (TS-2,3DHT-3). The TS-2,3DHT-2 is formed through the hydrogen transfer step of INT-2,3DHT-1. The corresponding activation energy barrier is 141.99 kJ mol$^{-1}$, which is nearly equal to the free energy of 141.14 kJ mol$^{-1}$ for the hydrogen transfer step (TS-2,5DHT-2) in the HYD of 2,5-DHT. At TS-2,3DHT-2 (Fig. 6b), the Cu–H bond is broken and a new S–H bond is formed; the bond lengths of S–H and Cu–H are 1.49 and 2.06 Å. The C–S bond cracking step for TS-2,3DHT-3 leads to the formation of 1-butene molecule and the regeneration of the catalyst. This step needs an activation energy barrier of 138.15 kJ mol$^{-1}$ that is higher than the energy barrier of 38.03 kJ mol$^{-1}$ in the C–S bond cracking step.
(TS-2,5DHT-3) in the HYD of 2,5-DHT. The higher energy barriers in TS-2,3DHT-1 and TS-2,3DHT-3 than those in TS-2,5DHT-1 and TS-2,5DHT-3 show that the ring-opening and C–S bond cracking steps are more favorable in HYD of 2,5-DHT. Guo et al. studied the HDS of 2,3-DHT on Pt(111) and found that the energy barrier for the C–S bond cracking was 82.98 kJ mol$^{-1}$ [41].

The predicted product 1-butene was found in the experimental work in Hensen [42] and Oyama et al. [52]. From TS-2,3DHT-3 (Fig. S5a), we can see that the S–H and C–S bonds are breaking and a new C–H bond is forming. The bond lengths of S–H, C–S and C–H are 3.50, 3.69 and 1.38 Å respectively. After TS-2,3DHT-3, the S atom of the S–H group replenishes the S vacancy on the zeolite, and the catalyst is regenerated (complex-2,3-DHT-3).

As mentioned above, a concerted DDS elimination pathway is easy to occur for the desulfurization of 2,5-DHT. Liu et al. reported a single concerted elimination pathway for the desulfurization of 2,3-DHT to form 1,3-butadiene in the Co-Mo zeolite L [17]. In present study, IRC calculations showed that this concerted transition state did not exist in the Cu-Mo FAU zeolite. In fact, Liu et al. pointed out that the concerted elimination pathway in the Co-Mo zeolite L was unfavorable due to high activation barrier.

In the energy profile of HYD of 2,3-DHT (Fig. S2), two sections are involved: complex-2,3DHT-2 to INT-2,3DHT-1 (164.72 kJ mol$^{-1}$, TS-2,3-DHT-1) and INT-2,3DHT-1 to complex-2,3DHT-3 (253.54 kJ mol$^{-1}$, TS-2,3DHT-3). The largest energy difference is obtained in the second section (INT-2,3DHT-1 to complex-2,3DHT-3, 253.54 kJ mol$^{-1}$) which shows that the rate-determining step is not the ring-opening and hydrogen transfer steps but C–S bond cracking of 2,3-DHT (TS-2,3DHT-3). It should be noted that for the same TS-2,3DHT-3, the energy barrier of 253.54 kJ mol$^{-1}$ is different from the energy barrier of 138.15 kJ mol$^{-1}$. The reason is that the former is calculated from the energy difference between TS-2,3DHT-3 and the first intermediate INT-2,3DHT-1 in the second section in the reaction sequence but the latter is calculated from the energy difference between TS-2,3DHT-3 and its previous intermediate INT-2,3DHT-2. The former is an apparent energy barrier for the whole HYD pathway of 2,3-DHT and the latter is only an energy barrier for an
individual step, i.e., the C-S bond cleavage. In addition, one can see that from the Fig. S2, the HYD of 2,3-DHT is thermodynamically exothermic reaction.

The enthalpy barriers, entropy losses, QM and MM contributions for the free energy barriers at 673.15 K for all TSs are listed in Table 4. First, positive entropy loss values for all TSs indicate that the HYD of 2,3-DHT is entropy-decreased. Second, most of MM energy values except TS-2,3DHT-2 are positive, suggesting that FAU zeolite framework is generally unfavorable for the formation of TSs in the HYD of 2,3-DHT. This prediction is the same as that for TS-2,5DHT-2. Third, all the free energy barriers are controlled by the QM contributions or the enthalpy barriers.

The HYD pathway of THT

Scheme 5 describes the HYD pathway of THT on the Cu-Mo FAU zeolite. The energy profile is given in Fig. S3. As shown in Scheme 5, THT is adsorbed on sulfur vacancy (complex-THT-1). Adding four H atoms to thiophene will lead to the complete destruction of the π-bond system of the thiophene ring; all C−S and C−C bonds in THT are elongated. The H2 and THT molecules are co-adsorbed on the Cu-S-Mo center to form complex-THT-2. At the TS-THT-1 (Fig. 6c), the H−H (0.83 Å) and C−S bonds (2.61 Å) are breaking and new C−H bond is forming (1.75 Å). The activation free energy barrier is calculated to be 174.24 kJ mol\(^{-1}\) (Table 5); this higher energy barrier than those in 2,3-DHT (164.72 kJ mol\(^{-1}\)) and 2,5-DHT (52.48 kJ mol\(^{-1}\)) indicating that the ring-opening step is unfavorable for the fully saturated thiophene. Jiao et al. studied the ring-opening of THT on Mo\(_3\)S\(_9\) cluster and reported that the calculated activation barrier was 170.6 kJ mol\(^{-1}\) [16]. Guo et al. studied the HYD of THT on Pt(111) and found that the energy barrier for the ring-opening of THT was 164.99 kJ mol\(^{-1}\) [41]. Their energy barriers are close to our result (174.24 kJ mol\(^{-1}\)).

