Hydrogenation Mechanism of 2-Methylthiophene over the Pt(111) Catalyst (Postprint)

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Abstract

The adsorption process and hydrogenation mechanisms of 2-methylthiophene on the Pt(111) surface have been elucidated using density functional theory (DFT). The optimal adsorption sites for reactants, intermediates, and products, as well as the activation energies and reaction energies for each elementary reaction, were investigated. The results revealed that the most stable configuration is 2-methylthiophene tilted on the Pt(111) catalyst with the C1-C2 double bond at the top site. During the hydrogenation process, the reaction enthalpies are predominantly negative, so lower temperatures favor the hydrogenation process. The hydrogenation steps of the mechanism proceed along C2→C3→C1→C4→S→C1 to generate the product pentane-2-thiol, in which the first step with the highest energy barrier is the rate-determining step.

Full Text

Theoretical Study on the Adsorption and Hydrogenation Mechanism of 2-Methylthiophene over the Pt(111) Catalyst

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ABSTRACT

The adsorption process and hydrogenation mechanisms of 2-methylthiophene on the Pt(111) surface have been elucidated using density functional theory (DFT). The optimal adsorption sites of reactants, intermediates, and products as well as the activation energy and reaction energy of each elementary reaction were investigated. The results revealed that 2-methylthiophene tilted toward the Pt(111) catalyst with the C1–C2 double bond at the top site was the most stable configuration. During the hydrogenation process, the heat of reaction was almost always negative, indicating that lowering the temperature favors the hydrogenation process. The hydrogenation steps of the mechanism proceed along C2→C3→C1→C4→S→C1 to generate the product pentane-2-thiol, in which the first step with the highest energy barrier is the rate-determining step.

Keywords: density functional theory; 2-methylthiophene; Pt(111); adsorption; hydrogenation mechanisms

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1 INTRODUCTION

In modern society, with increasing energy consumption demand, growing energy supply shortages, and rising awareness of the need to curb greenhouse gas emissions, many research efforts have focused on the exploitation of new types of energy resources [1-5]. Hydrogen is regarded as one of the high-performance, low-cost, and environmentally friendly energy resources [6-8], which has been widely applied in electronics, petrochemical, metallurgy, machinery, and other fields [9-11]. However, due to storage restrictions and low energy density of materials, there are still limitations in hydrogen usage [12, 13]. Consequently, numerous hydrogen storage materials with high energy density have been developed in recent years [14-17].

2-Methylthiophene (2MT) is a representative heteroatom aromatic compound, and the electron-donating effects of the methyl group favor hydrogen release both thermodynamically and kinetically under mild conditions [18, 19]. Furthermore, cleavage of one C–S bond during the hydrogenation process can store an additional mole of hydrogen. For these reasons, 2MT is considered an effective material for hydrogen storage. Celis-Cornejo et al. [20] investigated the adsorption of 2MT on a CoMo/ -Al O supported catalyst during hydrogenation and found that the adsorption mechanism follows the Langmuir-Hinshelwood model. Zhao et al. [19] compared 16 catalysts for hydrogenation and ring-opening of 2MT, finding that Pt exhibited the best reactivity and selectivity, and they proposed a possible reaction equation for the hydrogenation process. Although some research on 2MT hydrogenation exists, studies on the detailed hydrogenation mechanism remain scarce due to characterization limitations and reaction complexity.

Density functional theory (DFT) [21, 22] has become a unique and powerful research approach for examining individual elementary reaction steps at the molecular level. Gece [23] used DFT methods to find that thiophene has a considerable tendency for protonation, with the most probable site being the -position. Zhu et al. [24, 25] studied the most efficient hydrogenation route of thiophene on different crystal planes of Pt catalysts. Our previous theoretical calculations [26-28] investigated the adsorption and hydrogenation process of thiophene catalyzed on Au, Pd, and Au/Pd catalysts to identify the most favorable pathway for thiophene hydrodesulfurization.

Despite these efforts, to our knowledge, no theoretical reports are available on the adsorption behavior and hydrogenation process of 2MT on Pt catalysts. Therefore, in this study, the DMol^3 program package within DFT methods was used to calculate the hydrogenation storage of 2MT and its hydrogenated derivatives on a clean Pt(111) surface. The aim of this study is to analyze the possible hydrogenation storage pathways of 2MT and to better understand Pt catalysts at the molecular level for 2MT hydrogenation.

