Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Electronic Supplementary Material

A combined experimental and DFT study on catalysis performance of Co-doped MoS_2 monolayer for hydrodesulfurization reaction

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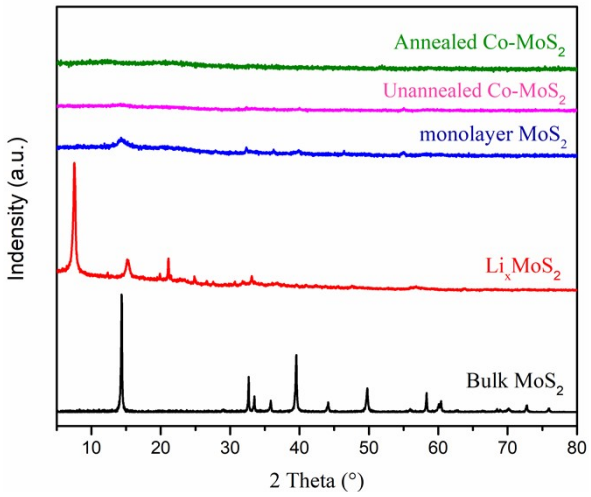

Fig. S1 X-ray diffractogram of Bulk MoS_2, Li_xMoS_2, monolayer MoS_2, Unannealed Co-MoS_2 and Annealed Co-MoS_2.

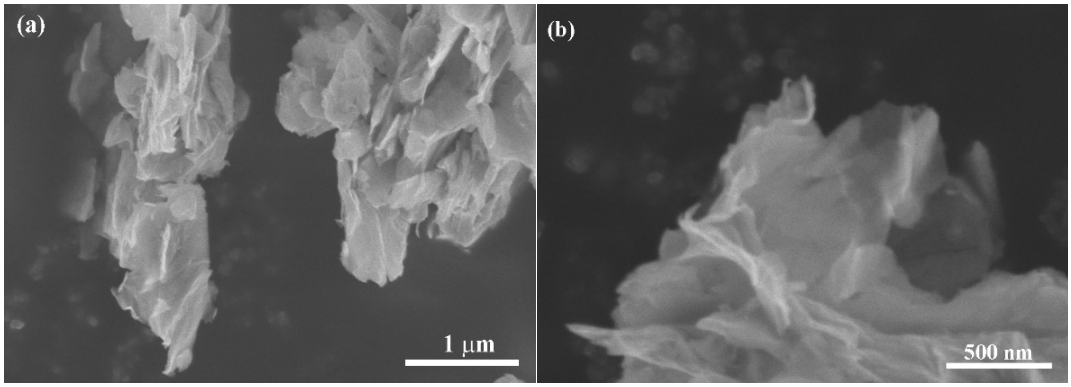

Fig. S2 SEM images of exfoliated MoS_2 monolayer without (a) and with (b) Co doping.

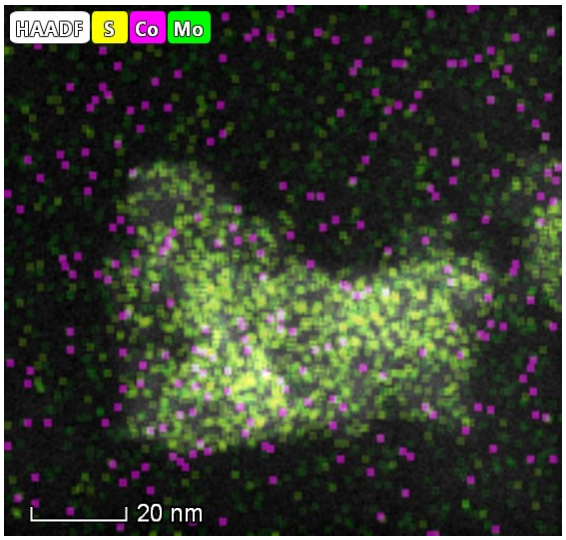

Fig. S3 HAADF-STEM image of prepared Co-MoS_2.

