

Supporting Information

Insight into the thiophene hydrodesulfurization on clean and S-modified MoP(010): a periodic density functional theory study

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Section 1. The calculation for surface energy

The exposed Mo-terminated surfaces of the MoP crystal mainly include (111), (100), (001), (010), (102) and (201) surfaces. Generally, a catalytic reaction starts from stable adsorption of reactants. For the (111), (102) and (201) surfaces, the average distance of the adjacent surface Mo-Mo is $\sim 5.38 \text{ \AA}$, which is significantly larger than the molecular dimension of thiophene (ca. 4.11 \AA) and not suitable for the stable adsorption of thiophene. In contrast, the (100), (001) and (010) surfaces involve more compact atomic arrangement of surface Mo atoms (ca. 3.24 \AA for the adjacent Mo-Mo distance), indicating that these surfaces could stably adsorb thiophene molecule and exhibit catalytic activity. Thus, the (100), (001) and (010) surfaces are appropriate models to simulate the MoP catalyst. Generally, the surface with high surface energy is unstable. We calculate the surface energies for the Mo-terminated (100), (001) and (010) surfaces based on the following formula^{1,2}:

$$E_{\text{surf}} = (E_{\text{slab}} - E_{\text{bulk}})/2S \quad (1)$$

where E_{surf} , E_{slab} , E_{bulk} and S represent the surface energy, the calculated electronic energies of the slab and the bulk, and the surface area, respectively. The calculated surface energies are 19.40, 10.74 and 11.08 eV/ \AA^2 for the (100), (001) and (010) surfaces, respectively. Thus, the (001) and (010) surfaces could be formed more easily compared to the (100) surface, and are more appropriate to be used as surface model for MoP catalyst.

Section 2. Test for the calculation parameters

We chose thiophene in the T-hollow-top adsorption geometry, the most stable configuration on clean MoP(010) (see Table 1), to carry out the following test calculations. (1) A $(3 \times 3 \times 2)$ k -points test showed that the employed $(2 \times 2 \times 1)$ k -points are accurate enough for the surface calculations (the adsorption energy difference was less than 0.03 eV). (2) We also tested the effect of zero point energy (ZPE) correction, which is less than 0.02 eV for the adsorption energy and less than 0.05 eV for the C-S bond scission energy barrier. Therefore, ZPE corrections were not included in the present study. The calculated geometrical parameters of the gas-phase thiophene, under the current computational conditions, are almost the same as

the experimental values (the largest difference is less than 0.02 Å, see Table S1).

Table S1 Bond lengths (in Å) calculated and experimental values for the free thiophene molecule

Thiophene	C ² -S/C ⁵ -S	C ² -C ³ /C ⁴ -C ⁵	C ³ -C ⁴
Theory	1.728	1.374	1.422
Exp. ³	1.714	1.378	1.427

Section 3. Energy barrier analysis

Upon adsorption, the geometry of the molecule and the surface are changed somewhat compared with those in the non-interacting systems. The adsorption energy of the adsorbates can be partitioned into three terms using the following formula:¹

$$\Delta E_{\text{ads}} = E_{\text{int}} + \delta E_{\text{ads}} + \delta E_{\text{surf}} \quad (2)$$

$$E_{\text{int}} = E_{\text{ads/surf}} - E_{\text{ads}^*} - E_{\text{surf}^*} \quad (3)$$

$$\delta E_{\text{ads}} = E_{\text{ads}^*} - E_{\text{ads}} \quad (4)$$

$$\delta E_{\text{surf}} = E_{\text{surf}^*} - E_{\text{surf}} \quad (5)$$

where E_{int} is the interaction energy between the surface and the adsorbate at the adsorbed geometries, E_{ads} and E_{ads^*} are the total energies of the adsorbate at the free and adsorbed structures, respectively. E_{surf} and E_{surf^*} are the total energies of the surface at the free and adsorbed geometries, respectively. Thus, δE_{ads} and δE_{surf} are the distortion energies of the adsorbate and the surface in the adsorption process, reflecting the energy cost for the adjustment of the relevant species structures in the adsorption process.

The energy barrier (E_a) of a step was calculated according to the following formula:

$$E_a = E_{\text{ads/surf}}^{\text{TS}} - E_{\text{ads/surf}}^{\text{IS}} \quad (6)$$

where $E_{\text{ads/surf}}^{\text{IS}}$ and $E_{\text{ads/surf}}^{\text{TS}}$ are total energies of the initial state (IS) and TS, respectively. The adsorption energy also can be expressed as:

$$\Delta E_{\text{ads}} = E_{\text{ads/surf}} - E_{\text{ads}} - E_{\text{surf}} \quad (7)$$

where, E_{ads} and E_{surf} correspond to the energy of the gas-phase thiophene and free surface, respectively.

According to the equations (2) – (7), the E_a can be expressed as follows:

$$E_a = \Delta E_{\text{ads}}^{\text{TS}} - \Delta E_{\text{ads}}^{\text{IS}} = (\delta E_{\text{ads}}^{\text{TS}} + \delta E_{\text{surf}}^{\text{TS}} + E_{\text{int}}^{\text{TS}}) - (\delta E_{\text{ads}}^{\text{IS}} + \delta E_{\text{surf}}^{\text{IS}} + E_{\text{int}}^{\text{IS}}) \quad (8)$$

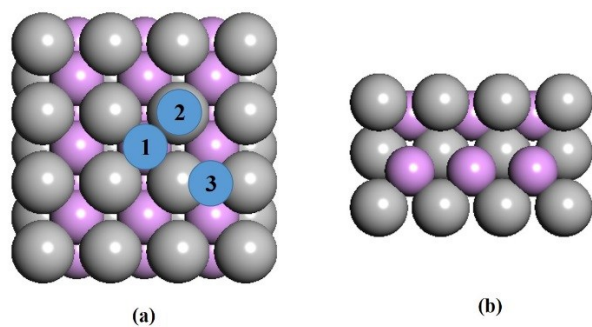


Fig. S1 The structures of Mo-terminated MoP(010) surface model: (a) top view and (b) side view, 1-3 represent the adsorption sites of hollow, top and bridge, respectively. Light-gray and purple denote Mo and P, respectively.