2 COMPUTATIONAL METHODS AND MODEL

2.1 Methods

All DFT simulations were conducted using the DMol^3 program package [29] in Materials Studio 6.0 (Accelrys Inc.). Throughout this study, the Perdew and Wang (PW91) [30-32] functional with the generalized gradient approximation (GGA) was adopted. The double numerical basis set with polarization functions (DNP) was employed to describe the valence atomic orbitals. The convergence criteria for energy, maximum force, maximum displacement, and maximum self-consistent-field (SCF) were set as 5×10 eV, 2×10^{2} eV/nm, 5×10 nm, and 2×10 eV/atom, respectively. Furthermore, transition states (TS) between reactants and products were searched using the complete LST (linear synchronous transit)/QST (quadratic synchronous transit) method [33]. The calculated TS was confirmed by the presence of a single imaginary vibrational frequency whose vibrational vector aligns with the reaction direction. During computations, the Fermi smearing method was employed to determine electron occupancies with a smearing width of 0.1 eV.

2.2 Catalyst Model

Based on the optimized structure of Pt bulk, we constructed a four-layer Pt(111) surface with a (4 × 4) unit cell (64 Pt atoms per cell), corresponding to 1/16 monolayer (ML) coverage for a single 2MT molecule on the surface, as shown in Fig. 1 [Figure 1: see original paper]. The reciprocal space was sampled with a (5 × 5 × 1) k-points grid generated automatically using the Monkhorst-Pack method, and a vacuum region thickness of 1 nm was added in the perpendicular direction to prevent interactions between periodic configurations. This created a repeating unit in space using the layer and vacuum region. During geometry optimization and TS searches, the bottom bilayer of Pt(111) was kept fixed while the remaining atoms were allowed to move freely. With these parameters, the calculated lattice constant for the Pt(111) surface was 0.3924 nm, which is consistent with the experimental value of 0.3923 nm [34, 35]. These simulation results demonstrate that the method used in this paper is correct and feasible.

3 RESULTS AND DISCUSSION

3.1 Adsorption

Calculation of adsorption energies is regarded as an efficient measure to illustrate changes in the adsorbate-substrate system before and after adsorption. In this work, the adsorption energy (E ds) is defined as follows:

$$E_{ads} = E(A/surface) - (E_A + E_{surface})$$

where E(A/surface) is the total energy of 2MT together with the Pt(111) surface, E_A is the total energy of a free 2MT molecule, and E_surface is the total energy of the bare surface. By this definition, more negative values of adsorption energy denote more stable binding between the 2MT molecule and the Pt(111) surface.

Based on the ring-plane structure of 2MT and our previous results [26-28, 36], 2MT adsorbed parallel to the Pt(111) surface is considered more stable than in the vertical orientation. Therefore, sixteen possible parallel adsorption sites were labeled by local coordination: (1) four top sites (0°, 30°, 60°, 90°), (2) four hcp sites (0°, 30°, 60°, 90°), (3) four fcc sites (0°, 30°, 60°, 90°), and (4) four bridge sites (0°, 30°, 60°, 90°), as shown in Fig. 1. Different angles represent 2MT rotated by 0°, 30°, 60°, and 90° around the symmetry axis of the ring-plane from the horizontal orientation.

Table 1 summarizes the calculated adsorption energies of 2MT on the Pt(111) surface. The data are divided into two groups with energies around -139.0 and -175.0 kJ · mol 1. The 2MT molecule prefers to adsorb in a tilted orientation through the double bond farthest from the methyl functional group. Among different initial positions, 2MT adsorbed at the Top-60° site with the lowest E ds of -175.0 kJ · mol 1 is the most stable configuration. The top and side views of this most stable structure are shown in Fig. 2 [Figure 2: see original paper].

In Fig. 2, the ring-plane rotates clockwise around the axis, while the methyl group associated with the C3-C4 double bond moves away from the Pt(111) surface during adsorption. Ultimately, 2MT adsorbs on the bridge site via the C1-C2 double bond. Table 2 lists the calculated structural parameters for the most stable adsorption site of 2MT on the Pt(111) surface.

Comparison of the results in Table 2 shows that the calculated bond lengths for 2MT agree well with experimental data [37]. These phenomena suggest that our method is suitable for studying 2MT adsorption on the Pt(111) catalyst. Furthermore, the bond length d shows the greatest change, suggesting that the C1-C2 double bond is the probable site for reaction initiation.