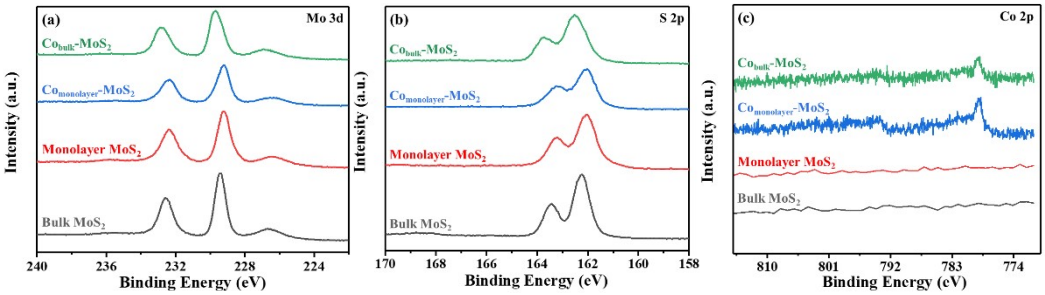

Fig. S4 XPS spectra of Mo 3d (a), S 2p (b) and Co 2p (c) regions of monolayer MoS_2 and Co-doped monolayer MoS_2.

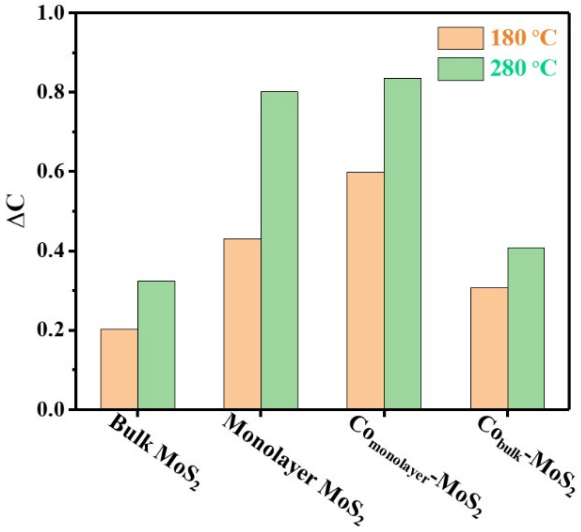

Fig. S5 Thiophene conversion of varied catalysts after reaction of 8 hours at different temperature.

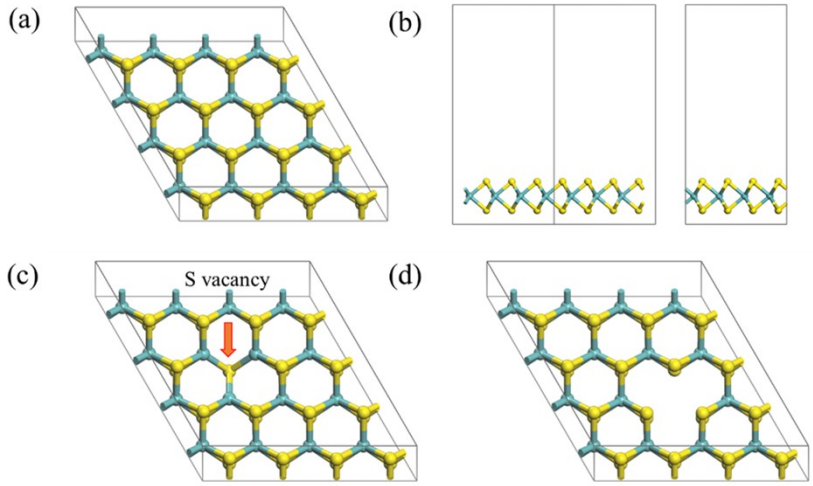

Fig. S6 Model images of MoS_2 monolayer. (a) MoS_2 monolayer, (b) side view of MoS_2 monolayer, (c) MoS_2 monolayer with S vacancy, (d) MoS_2 monolayer with Mo vacancy. (yellow color: sulfur atoms; blue color: molybdenum atoms)