The TS-THT-2 and TS-THT-3 undergo hydrogen transfer and C−S bond cracking steps respectively to produce a butane molecule. From TS-THT-2 (Fig. 6d), it can be seen that the Cu−H bond is broken and a new S−H bond is formed; the bond lengths of S−H and Cu−H are 1.52 and 2.18 Å respectively. The activation free energy barrier for TS-THT-2 is 111.33 kJ mol\(^{-1}\). After the C−S bond cracking step from TS-THT-3, the butane molecule is formed and the catalyst is regenerated. The corresponding activation energy barrier is 267.34 kJ mol\(^{-1}\) that is higher than energy barriers of
138.15 kJ mol\(^{-1}\) in TS-2,3DHT-3 and 38.03 kJ mol\(^{-1}\) in TS-2,5DHT-3, indicating that C−S bond cracking step is more difficult to occur in the fully saturated thiophene. Guo and Jiao reported the different results for the C−S bond cracking of THT on Pt(111) (111.93 kJ mol\(^{-1}\)) \[41\] and Mo\(_3\)S\(_9\) cluster (98.8 kJ mol\(^{-1}\)) \[16\]. The final product butane was observed in the experimental work in Hensen \[52\] and Oyama et al. \[42\]. From TS-THT-3 (Fig. S5b), the S−H and C−S bonds are broken and a new C−H bond is formed; the bond lengths of S−H, C−S and C−H bonds are 1.41, 2.23 and 1.66 Å respectively. After TS-THT-3, Mo−S and Cu−S bonds are formed; the S vacancy on the zeolite is replenished (complex-THT-3).

On Co-Mo zeolite L, Liu et al. reported a concerted DDS elimination pathway for the THT but the concerted transition state is unfavorable due to high activation barrier \[17\]. In current study, we obtained a concerted transition state in the Cu-Mo FAU zeolite that is structurally similar to the above-mentioned concerted TSs in Co-Mo zeolite L in the work of Liu et al. However, the corresponding IRC analysis suggested that the obtained TS in current work can not connect the relevant forward and reverse intermediates as given in the work of Liu et al. In the DDS of 2,3-DHT, the case is the same as that for the THT. Therefore, we predict that the desulfurization of 2,3-DHT and THT should occur by the HYD pathway.

In the energy profile (Fig. S3), three sections are involved: complex-THT-2 to INT-THT-1 (174.24 kJ mol\(^{-1}\), TS-THT-1) and INT-THT-1 to INT-THT-2 (111.33 kJ mol\(^{-1}\), TS-THT-2) and INT-THT-2 to complex-THT-3 (267.34 kJ mol\(^{-1}\), TS-THT-3). The largest energy difference is obtained in the third section (INT-THT-2 to complex-THT-3) with the free energy barrier of 267.34 kJ mol\(^{-1}\), showing that the rate-determining step is the C−S bond cracking of THT. The hydrogen transfer of INT-THT-1 is much easier than ring-opening and C−S bond cracking steps due to low energy barrier (111.33 kJ mol\(^{-1}\)). In addition, one can see that from the Fig. S3, the HYD of THT is thermodynamically exothermic reaction. In summary, for the HYD pathways of three hydrogenated thiophene, the rate-determining step is hydrogen transfer step for 2,5-DHT and C−S bond cracking step for 2,3-DHT and THT.

From the decomposition of free energy barriers in Table 5, two remarks can be found. First, all the free energy barriers are controlled by the enthalpy barriers or QM
contributions. Second, the entropy loss and MM energy value in TS-THT-3 are both negative, which indicates that the C–S bond cleavage step is entropy-increased and FAU framework is favorable for the formation of TS-THT-3.

**Understanding of the nature of transition state species**

In this work, the organic fragments in the TSs are cationlike and the zeolitic framework is anionlike. The charges will flow between different atoms and the electron density will change when the reaction steps occur, which reflects the nature of the elementary steps. We calculated the difference charge densities (DCDs), the reduced density gradients (RDGs) and localized orbital locators (LOLs) of the transition states to elucidate the migration of electrons for different elementary steps.

**The nature for the formation of sulfur vacancy**

The DCD plot of TS-1 for the H₂ cleavage is obtained from the following equation:

$$\Delta \rho = \rho^{TS} - \rho^{TS\text{ zeolite-framework(noH}_2\text{)}} - \rho^{TS\text{H}_2\text{gas}}$$

where $\rho^{TS}$ is the electron density of the TS. $\rho^{TS\text{ zeolite hydrocarbon(noH}_2\text{)}}$ and $\rho^{TS\text{H}_2\text{gas}}$ are the electron densities of the TS without the H₂ fragment and isolated gas H₂ molecule at their equilibrium structures of the TS. After H–H bond cracking, the INT-1 is formed. A DCD analysis (Figs. 7a and 7b) suggests that for TS-1, the electron density decreases in the H₂ fragment and increases in the Cu and S atoms, which reflects a clear electron transfer from the H₂ molecule to the Cu and S atoms when the H₂ molecule is cracked.