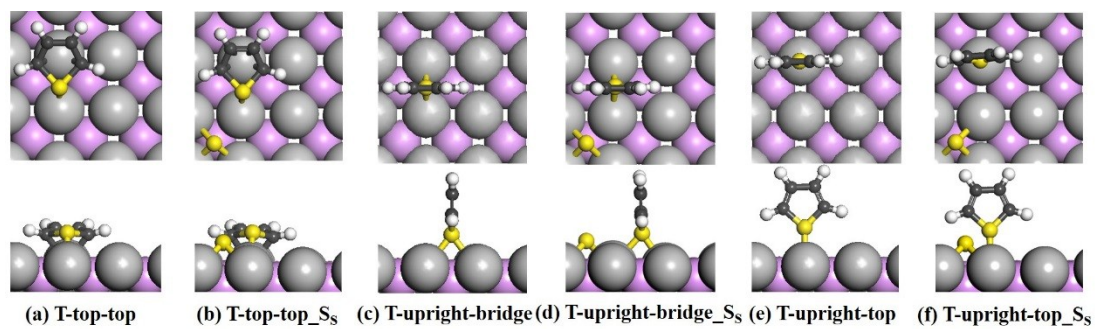


Fig. S2 The adsorption structures of the T-top-top, T-upright-bridge and T-upright-top configurations of thiophene on clean and S-modified MoP(010). Captions are the same as in Fig. 1.

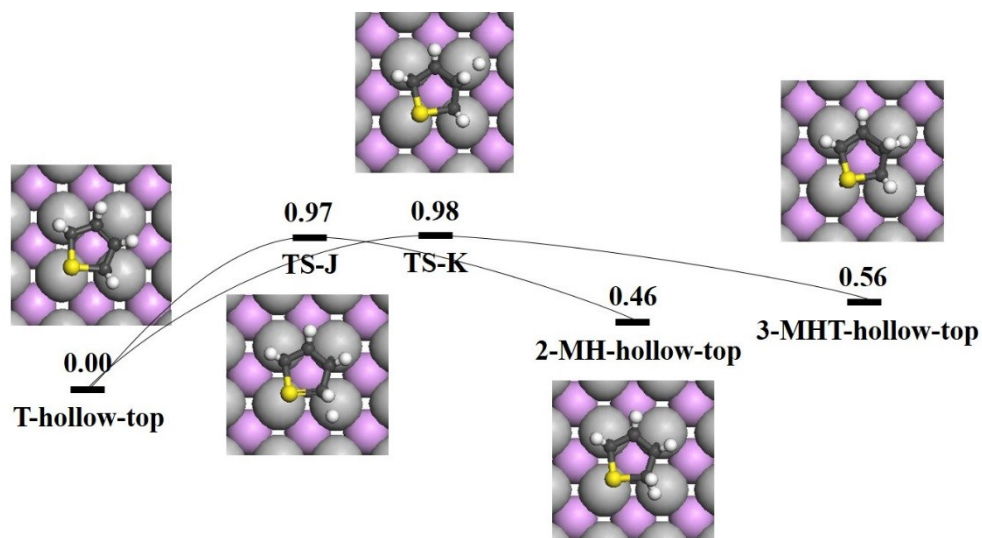


Fig. S3 Initial hydrogenation pathway of thiophene from T-hollow-top. Captions are the same as in Fig. 2.

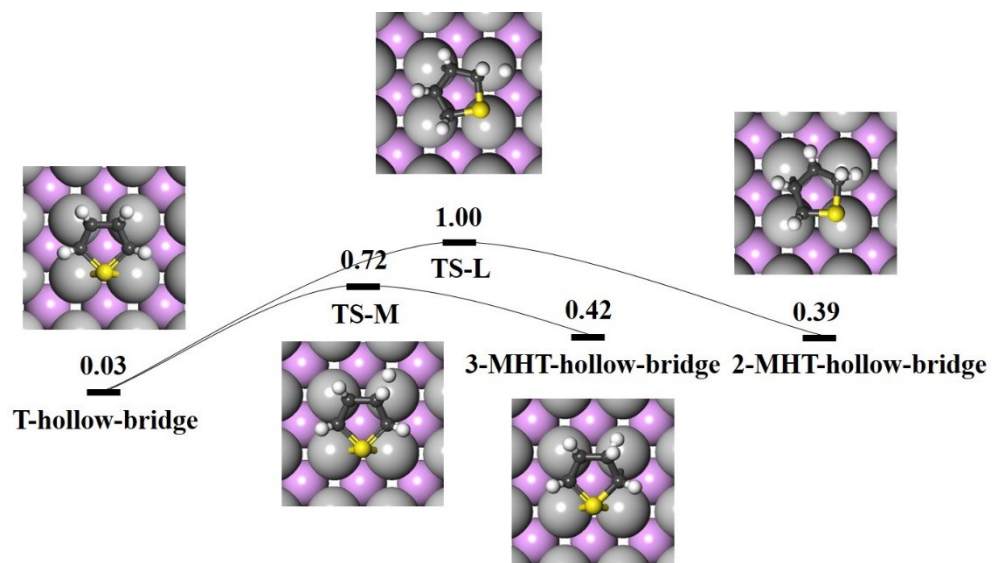


Fig. S4 Initial hydrogenation pathway of thiophene from T-hollow-bridge. Captions are the same as in Fig. 2.