3.2 Hydrogenation Mechanism of 2MT

Based on our previous research results [19], the hydrogenation products on the Pt catalyst were classified into two types of thiols during the reaction process. Fig. 3 [Figure 3: see original paper] shows the structures of all intermediates in sequence during the hydrogenation process of 2MT.

We simulated the optimal configurations of reactants (IS), products (FS), and corresponding transition states (TS) shown in Fig. 3. The activation energies and reaction energies at TS are tabulated in Table 3 . Based on different hydrogenation pathways, we considered the co-adsorption of 2MT and hydrogen as the first step, then compared the intermediate steps (steps 1-5 in Fig. 3).

3.2.1 IS1* + H* → C H S* (FS1-FS4) At the start of the reaction, we considered four possible initial hydrogenation products: FS1 through FS4. The calculated barriers (E), total energy changes (ΔE), and corresponding structures of IS, TS, and FS for step 1 are shown in Fig. 4 [Figure 4: see original paper]. According to our calculations, the H atom shifted from the adjacent fcc site to the bridge site while 2MT remained adsorbed on the bridge site via the C1-C2 double bond.

For product FS1, the molecule moved leftward horizontally, while the C1-H functional group tilted upward to become perpendicular to the Pt(111) surface and the C4 atom shifted downward. Finally, FS1 adsorbed on a hollow site via the C3-C4 double bond. TS1 was calculated between IS1 and FS1. During the reaction, the H atom transferred to the fcc site and the C1 atom moved downward slightly to form the C1-H bond. The first step forming FS1 was exothermic with ΔE of -52.2 kJ · mol ^{1} and the corresponding E was 167.7 kJ · mol ^{1}.

In FS2, the C2-H functional group tilted upward while the S atom and methyl group moved downward. Consequently, FS2 preferred to adsorb at the top site of the Pt surface via the S atom. During FS2 formation, the H atom gradually shifted to the fcc site to approach C2 for methylene C2-H formation in TS2. The generation of FS2 was exothermic with ΔE of -8.1 kJ · mol ^{1} and the corresponding E was 75.0 kJ · mol ^{1}.

In FS3, the methyl group of 2MT tilted upward and became almost vertical to the Pt surface, while the C3 atom shifted downward slightly to approach the surface. FS3 adsorbed on the hollow site via the C1-C2 double bond as the most stable configuration. In TS3, the H atom moved to the top site while the methyl functional group folded upward. The formation of FS3 was exothermic with ΔE of -54.9 kJ · mol ^{1} and the corresponding E was 130.9 kJ · mol ^{1}.

The FS4 molecule showed almost no change compared to IS1 when the reaction occurred. Finally, FS4 adsorbed on the bridge site via the C1-C2 double bond. In TS4, the H atom moved away from the Pt surface to the adjacent fcc site to approach C3. These phenomena facilitated the formation of another C3-H bond. The formation of FS4 was endothermic with ΔE of 29.7 kJ · mol ^{1} and the corresponding E was 187.1 kJ · mol ^{1}.

Comparing FS1, FS3, and FS4 from Table 3 and Fig. 4, the activation energy of FS2 is the minimum, indicating that FS2 formation is most likely in step 1. This result is consistent with the structural parameter analysis of 2MT. Thermodynamically, the relative energies of FS1-FS3 are exothermic with negative values, so reducing temperature can improve these hydrogenation reactions. In contrast, the relative energy of FS4 is endothermic with a positive value, so higher temperature is helpful for this hydrogenation pathway.

3.2.2 IS2* + H* → C H S* (FS5-FS7) FS2 was identified as the dominant product in the first step, and the further hydrogenation process in step 2 has three possible products: FS5, FS6, or FS7. The activation energies, reaction energies, and corresponding structures of IS, TS, and FS for step 2 are shown in Fig. 5 [Figure 5: see original paper]. Step 2 begins with the co-adsorption of FS2 and H. Through optimization, the H atom shifted away from the fcc site to the bridge site while FS2 adsorbed on the hollow site through the S atom.

For product FS5, the S atom shifted downward toward the Pt surface and the reacted methyne tilted upward to relieve steric hindrance for the H atom. Ultimately, FS5 adsorbed on the top site of the Pt surface through the S atom. In TS5, the H atom shifted to the hollow site to approach the reacted -C, finally forming a new C1-H bond. The formation of FS5 was endothermic with ΔE of 11.6 kJ · mol ^{1} and the corresponding E was 164.6 kJ · mol ^{1}.