Figures 7c and 7d show the LOL color-filled map of TS-1 on FAU. As shown in the Figs. 7c and 7d, the blue circle represents the region with low electron density between the valence shell and the inner shell. A yellow region between two hydrogen atoms indicates that there is a weak interaction between them and the H–H bond is forming or breaking, which is consistent with the nature of the transition state TS-1 (i.e., H–H bond cracking step).

The RDG plot for TS-1 over the FAU zeolite is given in Fig. 7e. A red region appears between two hydrogen atoms in the TS-1, which indicates that there is spatial repulsion between these two hydrogen atoms because they are close to each other.
The DCD plots for TS-2 are given in Figs. 8a and 8b. A careful DCD analysis suggests that the electron density decreases in the H$_2$S fragment, reflecting that the electron cloud is migrating from the organic fragment H$_2$S to the catalytic center during the formation of H$_2$S molecules. A green LOL region appears between H$_2$S and Cu atom for TS-2 in Figs. 8c and 8d, indicating that there is a weak attraction interaction between them. This weak interaction is consistent with the nature of the transition state for the formation of H$_2$S.

The RDG plot for TS-2 over the FAU zeolite is given in Fig. 8e. A red and blue region appears between the H$_2$S fragment and catalytic site; the red region represents a spatial repulsion and the blue region indicates a weak Mo···H$_2$S coordination attraction interaction. A careful comparison of RDGs between TS-1 (Fig. 7e) and TS-2 (Fig. 8e) suggests that there is a wider red region in TS-1 than TS-2, which indicates a stronger spatial hindrance and thus higher free energy barrier in TS-1 (178.62 kJ mol$^{-1}$) than TS-2 (113.62 kJ mol$^{-1}$).

The nature for the HYD of 2,5-DHT

The DCD plots of TS-2,5DHT-1 are given in Figs. S6a and S6b. The electron density on the organic framework decreases but the electron density in the catalytic center increases, which indicates that in the ring-opening process of 2,5-DHT, the electrons migrate from the organic chain to the catalytic center. The RDG plot for TS-2,5DHT-1 is given in Fig. S6c. There is a red region between the organic chain and catalytic center, showing a strong ring tension in the TS-2,5DHT-1. Figures S6d to S6f show the color-filled LOL map of TS-2,5DHT-1. In the LOL map, there are a red region between C atom of the organic fragment and H atom of H$_2$ fragment, which shows that the C–H covalent bond is nearly formed. A weak yellow region appears between two H atoms, indicating there is an weak attraction interaction between them.

The DCD plots of TS-2,5DHT-2 are given in Figs. S7a and S7b. The electron density on the H atom and the organic fragment decreases and the electron density on the Cu atom increases, which reflects that the electrons migrate from the organic fragment and the H atom to the Cu atom in the hydrogen transfer process. Figures S7c and S7d show the color-filled LOL map. In the LOL map, a yellow and green region
is formed between the migrating H atom and the Cu atom, showing a weak interaction between H and Cu atoms. A white region appears between the migrating H atom and the sulfur atom in the organic fragment, which indicates that the H–S covalent bond is nearly formed in the TS-2,5DHT-2. The RDG plot for TS-2,5DHT-2 is given in Fig. S7e. There is a blue and red region between organic fragment and Cu-S-Mo catalytic center, showing that both a steric hindrance and a weak van der Waals attractive interaction exist in the reactive center.

The DCD plots of TS-2,5DHT-3 are given in Figs. 9a and 9b. The electron density of the Cu-S\textsubscript{2}-Mo center decreases but the electron density of the thiophene fragment increases, indicating that for the formation of 2-butene, the electron cloud migrates from the Cu-S\textsubscript{2}-Mo center of the zeolite to the thiophene fragment. Figures 9c to 9e shows the color-filled LOL maps of TS-2,5DHT-3. In the LOL map, there is a red LOL region in the H–C atomic pair, which indicates a strong covalent interaction in the H–C region in the TS-2,5DHT-3. The RDG plot is given in Fig. 9f. There is a red region between thiophene fragment and the Cu-S\textsubscript{2}-Mo catalytic center, which indicates a strong steric hindrance between them. Although the short bond distances in the S···H···C region lead to steric hindrance, the short S···H···C bond distance increases the degree of covalent interaction for such as the H···C bond, which is consistent with the prediction of LOL.

The DCD plots of TS-2,5DHT-4 are given in Figs. 10a and 10b. The electron density of Cu-S\textsubscript{2}-Mo in the catalytic center of zeolite decreases, and the electron density on the carbon chain atoms of thiophene ring increases, suggesting that the electron cloud migrates from the Cu-S\textsubscript{2}-Mo center to the organic carbon chain. Figures 10c, 10e and 10f shows the color-filled LOL map of TS-2,5DHT-4. The LOL map describes the atomic interactions of organic fragment and Cu-S\textsubscript{2}-Mo catalytic center. The RDG plot for TS-2,5DHT-4 is given in Fig. 10d. A yellow and green region appears between the Cu-S\textsubscript{2}-Mo catalytic active center and the organic carbon chain atoms, indicating that there is a weak attraction between them. The yellow and green region is accompanied by a little red region, showing that there is weak steric
hindrance between the catalytic center and the organic carbon chain. The weak steric hindrance is consistent with the low energy barrier of TS-2,5DHT-4 (98.54 kJ mol$^{-1}$).