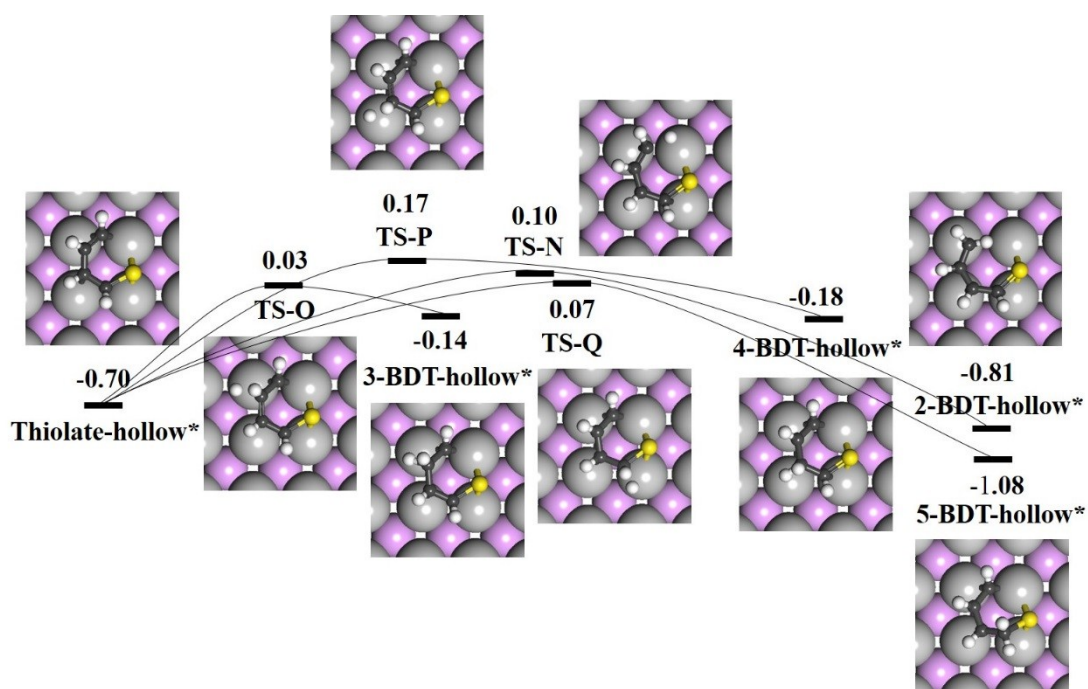


Fig. S5 Initial hydrogenation pathway of thiophene from Thiolate-hollow*, BDT represents the hydrogenation product (butadienethiolate). Captions are the same as in Fig. 2.