For product FS6, the methyl group moved upward slightly and the product remained adsorbed on the top site through the S atom. The configuration of TS6 was optimized as shown in Fig. 5. The H atom shifted away from the surface to approach C3 to form another C3-H bond, while the distance between H and C3 decreased from 0.4215 to 0.2644 nm. The formation of FS6 was endothermic with ΔE of 5.3 kJ · mol ^{1} and the corresponding E was 19.5 kJ · mol ^{1}.

For product FS7, the C1-C4 atoms located close to the surface and the methyl group migrated upward to become perpendicular to the surface due to H atom attack. Finally, FS7 adsorbed on the top site through the S atom. In TS7, the H atom shifted from the bridge site to the fcc site and the relevant C4-H distance decreased from 0.5057 to 0.2458 nm. The formation of FS7 was endothermic with ΔE of 76.4 kJ · mol ^{1} and E of 109.3 kJ · mol ^{1}.

As shown in Table 3 and Fig. 5, the relative energies of FS5-FS7 were endothermic with positive values, so raising the temperature benefits the second hydrogenation step. Moreover, the relative energy and reaction energy of FS6 are the lowest among the different products, implying that the process from IS2 to FS6 is most likely to occur in step 2.

3.2.3 IS3* + H* → C H S* (FS8 or FS9) In step 2, FS6 was deemed the dominant product, which would further hydrogenate to form FS8 or FS9. The activation and reaction energies of IS, TS, and FS for step 3 are illustrated in Fig. 6 [Figure 6: see original paper]. The process begins from the most favorable co-adsorption configuration of FS6 and the H atom. Through optimization, the H atom shifted away from the fcc site to the bridge site and FS6 adsorbed on the hollow site through the S atom.

For product FS8, the molecule transferred to the bottom right and the C1–C4 atoms shifted away from the Pt surface. Meanwhile, the C5 atom moved downward to make the C4–C5 bond parallel to the surface. Finally, FS8 adsorbed on the top site through the S atom. In TS8, the H atom migrated to approach the C1 atom and the relevant C1–H distance decreased from 0.4911 to 0.3581 nm. The formation of FS8 was exothermic with ΔE of –102.1 kJ · mol^{1} and the corresponding E was 67.9 kJ · mol^{1}.

During the IS3–FS9 process, significant distortion occurred in the C2 and C3 atoms. FS9 adsorbed on the top site via the S atom as the most stable configuration. The H atom shifted to the adjacent hollow site while the methylene group of C2 and C3 tilted upward, as shown in TS9. The formation of FS9 was endothermic with ΔE of 5.3 kJ · mol^{1} and the corresponding E was 97.3 kJ · mol^{1}.

According to these simulation results, IS3 prefers to hydrogenate at -C1 rather than -C2. The generation of FS8 is exothermic, while that of FS9 is endothermic. Additionally, a lower barrier of 67.9 kJ · mol^{1} along with a shorter bond length is present for the -C1–H bond formed in FS8. Consequently, the hydrogenation of IS3 to FS8 is most likely to occur.

3.2.4 IS4* + H* → C H S* (FS10) Based on the previous discussion in step 3, FS8 was identified as the optimal product. Only one possible pathway exists for further hydrogenation of FS8 to form the saturated product C H S. The activation and reaction energies of IS, TS, and FS for step 4 are shown in Fig. 7 [Figure 7: see original paper]. The initial hydrogenation channel of step 4 involves co-adsorption of FS8 and an H atom. After co-adsorption, the H atom located at the bridge site and FS8 maintained almost the same structure as in step 4.

The product FS10 slanted toward the Pt(111) surface through the S atom, while the methyl functional group tilted upward to decrease steric hindrance. In TS10, the H atom transferred to the adjacent top site to approach the C4 atom, finally forming a new C1–H bond. The formation of FS10 was exothermic with ΔE of -97.0 kJ · mol^{1} and the corresponding E was 112.6 kJ · mol^{1}.

3.2.5 IS5* + H* → C H S* (FS11-FS14) In step 5, FS10 is further hydrogenated to thiol with the assistance of an H atom. The activation and reaction energies of IS, TS, and FS for step 5 are shown in Fig. 8 [Figure 8: see original paper]. The hydrogenation began with FS10 located at the top site on the Pt(111) surface through the S atom and the H atom moving from the fcc site to the top site.