**The nature for the HYD of 2,3-DHT and THT**

Figures 11a and 11b for TS-2,3DHT-1 and 12a and 12b for TS-THT-1 show the DCD plots. We can see that the electron density on the thiophene ring decreases and the electron density on the catalytic center increases, indicating that the electrons migrate from the thiophene ring to the catalytic center in the ring-opening process of 2,3DHT and THT. Figures 12c−12e show the color-filled LOL map of TS-THT-1. There is a yellow LOL region between Cu atom, H$_2$ molecule and C atom of organic carbon chain, showing that there is a weak attractive interaction between them.

The RDG plots are given in Figures 11e (TS-2,3DHT-1) and 12f (TS-THT-1). In TS-2,3DHT-1 and TS-THT-1, there is a red region between the thiophene ring and catalytic active center, showing a strong ring tension in these two TSs. A comparison of their RDGs suggests that the RDG plot of TS-2,3DHT-1 is similar to that of TS-THT-1, which is consistent with similar free energy barriers between TS-2,3DHT-1 (164.72 kJ mol$^{-1}$) and TS-THT-1 (174.24 kJ mol$^{-1}$).

The DCD plots predict similar behaviors on the migration of electron for TS-2,3DHT-2 (Figs. S8a and S8b) and TS-THT-2 (Figs. S10a and S10b). The electron density on the H atom and the organic fragment decreases, while the electron density on the Cu and Mo atoms increases, which reflects the migration of electrons from the organic fragment to the Cu-Mo catalytic center. The RDG plots for TS-2,3DHT-2 and TS-THT-2 are given in Figs. S8c and S10c respectively. There are blue and red regions between the organic carbon chain and the Cu-S-Mo catalytic active center, which verified the existence of steric hindrance and weak van der Waals attraction interaction. The color-filled LOL maps of TS-2,3DHT-2 (Figs. S8d−S8f) and TS-THT-2 (Figs. S10d−S10f) show the similar nature of TSs. The yellow and green region between H atom and Cu atom indicates that there is a weak interaction in the H…Cu atomic pair. A white area appears between the migrating H and sulfur atoms, which shows that the H−S covalent bond is nearly formed in TS-2,3DHT-2 and TS-THT-2.
The DCD plots are given in Figs. S9a and S9b for TS-2,3DHT-3 and S11a and S11b for TS-THT-3. The electron density of the Cu-S2-Mo active center decreases, but the electron density of the organic fragment increases. Therefore, when 1-butene or butane is formed, the electron cloud migrates from the Cu-S2-Mo active center to the organic fragment. The RDG plots for TS-2,3DHT-3 and TS-THT-3 are given in Figs. S9e and S11c respectively. There is a red region between the organic chain and the Cu-S2-Mo catalytic center, which indicates that there is a strong steric hindrance between them. The LOL maps in Fig. S9c and S9d and S11d–S11f display a red and yellow LOL region in the S···H···C region, which suggests that there is a strong covalent interaction in the S···H···C region for the TS-2,3DHT-3 and TS-THT-3.

**Conclusions**

In this work, the catalytic ability of the Cu-Mo-supported FAU zeolite on HDS process of hydrogenated thiophene is investigated by a two-layer ONIOM method. The nature of TSs and the confinement effect of zeolitic nanospace are revealed in detail. The major conclusions are summarized as follows:

1. Thiophene can be hydrogenated to 2,5-DHT, 2,3-DHT and THT with relatively low free energy barriers. The sulfur atoms in the hydrogenated thiophene derivatives are removed as H₂S molecules and 1-butene, 2-butene, 1,3-butadiene and butane are produced. The rate-determining steps are the hydrogen transfer step for 2,5-DHT (TS-2,5DHT-2) and C–S bond cracking step for 2,3-DHT (TS-2,3DHT-3) and THT (TS-THT-3). The calculated free energy barriers increase in the following order: (TS-2,5DHT-2, 141.14 kJ mol⁻¹) < (TS-2,3DHT-3, 253.54 kJ mol⁻¹) < (TS-THT-3, 267.34 kJ mol⁻¹). From the energy profile, the HYD of 2,5-DHT, 2,3-DHT and THT are thermodynamically exothermic reactions and the formation of sulfur vacancy is endothermic reaction. The concerted DDS pathway is probably more favorable than the HYD pathway in the desulfurization of 2,5-DHT.

2. We can obtain useful information from the calculated enthalpy barriers, entropy losses, QM and MM contributions for the free energy barriers. Overall, all the free energy barriers are controlled by the enthalpy barriers or QM contributions except the
C–S bond cracking (TS-2,5DHT-3) and concerted elimination steps (TS-2,5DHT-4) in HYD of 2,5-DHT, and the formation step of THT in the hydrogenation of thiophene (TS-trans-6). The hydrogenation of thiophene to 2,5-DHT, 2,3-DHT and THT and their HDS process are entropy-decreased; the formation of sulfur vacancy is entropy-increased. FAU framework is favorable for the formation of sulfur vacancy and generally unfavorable for the hydrogenation of thiophene and HYD of 2,5-DHT, 2,3-DHT and THT.

(3) We studied the nature of transition states by the analysis from RDG, DCD, and LOL functional. The RDG plots indicate that both a steric hindrance and a weak van der Waals attractive interaction exist between organic fragment and catalytic center for all TSs. The steric hindrance is probably responsible for the calculated high activation free energy barriers in the HYD process. The DCD analysis reveals that for the ring-opening process of 2,5-DHT, 2,3-DHT and THT, the electrons are migrated from the organic chain to the Cu-Mo catalytic center; for the removal of S atom, the electrons migrate in the opposite direction. The LOL maps for all HYD TSs suggest that there is strong covalent interactions between the atoms in the forming chemical bonds and weak van der Waals interactions between the atoms in the breaking chemical bonds.