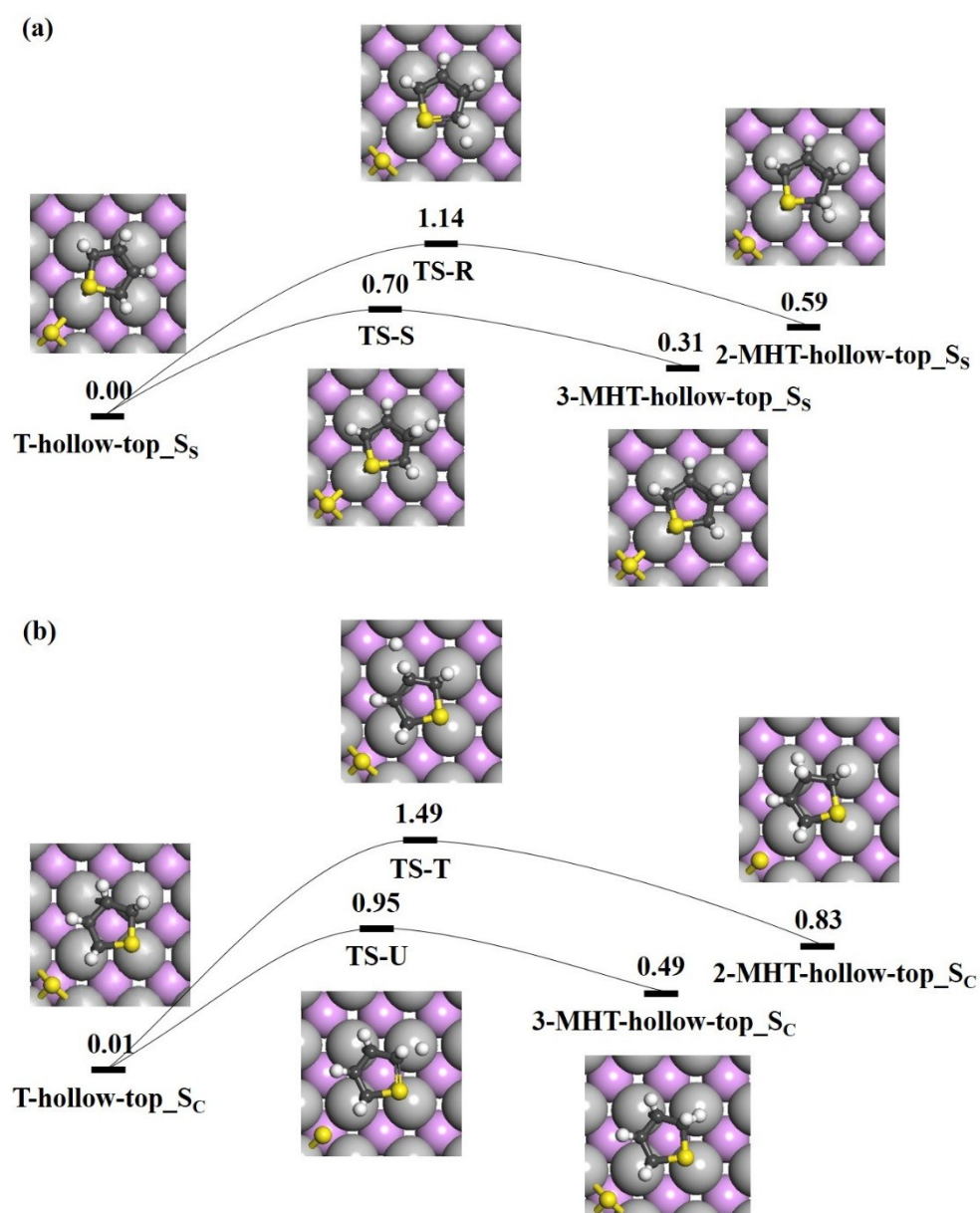


Fig. S6 Initial hydrogenation pathway of thiophene from (a) T-hollow-top_S_s and (b) T-hollow-top_S_c. Captions are the same as in Fig. 2.

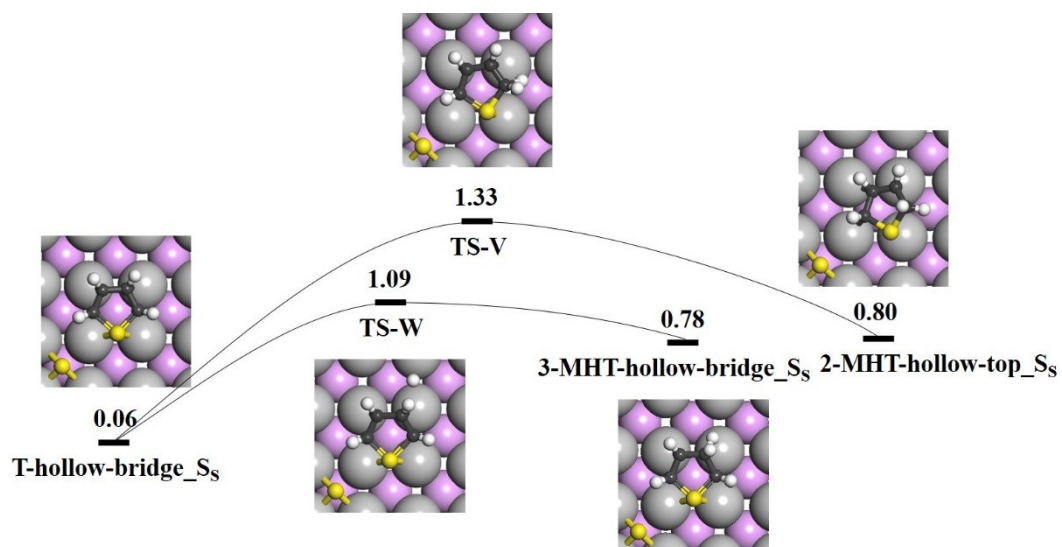


Fig. S7 Initial hydrogenation pathway of thiophene from T-hollow-bridge_Ss. Captions are the same as in Fig. 2.

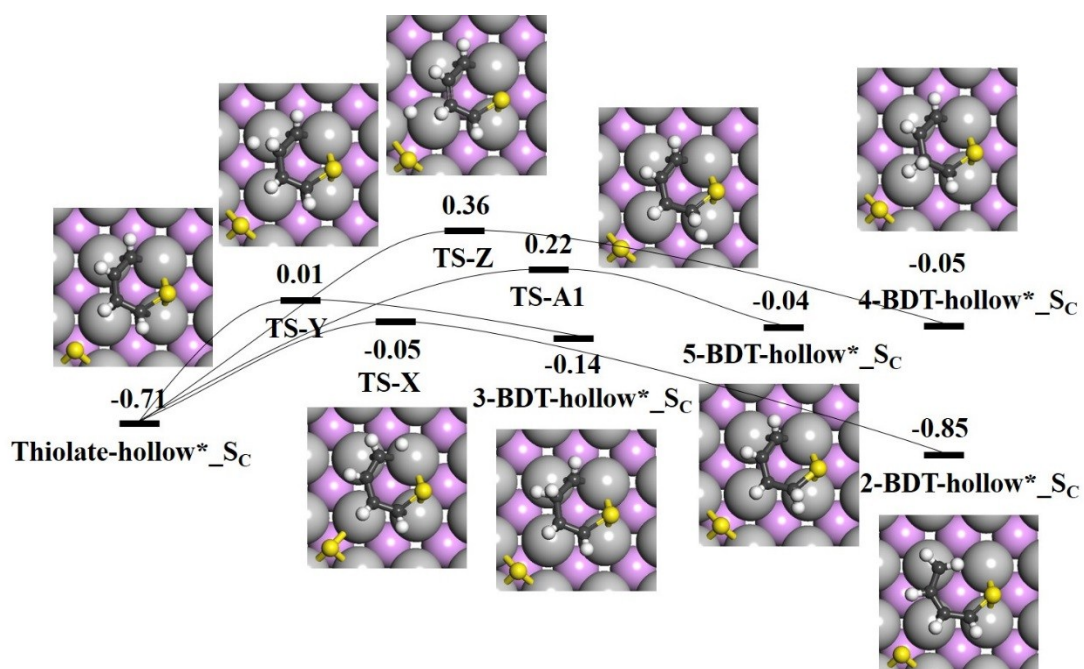


Fig. S8 Initial hydrogenation pathway of thiophene from Thiolate-hollow*_SC. Captions are the same as in Fig. 2.