In FS11, the C2-C5 atoms tilted upward and distorted significantly. Meanwhile, the C1 and S atoms moved downward, allowing FS11 to adsorb stably on the Pt surface. In TS11, the distance between H and S atoms decreased from 0.3600 to 0.2500 nm. This caused the d bond to break, accompanied by the H atom shifting to the adjacent top site and the S atom moving downward. The formation of FS11 was endothermic with ΔE of 48.9 kJ · mol ^{1} and the corresponding E was 116.9 kJ · mol ^{1}.

In FS12, the C1 methyl group shifted to the hcp site and the C2-C5 bonds remained in a straight line from the top view. Finally, FS12 adsorbed on the top site through the S atom. In TS12, the H atom moved to the adjacent bridge site and the C2-C3 bond rotated clockwise to approach the attacking H atom. The forming distance of the -C-H bond decreased from 0.2770 to 0.2065 nm. The formation of FS12 was endothermic with ΔE of 39.3 kJ · mol ^{1} and the corresponding E was 388.2 kJ · mol ^{1}.

The FS13 molecule rotated anticlockwise while the C3-C5 atoms tilted upward to move away from the Pt surface, causing FS13 to adsorb on the top site through the S atom. TS13 was calculated between IS5 and FS13. The H atom shifted to the adjacent fcc site to approach the S atom, decreasing the S-H distance from 0.3600 to 0.1970 nm. The formation of FS13 was endothermic with ΔE of 138.3 kJ · mol ^{1} and the corresponding E was 233.9 kJ · mol ^{1}.

Significant distortion occurred in the FS14 product when the reaction took place. The methyl group rotated anticlockwise around the C4 atom and the C2-C4 bond folded upward. In TS14, the H atom moved to the bridge site to approach C4 to generate the C4-H bond, while the distance between the dissociative H and C4 decreased from 0.4582 to 0.2987 nm. The formation of FS14 was endothermic with ΔE of 13.0 kJ · mol ^{1} and the corresponding E was 416.0 kJ · mol ^{1}.

Through comparative analysis of the IS, TS, and FS results in Fig. 8, the reaction energy of FS11 is 116.9 kJ · mol ^{1}, which is the smallest among FS11-FS14. Moreover, the relative energies of different products in step 5 are positive, thus high temperature is beneficial for the reaction. Based on kinetic and thermodynamic considerations, hydrogenation of FS10 on the Pt surface is more likely to produce FS11 rather than FS12-FS14, suggesting that FS11 is more competitive in step 5.

3.2.6 IS6* + H* → C H S* (FS15) FS11 is the dominant product in step 5. Fig. 9 [Figure 9: see original paper] illustrates the activation and reaction energies of IS, TS, and FS in the final hydrogenation step. The hydrogenation began with co-adsorption of FS11 and an H atom. When step 6 started, the

H atom shifted to the top site and the C H S structure remained the same as FS11.

For the final product FS15, the molecule twisted into a shape from the top view and adsorbed at the top site via the S atom. In the TS15 intermediate, the C1 methyl group moved upward while the H atom shifted to the adjacent hollow site to approach C1, decreasing the H–C1 distance from 0.3017 to 0.2460 nm. The formation of FS15 was exothermic with ΔE of –15.8 kJ · mol^{1} and the corresponding E was 210.8 kJ · mol^{1}.

3.3 Brief Summary of the Hydrogenation Process of 2MT

In this study, possible pathways involved in the hydrogenation mechanism of 2MT were investigated. The potential energy surface (PES) landscape for each step is shown in Fig. 10 [Figure 10: see original paper]. As shown in Fig. 10, the most favorable hydrogenation mechanism follows these steps: 2MT was hydrogenated to FS2, which then underwent a second hydrogenation to yield FS6. FS6 can be further hydrogenated to generate FS8, which then undergoes hydrogenation to form FS10. FS10 can undergo a fourth hydrogenation to produce FS11, and finally FS11 can be hydrogenated to generate pentane-2-thiol (FS15). These results are in agreement with previous experimental studies in the literature [19]. Among the different steps shown in Fig. 10, the first hydrogenation step to generate FS1 is the rate-determining step.

4 CONCLUSION

We have investigated and compared the adsorption and hydrogenation mechanisms of 2-methylthiophene using periodic density functional theory methods. Various adsorption modes of the intermediates involved in the reaction were studied from energetic and geometrical viewpoints, and the hydrogenation mechanism has been clarified. The major findings can be summarized as follows.