**Supplementary Information**

Free energy profiles and relative energies for the formation of sulfur vacancy and HYD pathways of 2,3-DHT and THT, Optimized structures of adsorbed thiophene molecule, TS-2,3DHT-3, and TS-THT-3, Plots of DCDs, RDGs, and LOLs for TS-2,5-DHT-1, TS-2,5-DHT-2, TS-2,3-DHT-2, TS-2,3-DHT-3, TS-THT-2, TS-THT-3 over Cu-Mo-FAU are provided.

**Declarations**

**Funding:** This work was funded by the National Natural Science Foundation of China (Project Number 21203118, 22008155, 22075183, 21878188 and 21975161), IIASA Young Scientists Summer Program (Project Number 21411140044), Science and Technology Commission of Shanghai Municipality Project (Project Number
18090503800), Shuguang Program of Shanghai Education Development Foundation and Shanghai Municipal Education Commission (Project Number 18SG52), Chenguang Program of Shanghai Education Development Foundation and Shanghai Municipal Education Commission (Project Number 19CG69), the Talent Development Foundation of Shanghai (Project Number 2018034), Shanghai Gaofeng & Gaoyuan Project for University Academic Program Development, the Research Fund of Department of Education of Sichuan Province (No. 18ZB0481), Development of integrated membrane technology for deep treatment of ammonia nitrogen wastewater from rare earth industry (J2018-61), Development of Metal-supported Catalysts for Thiophene Desulfurization (J2019-360), Simulation of Thermal Conductivity of Polymer Matrix Composites (J2020-50-2), Natural Science Foundation of Shanghai (No.19ZR1454900).

Conflicts of interest/Competing interests: The authors declare no competing interests.

Availability of data and material: The manuscript has full control of all primary data, and the authors agree to allow the journal to review their data if requested.

Code availability: Gaussian 09 package program.

Authors' contributions: Suyang Li: calculation, data analysis, writing. Yingxin Sun, Sheng Han, Qianggen Li: writing-review and editing.

References

1. Kumaran GM, Garg S, Soni K, Prasad VVDN, Sharma LD, Dhar GM (2006) Catalytic functionalities of H-β-zeolite-supported molybdenum hydrotreating catalysts. Energ Fuel 20: 1784–1790. https://doi.org/10.1021/ef060134j

2. Isoda K, Nagao S, Ma XL, Korai Y, Mochida I (1996) Hydrodesulfurization pathway of 4,6-dimethyldibenzothiophene through isomerization over Y-zeolite containing CoMo/Al₂O₃ catalyst. Energ Fuel 10: 1078–1082. https://doi.org/10.1021/ef960048r

3. Bian H, Zhang H, Li D, Duan Z, Zhang H, Zhang S, Xu B (2020) Insight into the oxidative desulfurization mechanism of aromatic sulfur compounds over
4. Samaniego ML, Luna MD, Ong DC, Wan MW, Lu MC (2019) Isotherm and thermodynamic studies on the removal of sulfur from diesel fuel by mixing-assisted oxidative–adsorptive desulfurization technology. Energ Fuel 33: 1098–1105. https://doi.org/10.1021/acs.energyfuels.8b04242

5. Mansouri A, Khodadadi A, Mortazavi Y (2014) Ultra-deep adsorptive desulfurization of a model diesel fuel on regenerable Ni-Cu/γ-Al2O3 at low temperatures in absence of hydrogen. J Hazard Mater 271: 120–130. https://doi.org/10.1016/j.jhazmat.2014.02.006

6. Silva PD, Andrake SKS, Zygourakis K, Wong MS (2019) Adsorptive desulfurization of liquid fuels at elevated temperatures using metal exchanged zeolite Y. Ind Eng Chem Res 58: 19623–19632. https://doi.org/10.1021/acs.iecr.9b03203

7. Zu Y, Guo ZS, Zheng J, Hui Y, Wang SH, Qin YC, Zhang L, Liu HH, Gao XH, Song LJ (2020) Investigation of Cu(I)-Y zeolites with different Cu/Al ratios towards the ultra-deep adsorption desulfurization: discrimination and role of the specific adsorption active sites. Chem Eng J 380: 122319. https://doi.org/10.1016/j.cej.2019.122319

8. Oliveira MLM, Miranda AAL, Barbosa CMBM, Cavalcante Jr CL, Azevedo DCS, Rodriguez-Castellon E (2009) Adsorption of thiophene and toluene on NaY zeolites exchanged with Ag(I), Ni(II) and Zn(II). Fuel 88: 1885–1892. https://doi.org/10.1016/j.fuel.2009.04.011

9. Hernandez-Maldonado AJ, Yang RT (2004) Desulfurization of diesel fuels via π-complexation with nickel(II)-exchanged X- and Y-zeolites. Ind Eng Chem Res 43: 1081–1089. https://doi.org/10.1021/ie034206v

10. Ren J, Wang A, Li X, Chen YY, Liu H, Hu YK (2008) Hydrodesulfurization of dibenzothiophene catalyzed by Ni-Mo sulfides supported on a mixture of MCM-41 and HY zeolite. Appl Catal A: Gen 344: 175–182. https://doi.org/10.1016/j.apcata.2008.04.017
11. Lee KX, Wang HD, Karakalos S, Tsilomelekis G, Valla JA (2019) Adsorptive desulfurization of 4,6-dimethyldibenzothiophene on bimetallic mesoporous Y zeolites: effects of Cu and Ce composition and configuration. Ind Eng Chem Res 58: 18301–18312. https://doi.org/10.1021/acs.iecr.9b02346