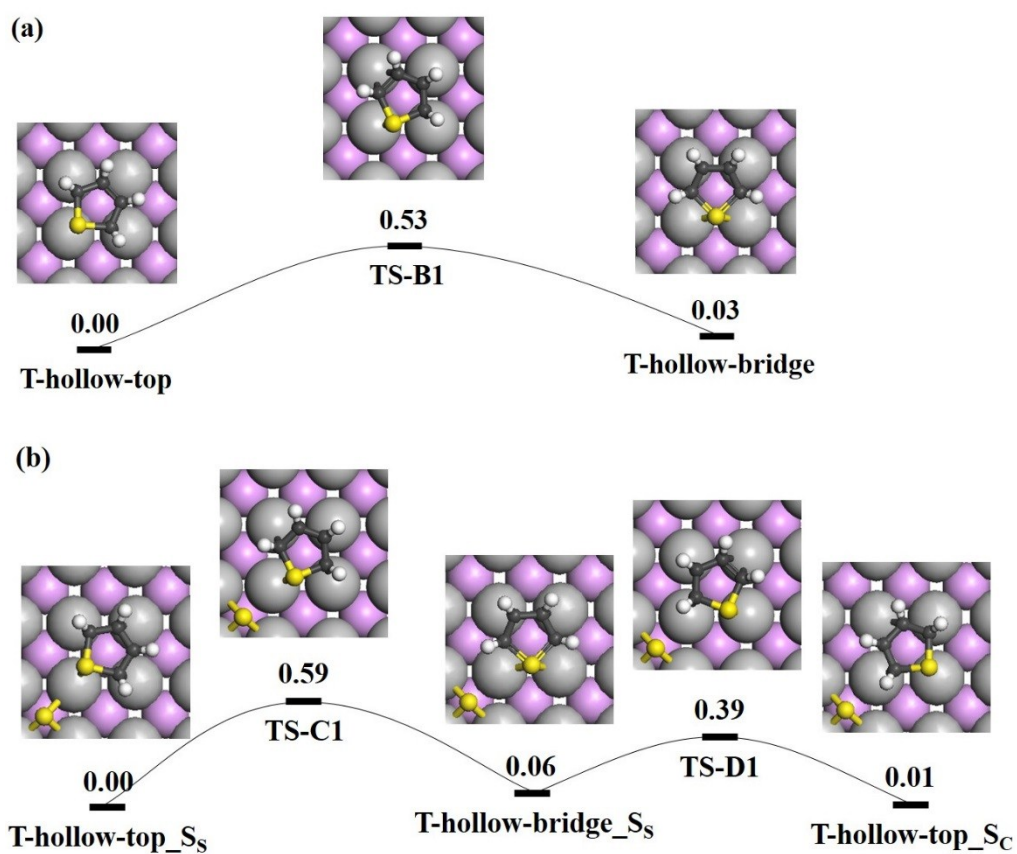


Fig. S9 Conversion pathways between the T-hollow-top and T-hollow-bridge configurations of thiophene on (a) clean and (b) S-modified MoP(010). Captions are the same as in Fig. 2.

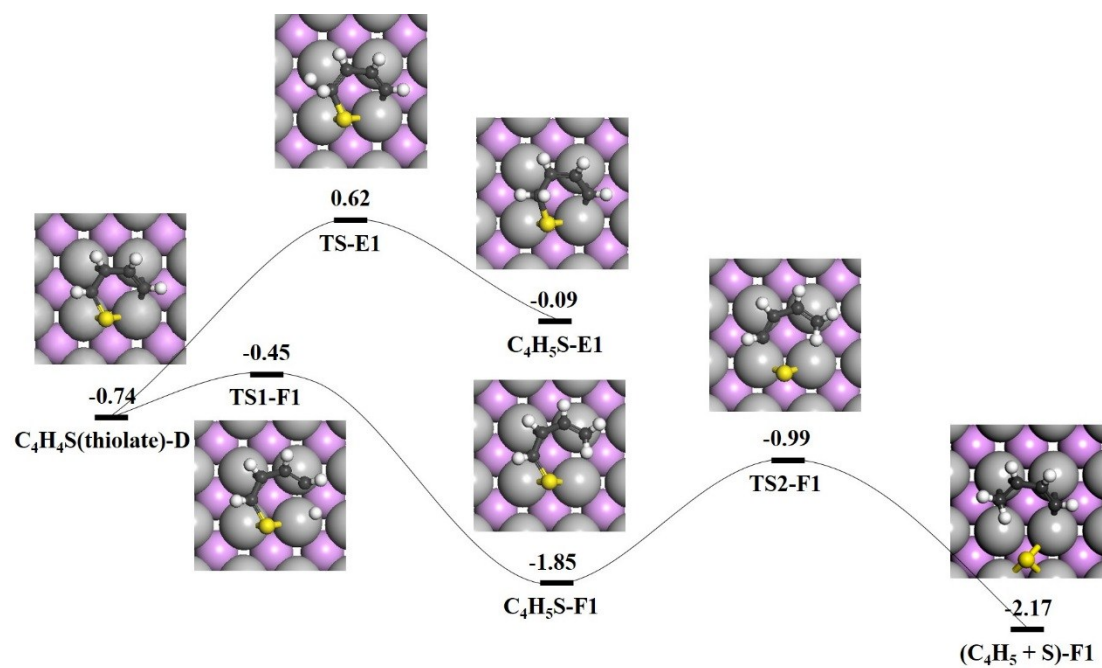


Fig. S10 Hydrogenation and subsequent C-S bond scission pathways of thiolate from $\text{C}_4\text{H}_4\text{S}$ (thiolate-D). Captions are the same as in Fig. 2.