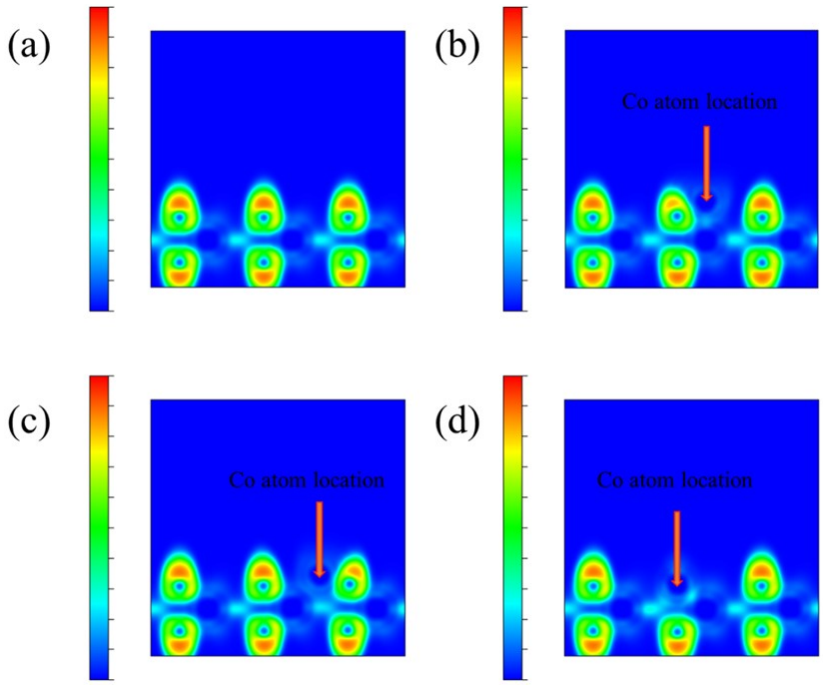

Fig. S7 Electron localization function of the electron density on the side. (a) MoS_2 single sheet, (b) MoS_2 single sheet with Co on Mo site, (c) MoS_2 single sheet with Co atom in hollow site, (d) MoS_2 single sheet with Co filled in S-vacancy. The coordinate axis ranges from 0 to 1.

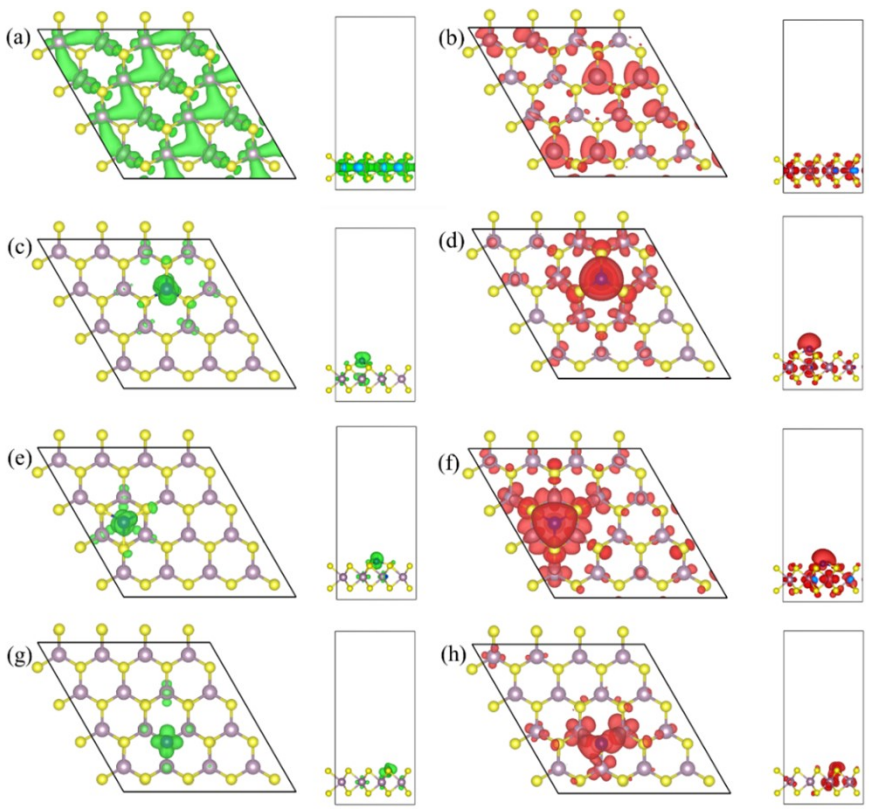

Fig. S8 The top and side views of the distribution of frontal tracks on the MoS_2 catalyst before and after Co atom doping. (a) VBM orbit of MoS_2; (b) CBM orbit of MoS_2; (c) VBM orbit of Co_{Mo}-MoS_2; (d) CBM orbit of Co_{Mo}-MoS_2; (e) VBM orbit of Co_{hollow}-MoS_2; (f) Co_{hollow}-MoS_2 CBM track; (g) Co_{Vs}-MoS_2 VBM track; (h) Co_{Vs}-MoS_2 CBM track.