Our calculations show that tilted adsorption of 2MT at the top site through the C1–C2 double bond is the most stable configuration. With the increase in bond length of 2MT after adsorption, the H atom will most likely attack the C1–C2 double bond of 2MT. The dominant hydrogenation mechanism follows the steps C2→C3→C1→C4→S→C1 to generate pentane-2-thiol from a kinetic perspective. The hydrogenation process of 2MT is almost exothermic, so reducing the temperature is beneficial for the reaction. In addition, the first hydrogenation step of 2MT, which has the highest activation barrier, is the rate-determining step.

REFERENCES

(1) Konda, S. K.; Chen, A. C. Palladium based nanomaterials for enhanced hydrogen spillover and storage. *Mater. Today* 2016, 19, 2–9.

(2) Zhang, Q.; Zheng, D. D.; Xu, L. S.; Chang, C. T. Photocatalytic conversion of terephthalic acid preparation wastewater to hydrogen by graphene-modified TiO . *Catal. Today* 2016, 274, 8-14.

(3) Contreras, M. L.; Villarroel, I.; Rozas, R. Hydrogen physisorption energies for bumpy, saturated, nitrogen-doped single-walled carbon nanotubes. *Struct. Chem.* 2016, 27, 1-12.

(4) Li, X. D.; Zhang, H.; Miyamoto, Y.; Tang, Y. J.; Wang, C. Y. Computational design of tetrahedral silsesquioxane-based porous frameworks with diamond-like structure as hydrogen storage materials. *Struct. Chem.* 2014, 25, 177-185.

(5) Jiang, H.; Cheng, X. L.; Zhang, H.; Tang, Y. J.; Wang, J. Molecular dynamic investigations of hydrogen storage efficiency of graphene. *Struct. Chem.* 2015, 26, 531-537.

(6) Toklu, E.; Avci, A. C.; Kaygusuz, K.; Gur, M. A research on hydrogen production from industrial waste heat by thermal water splitting. *Int. J. Hydrogen. Energ.* 2016, 41, 10071-10079.

(7) Hosseini, S. E.; Wahid, M. A. Hydrogen production from renewable and sustainable energy resources: promising green energy carrier for clean development. *Renew. Sust. Energ. Rev.* 2016, 57, 850-866.

(8) Ren, J.; Zhang, N. C.; Zhang, H.; Peng, X. J. First-principles study of hydrogen storage on Pt (Pd)-doped boron nitride sheet. *Struct. Chem.* 2015, 26, 731-738.

(9) Iulianelli, A.; Liguori, S.; Huang, S.; Basile, A. Model biogas steam reforming in a thin Pd-supported membrane reactor to generate clean hydrogen for fuel cells. *J. Power. Sour.* 2015, 273, 25-32.

(10) Moradi, M.; Naderi, N. First principle study of hydrogen storage on the graphene-like aluminum nitride nanosheet. *Struct. Chem.* 2014, 25, 1289-1296.

(11) Zhang, S. L.; Feng, Y.; Zhang, D.; Jiang, Y. G.; Qin, J.; Bao, W. Parametric numerical analysis of regenerative cooling in hydrogen fueled scramjet engines. *Int. J. Hydrogen. Energ.* 2016, 41, 10942-10960.

(12) Mazzucco, A.; Dornheim, M.; Sloth, M.; Jensen, T. R.; Jensen, J. O.; Rokni, M. Bed geometries, fueling strategies and optimization of heat exchanger designs in metal hydride storage systems for automotive applications: a review. *Int. J. Hydrogen. Energ.* 2014, 39, 17054-17071.

(13) Zhang, Z. H.; Hu, C. System design and control strategy of the vehicles using hydrogen energy. *Int. J. Hydrogen. Energ.* 2014, 39, 17072–17079.

(14) Shafiee, S.; McCay, M. H. Different reactor and heat exchanger configurations for metal hydride hydrogen storage systems—a review. *Int. J. Hydrogen. Energ.* 2016, 41, 9462–9470.

(15) Niaz, S.; Manzoor, T.; Pandith, A. H. Hydrogen storage: materials, methods and perspectives. *Renew. Sust. Energ. Rev.* 2015, 50, 457–469.

(16) Liu, W.; Webb, C. J.; Gray, E. M. Review of hydrogen storage in AB alloys targeting stationary fuel cell applications. *Int. J. Hydrogen. Energ.* 2016, 41, 3485–3507.

(17) Sun, W. P.; Zhang, Y.; Zhu, Y. F.; Zhuang, X. Y.; Dong, J.; Qu, Y.; Guo, X. L.; Chen, J.; Wang, Z. M.; Li, L. Q. The hydrogen storage performance of a 4MgH -LiAlH -TiH composite system. *J. Alloy. Compd.* 2016, 676, 557–564.