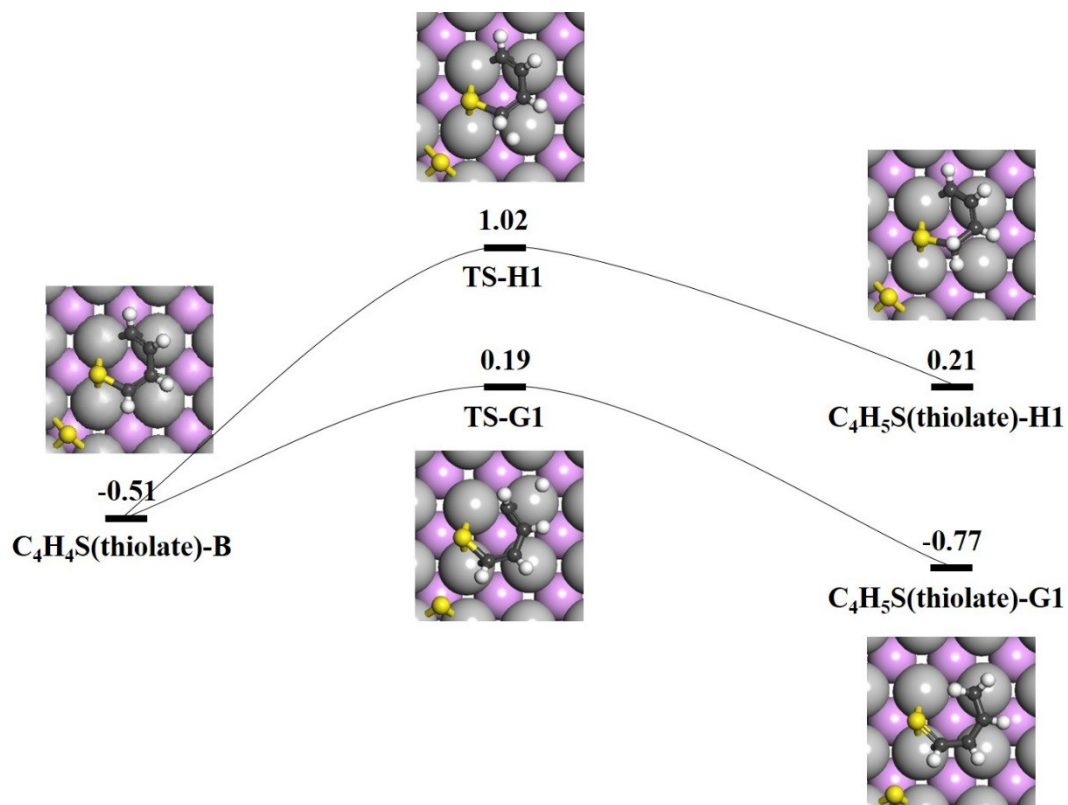


Fig. S11 Hydrogenation and subsequent C–S bond scission pathways of thiolate from C₄H₄S (thiolate–B). Captions are the same as in Fig. 2.

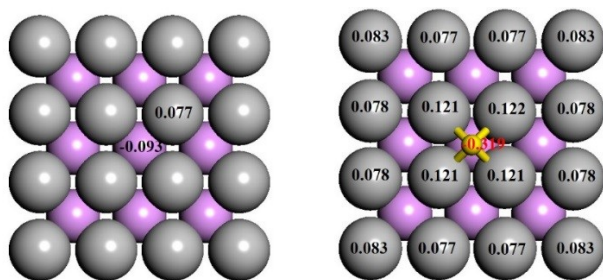


Fig. S12 Mulliken charges (in e) of the surface metal atoms and surface S atom on clean and S-modified MoP(010) surfaces.