12. Jayaraman A, Yang FH, Ralph TY (2006) Effects of nitrogen compounds and polyaromatic hydrocarbons on desulfurization of liquid fuels by adsorption via \( \pi \)-complexation with Cu(I)Y zeolite. Energ Fuel 20: 909–914. https://doi.org/10.1021/ef050308h

13. Wang L, Sun ZL, Ding L, Chen Y, Li Q, Xu M, Li H, Song LJA (2011) A theoretical study of thiophenic compounds adsorption on cation-exchanged Y zeolites. Adv Surf Sci 257: 7539–7544. https://doi.org/10.1016/j.apsusc.2011.03.115

14. Bian H, Zhang H, Li D, Duan Z, Zhang H, Zhang S, Xu B (2020) Insight into the oxidative desulfurization mechanism of aromatic sulfur compounds over Ti-MWW zeolite: a computational study. Micropor Mesopor Mat 294: 109837. https://doi.org/10.1016/j.micromeso.2019.109837

15. Song H, Chang YX, Wan X, Dai M, Song HL, Jin ZS (2014) Equilibrium, kinetic, and thermodynamic studies on adsorptive desulfurization onto Cu\(^{I}\)Ce\(^{IV}\)Y zeolite. Ind Eng Chem Res 53: 5701–5708. https://doi.org/10.1021/ie403177t

16. Yao XQ, Li YW, Jiao HJ (2005) Mechanistic aspects of catalyzed benzothiophene hydrodesulfurization. A density functional theory study. J Mol Struc-Theochem 726: 67–80. https://doi.org/10.1016/j.theochem.2005.02.073

17. Liu B, Zhao Z, Wang DX, Liu J (2015) A theoretical study on the mechanism for thiophene hydrodesulfurization over zeolite L-supported sulfided CoMo catalysts: Insight into the hydrodesulfurization over zeolite-based catalysts. Comput Theor Chem 1052: 47–57. https://doi.org/10.1016/j.comptc.2014.12.001

18. Hriljac JA, Eddy MM, Cheetham AK, Donohue JA, Ray GJ (1993) Power neutron diffraction and \(^{29}\)Si MAS NMR studies of siliceous zeolite-Y. J Solid State Chem 106: 66–72. https://doi.org/10.1006/jssc.1993.1265
19. Maseras F, Morokuma K (1995) IMOMM: a new integrated ab initio + molecular mechanics geometry optimization scheme of equilibrium structures and transition states. J Comput Chem 16: 1170–1179. https://doi.org/10.1002/jcc.540160911

20. Zhao Y, Truhlar DG (2008) The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. Theor Chem Acc 120: 215–241. https://doi.org/10.1007/s00214-007-0310-x

21. Rappe AK, Casewit CJ, Colwell KS, Goddard WA, Skiff WM (1992) UFF, a full periodic table force field for molecular mechanics and molecular dynamics simulations. J Am Chem Soc 114: 10024–10035. https://doi.org/10.1021/ja00051a040

22. Zhao Y, Truhlar DG (2008) ChemInform abstract: density functionals with broad applicability in chemistry. Acc Chem Res 41: 157–167. https://doi.org/10.1002/chin.200821274

23. Zhao Y, Truhlar DG (2006) A new local density functional for main-group thermochemistry, transition metal bonding, thermochemical kinetics, and noncovalent interactions. J Chem Phys 125: 194101–194118. https://doi.org/10.1063/1.2370993

24. Zhao Y, Truhlar DG (2006) Density functional for spectroscopy: no long-range self-interaction error, good performance for Rydberg and charge-transfer states, and better performance on average than B3LYP for ground states. J Phys Chem A 110: 13126–13130. https://doi.org/10.1021/jp066479k

25. Zhao Y, Schultz NE, Truhlar DG (2006) Design of density functionals by combining the method of constraint satisfaction with parametrization for thermochemistry, thermochemical kinetics, and noncovalent interactions. J Chem Theory Comput 2: 364–382. https://doi.org/10.1021/ct0502763

26. Jungsuttiwong S, Limtrakul J, Truong TN (2005) Theoretical study of modes of adsorption of water dimer on H-ZSM-5 and H-Faujasite zeolites. J Phys Chem B 109: 13342–13351. https://doi.org/10.1021/jp045021k
27. Dumont E, Loos PF, Assfeld X (2008) Factors governing electron capture by small disulfide loops in two-cysteine peptides. J Phys Chem B 112: 13661–13669. https://doi.org/10.1021/jp806465e

28. He DS, Ma M (2014) Impact of Lewis Base on chemical reactivity and separation efficiency for hydrated fourth-row transition metal (II) complexes: an ONIOM DFT/MM study. J Phys Chem A 118: 2984–2994. https://doi.org/10.1021/jp500447m

29. Guo XX, Mao XF, Deng C, Sun YX, Han S (2019) Understanding the nature of transition states in the confined nanospace of different acidic zeolites on the desulfurization mechanism of thiophene. J Phys Chem C 123: 1260–1278. https://doi.org/10.1021/acs.jpcc.8b09924

30. Sun YX, Mao XF, Pei SP (2016) A two-layer ONIOM study of thiophene cracking catalyzed by proton- and cation-exchanged FAU zeolite. J Mol Model 22: 51–66. https://doi.org/10.1007/s00894-016-2916-1