(18) Song, X. L.; Fanelli, M. G.; Cook, J. M.; Bai, F. R.; Parish, C. A. Mechanisms for the reaction of thiophene and methylthiophene with singlet and triplet molecular oxygen. *J. Phys. Chem. A* 2012, 116, 4934–4946.

(19) Zhao, H. Y.; Oyama, S. T.; Naeemi, E. D. Hydrogen storage using heterocyclic compounds: the hydrogenation of 2-methylthiophene. *Catal. Today* 2010, 149, 172–184.

(20) Celis-Cornejo, C. M.; Granados-Zarta, G. A.; Bravo-Villarreal, C. E.; Perez-Martinez, D. D.; Giraldo-Duarte, S. A. Kinetic parameters determination of fcc gasoline hydrotreating using genetic algorithms. *CT. F-Cienc. Tecn. Fut.* 2016, 5, 79–93.

(21) Heermann, D. W. *Computer Simulation Methods in Theoretical Physics.* Springer-Verlag Press, 1990.

(22) Leach, A. R. *Molecular Modelling: Principles and Applications.* Addison Wesley Longman Limited Press, 2001.

(23) Gece, G. Theoretical evaluation of the inhibition properties of two thiophene derivatives on corrosion of carbon steel in acidic media. *Mater. Corros.* 2013, 64, 940–944.

(24) Zhu, H. Y.; Lu, X. Q.; Guo, W. Y.; Li, L. F.; Zhao, L. M.; Shan, H. H. Theoretical insight into the desulfurization of thiophene on Pt(110): a density functional investigation. *J. Mol. Catal. A-Chem.* 2012, 363–364,

18–25.

(25) Zhu, H. Y.; Guo, W. Y.; Li, M.; Zhao, L. M.; Li, S. R.; Li, Y.; Lu, X. Q.; Shan, H. H. 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.* 2011, 11, 1498–1510.

(26) Zhang, L. Y.; Shi, W.; Xia, S. J.; Ni, Z. M. Hydrodesulfurization mechanisms of thiophene catalyzed by Au/Pd(111) bimetallic surface. *Acta. Phys-Chim. Sin.* 2014, 30, 1847–1854.

(27) Ni, Z. M.; Shi, W.; Xia, M. Y.; Xue, J. L. Theoretical studies on reaction mechanism of hydrodesulfurization of thiophene catalyzed by Au(111) plane. *Chem. J. Chin. U* 2013, 34, 2353–2362.

(28) Shi, W.; Zhang, L. Y.; Ni, Z. M.; Xia, S. J.; Xiao, X. C. DFT investigations of the adsorption and hydrodesulfurization mechanism of thiophene catalyzed by Pd(111) surface. *RSC. Adv.* 2014, 4, 58315–58324.

(29) Delley, B. From molecules to solids with the DMol^3 approach. *J. Chem. Phys.* 2000, 113, 7756–7764.

(30) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. Atoms, molecules, solids, and surfaces—applications of the generalized gradient approximation for exchange and correlation. *Phys. Rev. B* 1992, 46, 6671–6687.

(31) White, J. A.; Bird, D. M.; Payne, M. C.; Stich, I. Surface corrugation in the dissociative adsorption of H on Cu(100). *Phys. Rev. Lett.* 1994, 73, 1404–1407.

(32) Perdew, J. P.; Wang, Y. Accurate and simple analytic representation of the electron-gas correlation-energy. *Phys. Rev. B* 1992, 45, 13244–13249.

(33) Halgren, T. A.; Lipscomb, W. N. The synchronous-transit method for determining reaction pathways and locating molecular transition states. *Phys. Lett.* 1977, 49, 225–232.

(34) Kittel, C. *Solid State Physics.* John Wiley & Sons Press, 1976.

(35) Mai, S. W.; Zhou, G. D.; Li, W. J. *Advanced Inorganic Structural Chemistry.* Peking University Press, 2001.

(36) Chen, Z. H.; Ding, K. N.; Xu, X. L.; Li, J. Q. DFT study of thiophene adsorption on the Pd(111) and Pt(111) surfaces. *Chin. J. Struct. Chem.*

2010, 29, 365-376.