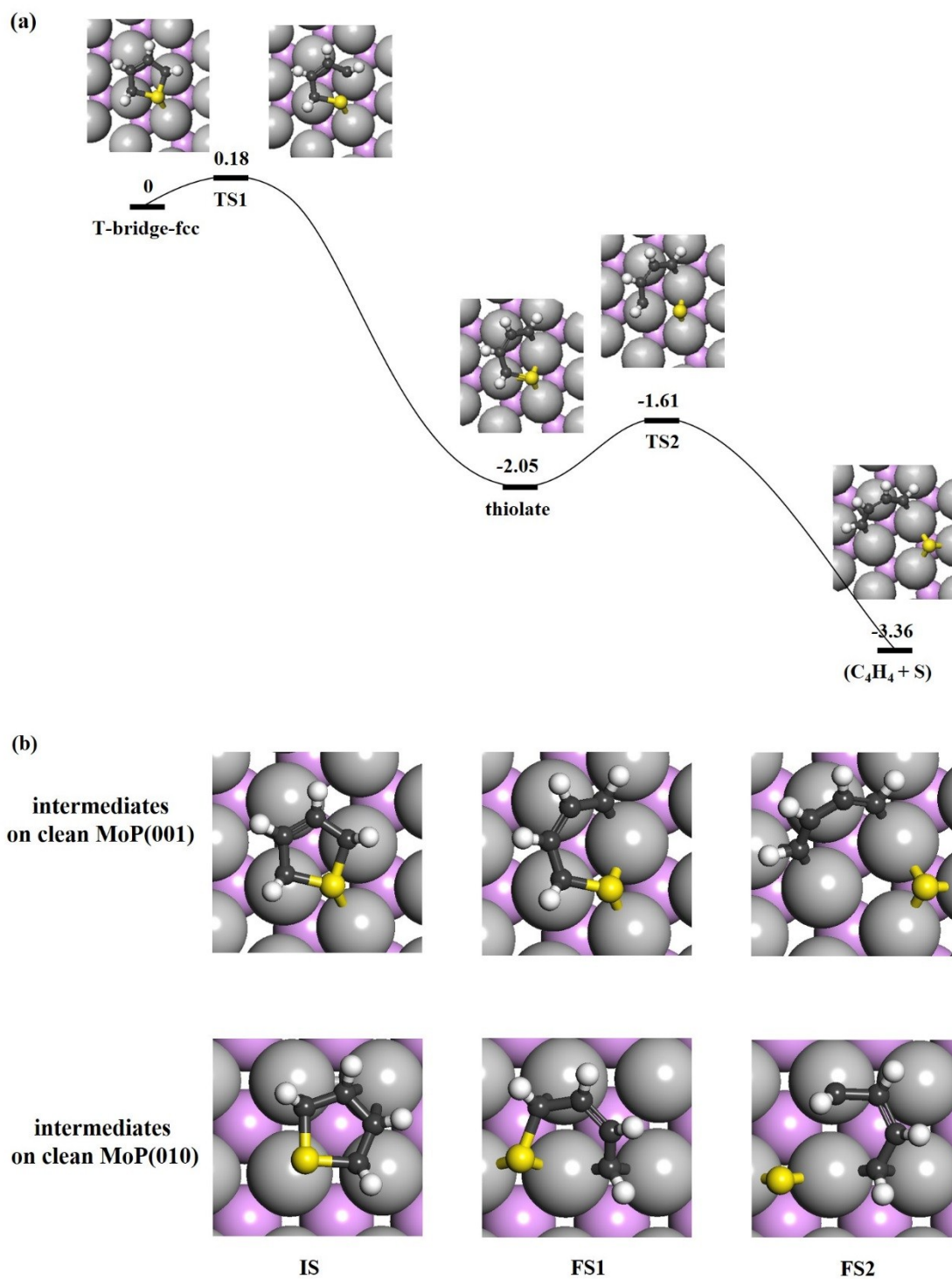


Fig. S13 (a) The direct desulfurization pathway of thiophene from T-bridge-fcc on clean MoP(001).⁴ (b) The intermediates involved in the desulfurization of thiophene from T-bridge-fcc and T-hollow-top configurations on clean MoP(001) and MoP(010) surfaces, respectively.

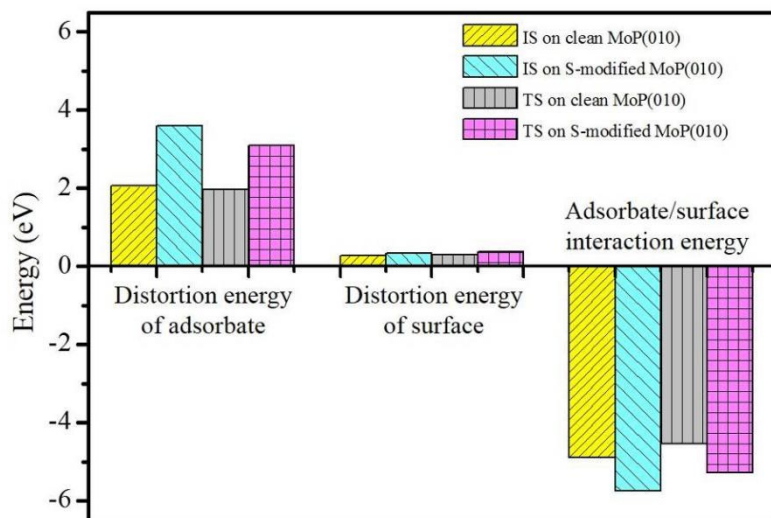


Fig. S14 Decomposition of the adsorption energies for the IS and TS of the initial C–S bond scission of thiophene from T-hollow-top on the clean and S-modified MoP(010) surfaces.

Table S2 Adsorption configurations, adsorption energies (ΔE_{ads} , eV), structural parameters (Å), and Mulliken populations (e) for thiophene on clean and S-modified MoP(010)

Sites	ΔE_{ads}	$d(\text{S-Mo})$	$d(\text{C-Mo})$	$d(\text{C}^2\text{-S})$	$d(\text{C}^5\text{-S})$	$d(\text{C}^2\text{-C}^3)$	$d(\text{C}^3\text{-C}^4)$	$d(\text{C}^4\text{-C}^5)$	Charges
gas	–	–	–	1.728	1.728	1.374	1.422	1.374	0
top-top	–1.51	2.400	2.244, 2.400, 2.400, 2.244	1.909	1.908	1.431	1.404	1.430	0.017
top-top_S _S	–1.25	2.490	2.271, 2.393, 2.397, 2.266	1.862	1.887	1.433	1.400	1.431	0.118
upright-bridge	–1.02	2.541, 2.538	–	1.758	1.757	1.360	1.442	1.360	0.144
upright-bridge_S _S	–0.92	2.623, 2.498	–	1.758	1.756	1.360	1.440	1.360	0.170
upright-top	–0.90	2.403	–	1.729	1.728	1.375	1.425	1.374	0.082
upright-top_S _S	–0.90	2.392	–	1.731	1.730	1.372	1.428	1.372	0.096