31. Gonzalez C, Schlegel HB (1990) Reaction path following in mass-weighted internal coordinates. J Phys Chem 94: 5523–5527. https://doi.org/10.1021/j100377a021

32. Chu YY, Han B, Zheng AM, Yi XF, Deng F (2013) Pore selectivity for olefin protonation reactions confined inside mordenite zeolite: a theoretical calculation study. J Phys Chem C 117: 2194–2202. https://doi.org/10.1021/jp311264u

33. Liu JW, Liu ZF, Feng G, Kong DJ (2014) Dimerization of propene catalyzed by Brønsted acid sites inside the main channel of zeolite SAPO-5: a computational study. J Phys Chem C 118: 18496–18504. https://doi.org/10.1021/jp502768d

34. Johnson ER, Keinan S, Mori-Sánchez P, Contreras-García J, Cohen AJ, Yang WT (2010) Revealing noncovalent interactions. J Am Chem Soc 132: 6498–6506. https://doi.org/10.1021/ja100936w

35. Becke AD (2000) Simulation of delocalized exchange by local density functionals. J Chem Phys 112: 4020–4026. https://doi.org/10.1063/1.480951

36. Sun YX, Zheng D, Pei SP, Fan DL (2017) New theoretical insights into the contributions of polymethylbenzene and alkene cycles to methanol-to-propene in
H-FAU zeolite. J Phys Chem C 121: 16216–16237. https://doi.org/10.1021/acs.jpcc.7b01991

37. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Mennucci B, Petersson GA, Nakatsuji H, Caricato M, Li X, Hratchian HP, Izmaylov AF, Bloino J, Zheng G, Sonnenberg JL, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Montgomery Jr JA, Peralta JE, Ogliaro F, Bearpark M, Heyd JJ, Brothers E, Kudin KN, Staroverov VN, Kobayashi R, Normand J, Raghavachari K, Rendell A, Burant JC, Iyengar SS, Tomasi J, Cossi M, Rega N, Millam NJ, Klene M, Knox JE, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Martin RL, Morokuma K, Zakrzewski VG, Voth GA, Salvador P, Dannenberg JJ, Dapprich S, Daniels AD, Farkas Ö, Foresman JB, Ortiz JV, Cioslowski J, Fox DJ (2009) Gaussian 09, Revision A.01, Gaussian, Inc., Wallingford CT.

38. Lu T, Chen FW (2012) Multiwfn: a multifunctional wavefunction analyzer. J Comput Chem 33: 580–592. https://doi.org/10.1002/jcc.22885

39. Kogan VM, Nikulshin PA (2010) On the dynamic model of promoted molybdenum sulfide catalysts. Catal Today 149: 224–231. https://doi.org/10.1016/j.cattod.2009.03.023

40. Kogan VM, Nikulshin PA, Rozhdestvenskaya NN (2012) Evolution and interlayer dynamics of active sites of promoted transition metal sulfided catalysts under hydrodesulfurization conditions. Fuel 100: 2–16. https://doi.org/10.1016/j.fuel.2011.11.016

41. Zhu HY, Guo WY, Li M, Zhao LM, Li SR, Li Y, Lu XQ, Shan HH (2011) Density functional theory study of the adsorption and desulfurization of thiophene and its hydrogenated derivatives on Pt(111): implication for the mechanism of hydrodesulfurization over noble metal catalysts. ACS Catal 1: 1498–1510. https://doi.org/10.1021/cs2002548
42. Hensen EJM, Vissenberg MJ, Beer VHJ, Veen JAR, Santen RA (1996) Kinetics and mechanism of thiophene hydrodesulfurization over carbon-supported transition metal sulfides. J Catal 163: 429–435. https://doi.org/10.1006/jcat.1996.0344

43. Weber T, Veen JAR (2008) A density functional theory study of the hydrodesulfurization reaction of dibenzothiophene to biphenyl on a single-layer NiMoS cluster. Catal Today 130: 170–177. https://doi.org/10.1016/j.cattod.2007.06.078

44. Murdoch JR (1981) What Is the Rate-limiting Step of A Multistep Reaction? J Chem Educ 58: 32–36. https://doi.org/10.1021/ed058p32

45. Yin JB, Guo XX, Sun YX, Han S, Li QG (2021) Understanding the nanoconfinement effect on the ethanol-to-propene mechanism catalyzed by acidic ZSM-5 and FAU zeolites. J Phys Chem C 125: 310–334. https://doi.org/10.1021/acs.jpcc.0c07614

46. Karvan O, Atakül H (2008) Investigation of CuO/mesoporous SBA-15 sorbents for hot gas desulfurization. Fuel Process Technol 89: 908–915. https://doi.org/10.1016/j.fuproc.2008.03.004

47. Baeza P, Aguila G, Vargas G, Ojeda J, Araya P (2012) Adsorption of thiophene and dibenzothiophene on highly dispersed Cu/ZrO₂ adsorbents. Appl Catal B: Environ 111-112: 133–140. https://doi.org/10.1016/j.apcatb.2011.09.026

48. Lee KX, Tsilomelekis G, Valla JA (2018) Removal of benzothiophene and dibenzothiophene from hydrocarbon fuels using CuCe mesoporous Y zeolites in the presence of aromatics. Appl Catal B: Environ 234: 130–142. https://doi.org/10.1016/j.apcatb.2018.04.022

49. Song H, Wan X, Dai M, Zhang JJ, Li F, Song HL (2013) Deep desulfurization of model gasoline by selective adsorption over Cu-Ce bimetal ion-exchanged Y zeolite. Fuel Process Technol 116: 52–62. https://doi.org/10.1016/j.fuproc.2013.04.017