For the original MoS_2, the orbits of VBM and CBM are both distributed on the molybdenum atomic layer, which explains that it is generally inert in the catalytic reaction. When Co atoms are doped on the basal surface of the catalyst, these two orbitals are distributed on the Co atoms and the S atom sites around Co center. Therefore, it can be speculated that these sites may be catalytically active centers.

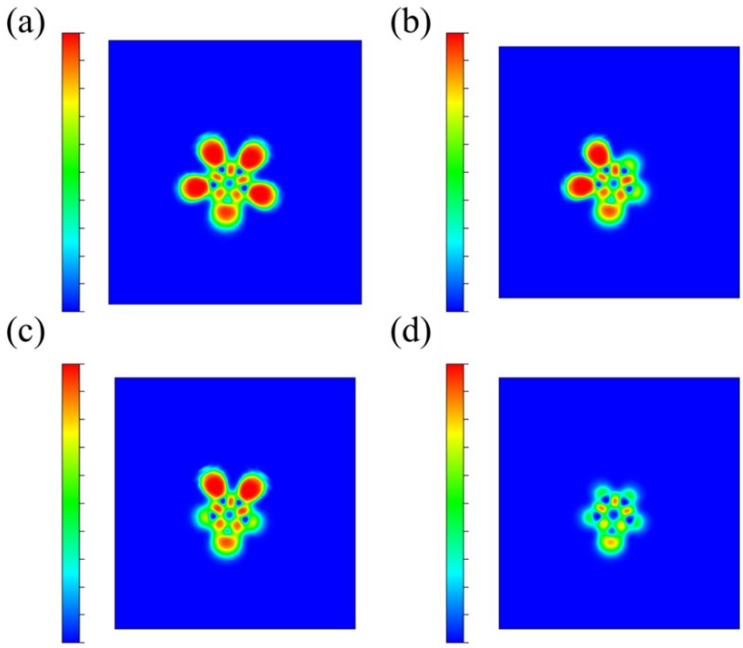

Fig. S9 ELF charge of thiophene and important intermediates. (a) thiophene, (b) 2,3-DHT, (c) 2,5-DHT, (d) THT. The coordinate axis ranges from 0 to 1.

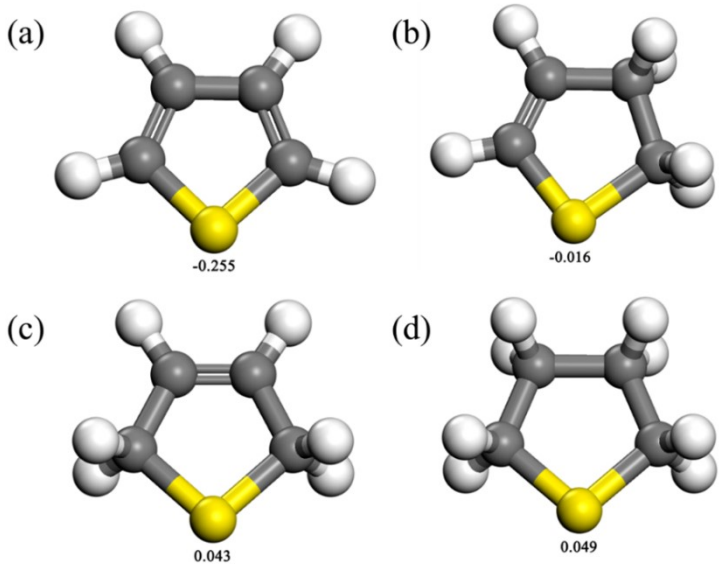

Fig. S10 Bader charge analysis of S atom at the adsorption site. (a) thiophene, (b) 2,3-DHT, (c) 2,5-DHT, (d) THT. Negative sign means losing electrons, positive sign means gaining electrons.

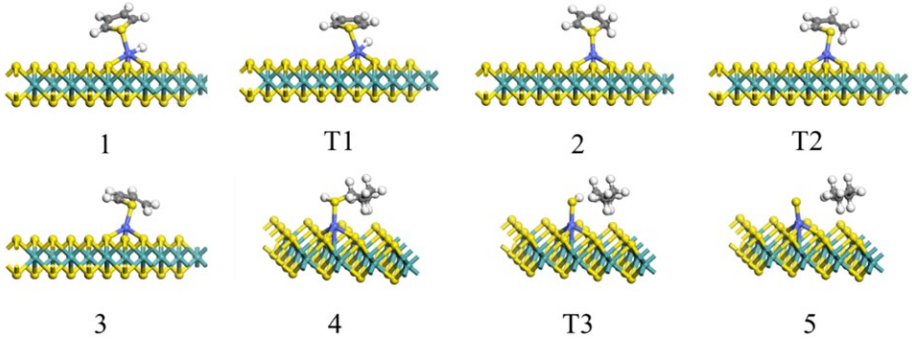

Fig. S11 Reaction structure models of the DDS pathway of thiophene on Co_{Mo}-MoS_2.