Table S3 Adsorption energy (ΔE_{ads} , eV) for surface S atom, and the hydrogenation products of C_4H_4 on clean MoP(010), MoP(001) and S-modified MoP(010)

Species	Sites	ΔE_{ads}		
		Clean MoP(010)	S-modified MoP(010)	Clean MoP(001) ⁴
S	hollow	-5.17	-4.94	-6.23/-6.47
	bridge	-5.13	-4.83	-
	top	-4.53	-	-
C_4H_4	hollow	-4.77/-4.53	-4.55	-5.67/-5.96
C_4H_6	hollow	-2.64	-2.41	-2.84/-3.44
	top	-2.23	-1.79	-
<i>trans</i> -2- C_4H_8	hollow-top	-1.30	-1.28	-1.53
<i>cis</i> -2- C_4H_8	-	-1.30/-0.98	-0.78/-0.76	-1.22

Table S4 C–S distances (Å) in desulfurization reactions of adsorbed thiophene on clean and S-modified MoP(010)

Reactants	Intermediates	$d(\text{C}^2\text{--S})$	$d(\text{C}^5\text{--S})$
T-hollow-top	T-hollow-top	1.835	1.840
	TS1-A	2.391	1.774
	C ₄ H ₄ S(thiolate)-A	3.060	1.850
	TS2-A	3.177	2.483
	(C ₄ H ₄ + S)-A	3.408	3.570
T-hollow-top_S _S	T-hollow-top_S _S	1.819	1.844
	TS1-B	1.814	2.229
	C ₄ H ₄ S (thiolate)-B	1.817	2.848
	TS2-B	2.348	2.966
	(C ₄ H ₄ + S)_S _S -B	3.675	3.500
T-hollow-top_S _C	T-hollow-top_S _C	1.838	1.830
	TS1-C	1.811	2.555
	C ₄ H ₄ S (thiolate)-C	1.800	3.174
	TS2-C	2.374	3.328
	(C ₄ H ₄ + S)_S _C -C	3.235	3.621
T-hollow-bridge	T-hollow-bridge	1.902	1.898
	TS1-D	1.991	1.888
	C ₄ H ₄ S(thiolate)-D	2.897	1.805
	TS2-D	3.228	2.620
	(C ₄ H ₄ + S)-D	3.578	3.589
T-hollow-bridge_S _S	T-hollow-bridge_S _S	1.866	1.919
	TS1-E	1.860	2.007
	C ₄ H ₄ S (thiolate)-E	1.806	2.919
	TS2-E	2.389	3.129
	(C ₄ H ₄ + S)_S _S -E	3.557	3.696
Thiolate-hollow*	Thiolate-hollow*	2.890	1.820
	TS-F	3.045	2.340
	(C ₄ H ₄ + S)-F	3.577	3.582
Thiolate-hollow*_S _C	Thiolate-hollow*_S _C	2.896	1.818
	TS-G	3.046	2.310
	(C ₄ H ₄ + S)_S _C -G	3.525	3.499

Table S5 Distortion energy of adsorbate (δE_{ads} , eV), distortion energy of surface (δE_{surf} , eV), adsorbate/surface interaction energy (E_{int} , eV), adsorption energy (ΔE_{ads} , eV) for the IS, FS1 and FS2 involved in products of the first and second C–S scissions of thiophene from T-bridge-fcc on clean MoP(001)⁴ and T-hollow-top on clean MoP(010) surfaces

Configurations	IS ^a				FS1 ^a				FS2 ^b			
	δE_{ads}	δE_{surf}	E_{int}	ΔE_{ads}	δE_{ads}	δE_{surf}	E_{int}	ΔE_{ads}	δE_{ads}	δE_{surf}	E_{int}	ΔE_{ads}
T-bridge-fcc	1.85	0.12	-4.57	-2.60	5.00	0.45	-10.10	-4.65	1.57	0.63	-16.02	-13.82
T-hollow-top	2.06	0.28	-4.89	-2.55	4.99	0.29	-8.25	-2.97	1.86	0.57	-13.65	-11.22

^aThe gas-phase adsorbate in δE_{ads} and ΔE_{ads} corresponds to the gas-phase thiophene. ^bThe gas-phase adsorbate in δE_{ads} and ΔE_{ads} corresponds to gas-phase (C₄H₄ + S), respectively.

Table S6 Distortion energy of adsorbate (δE_{ads} , eV), distortion energy of surface (δE_{surf} , eV), and adsorbate/surface interaction energy (E_{int} , eV) in the IS and TS involved in the first C–S bond scission of thiophene from T-hollow-top on clean and S-modified MoP(010) surfaces

Surfaces	δE_{ads}		δE_{surf}		E_{int}		E_{a1}	E_{a2}	E_{a3}	E_{a}
	IS	TS	IS	TS	IS	TS				
Clean MoP(010)	2.06	3.60	0.28	0.33	-4.89	-5.74	1.54	0.05	-0.85	0.74
S-modified MoP(010)	1.96	3.10	0.30	0.37	-4.54	-5.26	1.14	0.07	-0.72	0.49

$E_{\text{a1}} = (\delta E_{\text{ads}}^{\text{TS}} - \delta E_{\text{ads}}^{\text{IS}})$, $E_{\text{a2}} = (\delta E_{\text{surf}}^{\text{TS}} - \delta E_{\text{surf}}^{\text{IS}})$ and $E_{\text{a3}} = (E_{\text{int}}^{\text{TS}} - E_{\text{int}}^{\text{IS}})$

Notes and references

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- 2 H.-T. Chen, Y. M. Choi and M. L. Liu, *ChemPhysChem*, 2007, **8**, 849–855.
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