50. Hernandez-Maldonado AJ, Yang RT, Cannella W (2004) Desulfurization of commercial jet fuels by adsorption via π-complexation with vapor phase ion
exchanged Cu(I)-Y zeolites. Ind Eng Chem Res 43: 6142–6149. https://doi.org/10.1021/ie049533x

51. Lee KX, Valla JA (2017) Investigation of metal-exchanged mesoporous Y zeolites for the adsorptive desulfurization of liquid fuels. Appl Catal B: Environ 201: 359–369. https://doi.org/10.1016/j.apcatb.2016.08.018

52. Oyama ST, Gott T, Asakura K, Takakusagi S, Miyazaki K, Koike Y, Bando KK (2009) In situ FTIR and XANES studies of thiophene hydrodesulfurization on Ni3P/MCM-41. J Catal 268: 209–222. https://doi.org/10.1016/j.jcat.2009.09.018

53. Wang HM, Prins R (2008) HDS of benzothiophene and dihydrobenzothiophene over sulfided Mo/γ-Al2O3. Appl Catal A 350: 191–196. https://doi.org/10.1016/j.apcata.2008.08.010

54. Wang HM, Prins R (2008) Hydrodesulfurization of dibenzothiophene and its hydrogenated intermediates over sulfided Mo/γ-Al2O3. J Catal 258: 153–164. https://doi.org/10.1016/j.jcat.2008.06.005

55. Sun YY, Prins R (2009) Mechanistic studies and kinetics of the hydrodesulfurization of dibenzothiophene on Co-MoS2/γ-Al2O3. J Catal 267: 193–201. https://doi.org/10.1016/j.jcat.2009.08.013
Figures

Figure 1

A 156T nanocluster model of Cu-Mo-FAU zeolite cluster divided into two areas: the inner 18T region, shown by colored balls, and the outer region by sticks. a the whole ONIOM model, b the 18T QM region.
Figure 2

Free energy profile and relative energies of HYD and DDS pathways of 2,5-DHT over Cu-Mo-FAU at 673.15 K
Figure 3

Optimized structures of transition states: a TS-1 and b TS-2 over Cu-Mo-FAU zeolite
Figure 4

Optimized structures of transition states: a TS-trans-1, b TS-trans-2, c TS-trans-3, d TS-trans-4, e TS-trans-5, f TS-trans-6 over Cu-Mo-FAU zeolite
Figure 5

Optimized structures of transition states: a TS-2,5DHT-1, b TS-2,5DHT-2, c TS-2,5DHT-3, d TS-2,5DHT-4 over Cu-Mo-FAU zeolite
Figure 6

Optimized structures of transition states: a TS-2,3DHT-1, b TS-2,3DHT-2, c TS-THT-1, d TS-THT-2 over Cu-Mo-FAU zeolite
Figure 7

Plots of DCDs (isovalue = 0.0004) for TS-1 over Cu-Mo-FAU. a positive DCD, b negative DCD. The positive DCD (light blue) represents where the electron density increases, and the negative DCD (light green) represents where the electron density decreases. c Optimized structure of TS-1, d Color-filled maps of LOL of TS-1, e Isosurface plot RDG of TS-1 (isovalue = 0.5)
Figure 8

Plots of DCDs (isovalue = 0.0004) for TS-2 over Cu-Mo-FAU. a positive DCD, b negative DCD. The positive DCD (light blue) represents where the electron density increases, and the negative DCD (light green) represents where the electron density decreases. c Optimized structure of TS-2, d Color-filled maps of LOL of TS-2, e Isosurface plot RDG of TS-2 (isovalue = 0.5)
Plots of DCDs (isovalue = 0.0004) for TS-2,5-DHT-3 over Cu-Mo-FAU. a positive DCD, b negative DCD. The positive DCD (light blue) represents where the electron density increases, and the negative DCD (light green) represents where the electron density decreases. c Optimized structure, d,e Color-filled maps of LOLs, f Isosurface plot RDG (isovalue = 0.5)
Figure 10

Plots of DCDs (isovalue = 0.0004) for TS-2,5-DHT-4 over Cu-Mo-FAU. a positive DCD, b negative DCD. The positive DCD (light blue) represents where the electron density increases, and the negative DCD (light green) represents where the electron density decreases. c,f Color-filled maps of LOLs, d Isosurface plot RDG (isovalue = 0.5), e Optimized structure of TS-2,5-DHT-4
Figure 11

Plots of DCDs (isovalue = 0.0004) for TS-2,3-DHT-1 over Cu-Mo-FAU. a positive DCD, b negative DCD. The positive DCD (light blue) represents where the electron density increases, and the negative DCD (light green) represents where the electron density decreases. c Optimized structure of TS-2,3-DHT-1, d Color-filled maps of LOL, e Isosurface plot RDG (isovalue = 0.5)
Figure 12

Plots of DCDs (isovalue = 0.0004) for TS-THT-1 over Cu-Mo-FAU. a positive DCD, b negative DCD. The positive DCD (light blue) represents where the electron density increases, and the negative DCD (light green) represents where the electron density decreases. c Optimized structure, d,e Color-filled maps of LOLs, f Isosurface plot RDG (isovalue = 0.5)
Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- scheme1.jpg
- scheme2.jpg
- scheme3.jpg
- scheme4.jpg
- scheme5.jpg
- SupplementaryInformation.doc