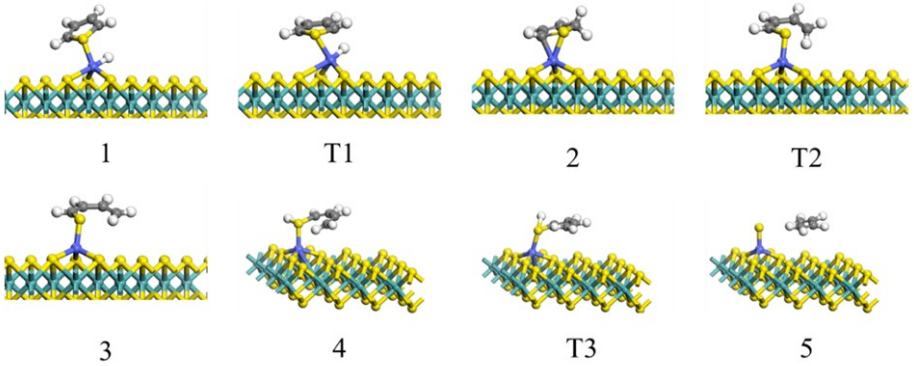

Fig. S12 Reaction structure models of the DDS pathway of thiophene on Co_{hollow}-MoS_2.

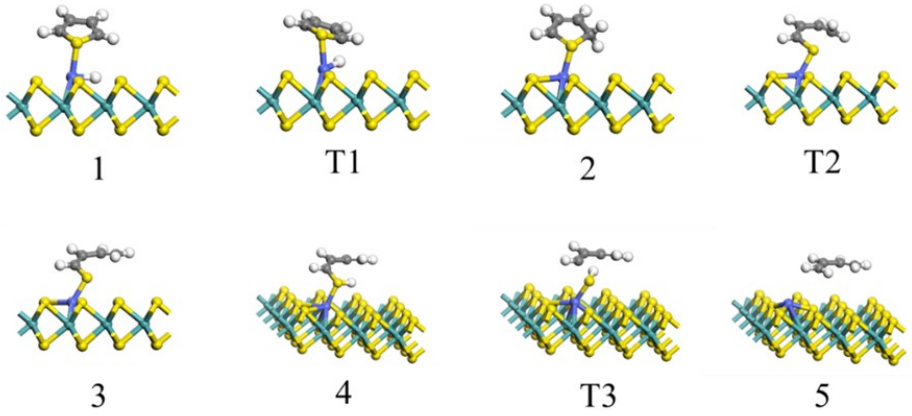

Fig. S13 Reaction structure models of the DDS pathway of thiophene on Co_{Vs}-MoS_2.

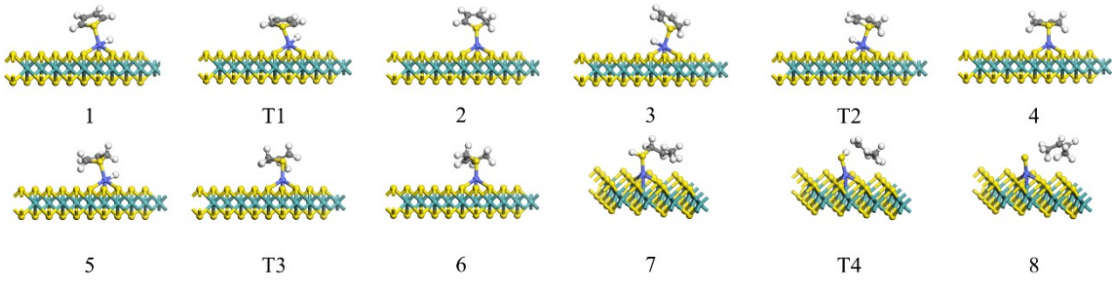

Fig. S14 Reaction structure models of the first PH pathway of thiophene on Co_{Mo}-MoS_2.