(37) Tanabe, M.; Kuze, N.; Fujiwara, H.; Takeuchi, H.; Konaka, S. Molecular structure of 2-methylthiophene studied by gas electron diffraction combined with microwave spectroscopic data. *J. Mol. Struct.* 1995, 372, 173-180.

Table 1. Adsorption Energies of 2MT on the Pt(111) Surface

Adsorption site	E ds (kJ · mol ^{1})	Adsorption site	E ds (kJ · mol ^{1})
Top-0°		Fcc-0°	
Top-30°		Fcc-30°	
Top-60°		Fcc-60°	
Top-90°		Fcc-90°	
Hcp-0°		Bri-0°	
Hcp-30°		Bri-30°	
Hcp-60°		Bri-60°	
Hcp-90°		Bri-90°	

The adsorption positions in Table 1 represent the initial adsorption sites of 2MT.

Table 2. Adsorption Energy and Bond Lengths of 2MT Molecule on Pt(111) for the Most Stable Adsorption Geometry

Model	E ds (kJ · mol ^{1})	d (nm)	d (nm)	d (nm)	d (nm)	d (nm)	d (nm)
2MT (Expt) [37]							
2MT (Calc.)							
2MT/Pt(111)							
	Δd						

Table 3. Activation Energy (E) and Reaction Energy (ΔE) of Elementary Reactions on the Pt(111) Surface

Reaction	E (kJ · mol ^{1})	ΔE (kJ · mol ^{1})
C H S* + H* → FS1* + *		
C H S* + H* → FS2* + *		
C H S* + H* → FS3* + *		
C H S* + H* → FS4* + *		

Reaction	E (kJ · mol ^{1})	ΔE (kJ · mol ^{1})
FS2* + H* → FS5* + *		
FS2* + H* → FS6* + *		
FS2* + H* → FS7* + *		
FS6* + H* → FS8* + *		
FS6* + H* → FS9* + *		
FS9* + H* → FS10* + *		
FS10* + H* → FS11* + *		
FS10* + H* → FS12* + *		
FS10* + H* → FS13* + *		
FS10* + H* → FS14* + *		
FS10* + H* → FS15* + *		

Fig. 1. Top (left) and side (right) view of Pt(111) surface models (4×4)

Fig. 2. The most stable configurations of 2MT on the Pt(111) surface: (a) 2MT; (b) top view; (c) side view

Fig. 3. Different reaction pathways for the hydrogenation storage of 2MT (FS represents the product)

Fig. 4. IS, TS, FS, activation energy and reaction energy (kJ · mol ^{1}) of step 1
Note: FS1: E = 167.7; ΔE = -52.2, FS2: E = 75.0; ΔE = -8.1, FS3: E = 130.9; ΔE = -54.9, FS4: E = 187.1; ΔE = 29.7

Fig. 5. IS, TS, FS, activation energy, reaction energy (kJ · mol ^{1}) and bond length (nm) of step 2
Note: FS5: E = 164.6; ΔE = 11.6, FS6: E = 19.5; ΔE = 5.3, FS7: E = 109.3; ΔE = 76.4

Fig. 6. IS, TS, FS, activation energy, reaction energy (kJ · mol ^{1}) and bond length (nm) of step 3
Note: FS8: E = 67.9; ΔE = -102.1, FS9: E = 97.3; ΔE = 5.3

Fig. 7. IS, TS, FS, activation energy and reaction energy (kJ · mol ^{1}) of step 4
Note: FS10: E = 112.6; ΔE = -97.0

Fig. 8. IS, TS, FS, activation energy, reaction energy (kJ · mol ^{1}) and bond length (nm) of step 5
Note: FS11: E = 116.9; ΔE = 48.9, FS12: E = 388.2; ΔE = 39.3, FS13: E = 233.9; ΔE = 138.3, FS14: E = 416.0; ΔE = 13.0

Fig. 9. IS, TS, FS, activation energy, reaction energy (kJ · mol ^{1}) and bond length (nm) of step 6
Note: FS15: E = 210.8; ΔE = -15.8

Fig. 10. Sketch for potential relative energy (E_R) of hydrogenation mechanisms on the Pt(111) surface

Potential energy diagram showing: 2MT() → TS2 (75.0) → FS2 (-8.1) → TS6 (11.4) → FS6 (-2.8) → TS8 (65.1) → FS8 (-104.9) → TS10 (7.7) → FS10 (-201.9) → TS11 (-85.0) → FS11 (-153.0) → TS15 (57.8) → FS15 (-168.8)*

Note: Figure translations are in progress. See original paper for figures.