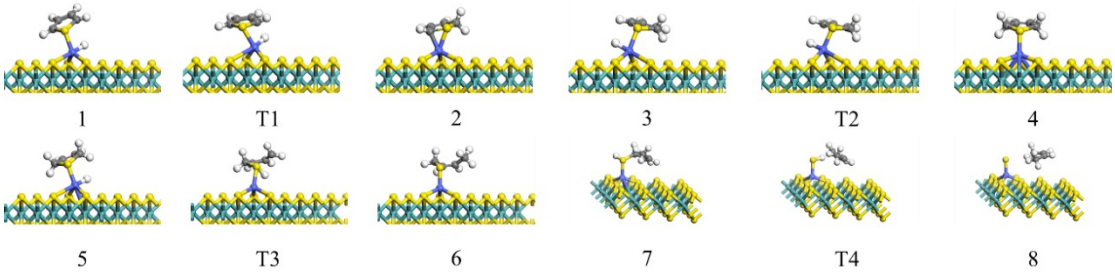

Fig. S15 Reaction structure models of the first PH pathway of thiophene on Co_{hollow}-MoS_2.

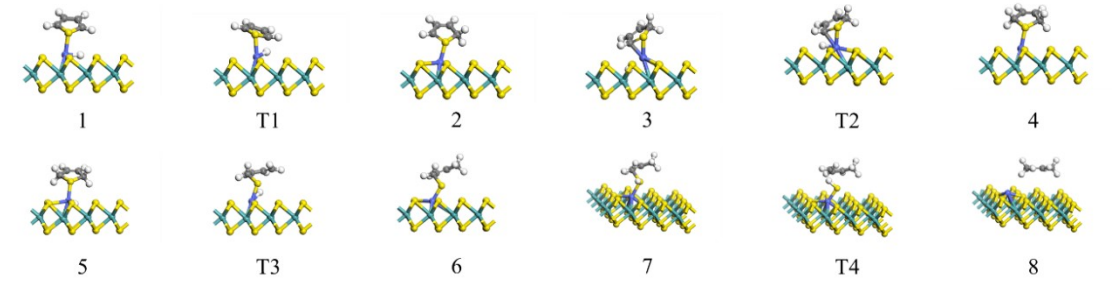

Fig. S16 Reaction structure models of the first PH pathway of thiophene on Co_{Vs}-MoS_2.

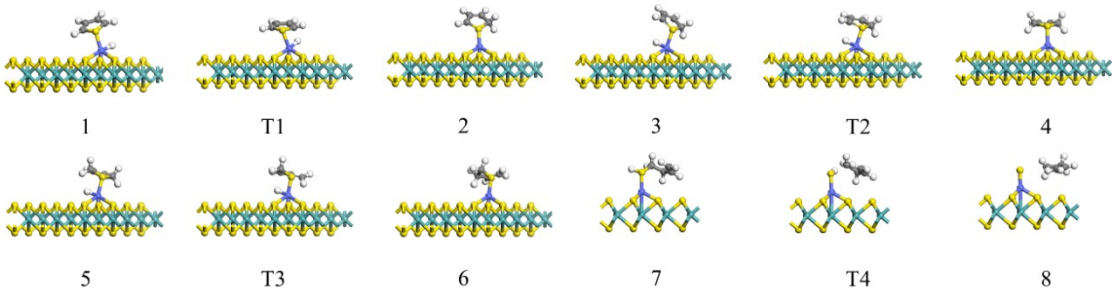

Fig. S17 Reaction structure models of the second PH pathway of thiophene on Co_{Mo}-MoS_2.

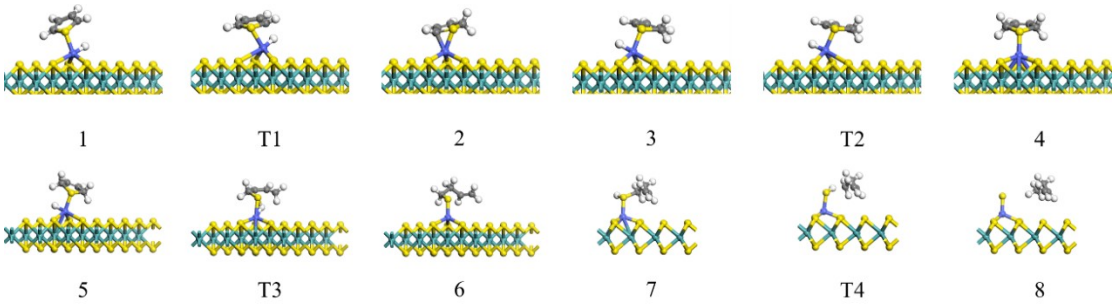

Fig. S18 Reaction structure models of the second PH pathway of thiophene on Co_{hollow}-MoS_2.

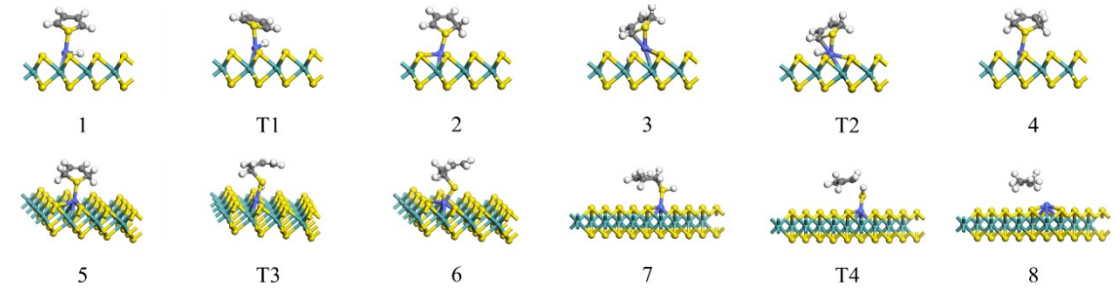

Fig. S19 Reaction structure models of the second PH pathway of thiophene on Co_{Vs}-MoS_2.

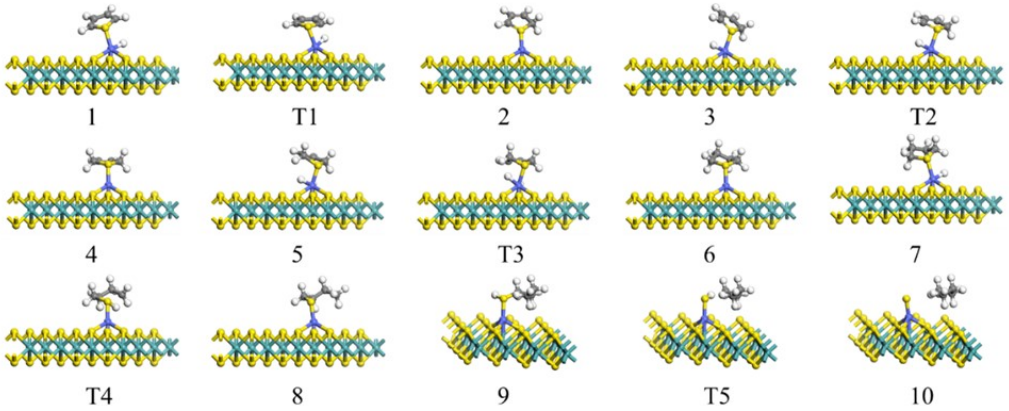

Fig. S20 Reaction structure models of the FH pathway of thiophene on Co_{Mo}-MoS_2.

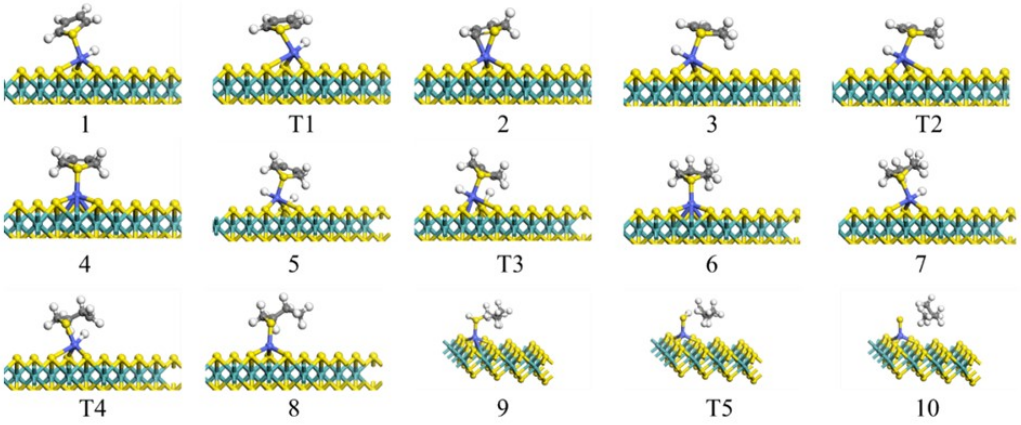

Fig. S21 Reaction structure models of the FH pathway of thiophene on Co_{hollow}-MoS_2.

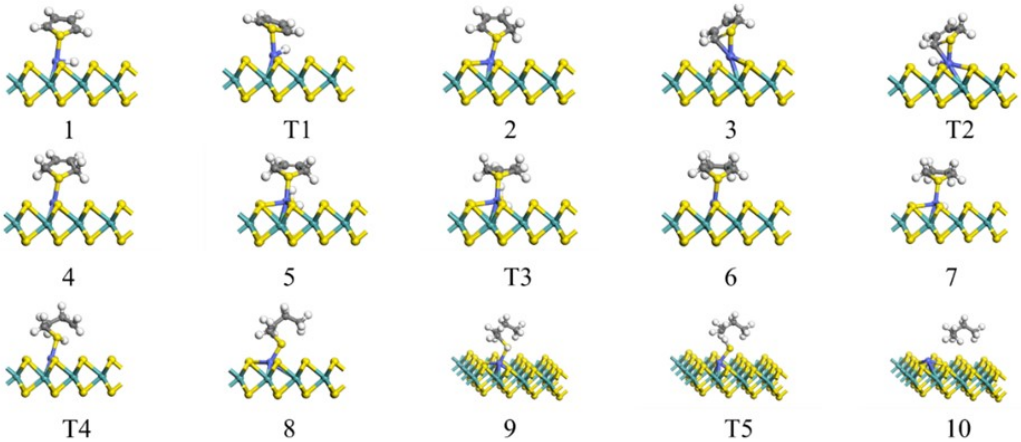

Fig. S22 Reaction structure models of the FH pathway of thiophene on Co_{Vs}-MoS_2.

Table S1 Vacancy formation energy on MoS_2 single sheet

MoS_2 single sheet	Energy (eV)	Atomisation Energy (eV)	Bond Energy	Vacancy Formation Energy (eV)
MoS_2	-356.64	-253.96	-3.97	
MoS_2 with a S-vacancy	-349.56	-247.79		2.20
MoS_2 with a Mo-vacancy	-361.51	-239.97		6.05

The calculation of atomization energy, bond energy and vacancy formation energy are referenced from previous study.[1]

Table S2 Analysis of Co bonding configuration

MoS_2 single sheet with isolated Co atom	Energy(eV)	Atomisation Energy (eV)	Bonding energy of Co atom (eV)	Vacancy Formation Energy (eV)
Co on S site	-360.11	-255.66	-1.26	
Co on Mo site	-361.80	-257.34	-3.38	
Co in hollow site	-361.51	-257.05	-3.10	
Co filled in S-vacancy	-355.70	-252.15	-4.36	-2.17

Table S3 Imaginary frequency information of the transition state.

Pathway	Location	Imaginary frequency/cm^{-1}				
		T1	**T2**	**T3**	**T4**	**T5**
DDS route	Co_{hollow}-MoS_2	604	290	1258		
	Co_{Mo}-MoS_2	595	295	1235		
	Co_{Vs}-MoS_2	739	267	1068		
PH pathway one	Co_{hollow}-MoS_2	604	183	233	777	
	Co_{Mo}-MoS_2	595	165	225	707	
	Co_{Vs}-MoS_2	739	757	242	732	
PH pathway two	Co_{hollow}-MoS_2	604	183	334	987	
	Co_{Mo}-MoS_2	595	165	264	1165	
	Co_{Vs}-MoS_2	739	757	276	1080	
FH pathway	Co_{hollow}-MoS_2	604	183	1014	803	1018
	Co_{Mo}-MoS_2	595	165	1298	1286	1069
	Co_{Vs}-MoS_2	739	757	1258	877	1104

References:

1. G. Liu, A. W. Robertson, M. M.-J. Li, W. C. H. Kuo, M. T. Darby, M. H. Muhieddine, Y.-C. Lin, K. Suenaga, M. Stamatakis, J. H. Warner, S. C. E. Tsang, *Nat. Chem.*, 2017, **9**, 810-816.