Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Identification of linear scaling relationships in polysulfide conversion on α-In_2Se_3 supported single-atom catalysts

Hui Wang, Lin Zou, Min Li, Long Zhang*

School of Physics and Electronics, Hunan Key Laboratory of Super Microstructure and Ultrafast Process, Hunan Key Laboratory of Nanophotonics and Devices, State Key Laboratory of Powder Metallurgy, Central South University, Changsha 410083, China

*E-mail: L.zhang@csu.edu.cn

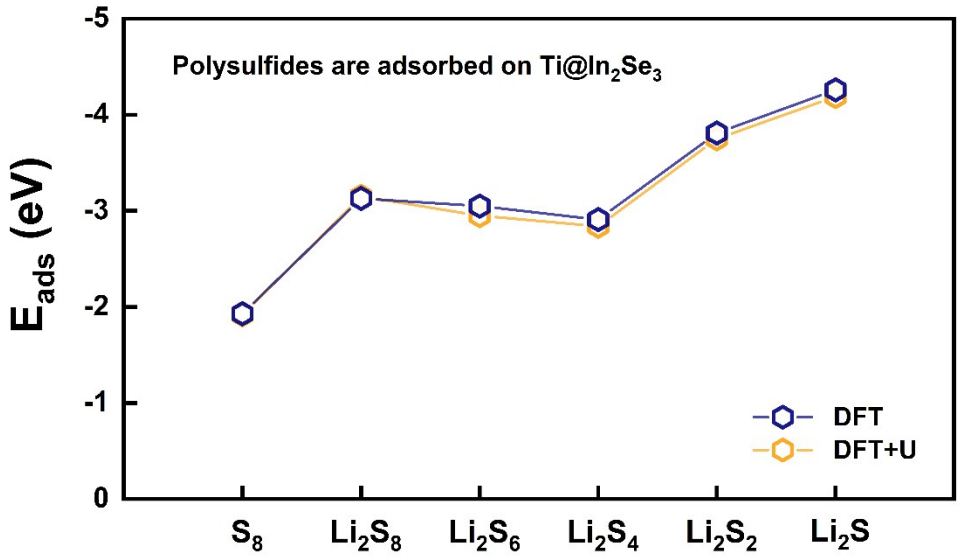

Fig. S1 Adsorption energies for Li_2S_n via DFT and DFT+U (U_{eff} = 2.58 eV).

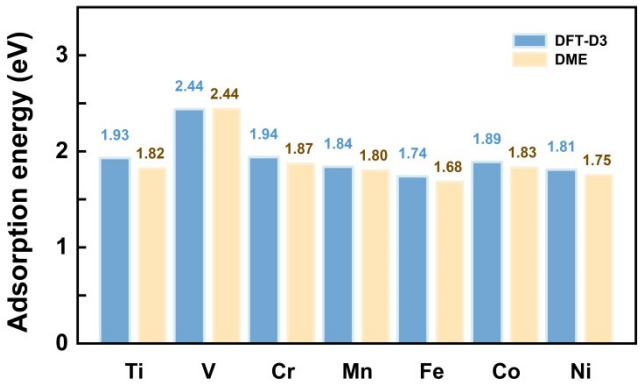

Fig. S2 Adsorption energies of S_8 with and without consideration of the effect of DME solvent.

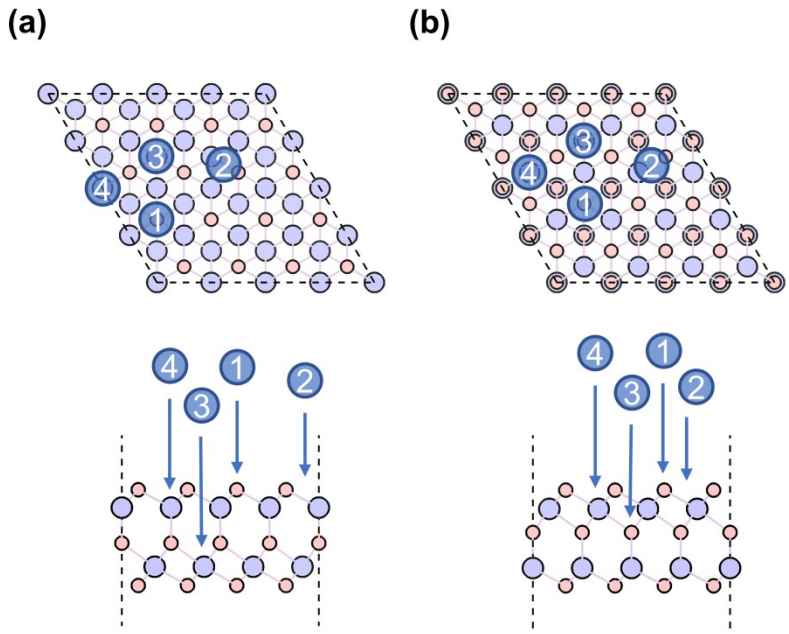

Fig. S3 Top and side views of (a) $P_{\uparrow}In_2Se_3$ and (b) $P_{\downarrow}In_2Se_3$ (color code: pink, Se; purple, In; blue, TM). Four different surface sites, namely, Se top site (site 1), bridge site (site 2), fcc hollow site (site 3), and hcp hollow site (site 4), are labeled.

Table S1 The values of U paramaters for DFT+U calculations (U in eV)

TM	Ti	V	Cr	Mn	Fe	Co	Ni
U	2.58	2.72	2.79	3.06	3.29	3.42	3.40

Table S2 Binding energies (E_b in eV) for TM atoms adsorbs on P ↓ In_2Se_3

catalysts	site 1	site 2	site 3	site 4
Ti@In_2Se_3	-4.98	-5.14	-5.84	-6.35
V@In_2Se_3	-2.43	-2.52	-4.85	-5.12
Cr@In_2Se_3	-1.94	-2.14	-3.17	-3.41
Mn@In_2Se_3	-2.44	-2.45	-3.76	-3.86
Fe@In_2Se_3	-2.20	-3.10	-4.14	-4.54
Co@In_2Se_3	-1.95	-1.91	-3.76	-4.28
Ni@In_2Se_3	-2.55	-2.33	-4.34	-4.73

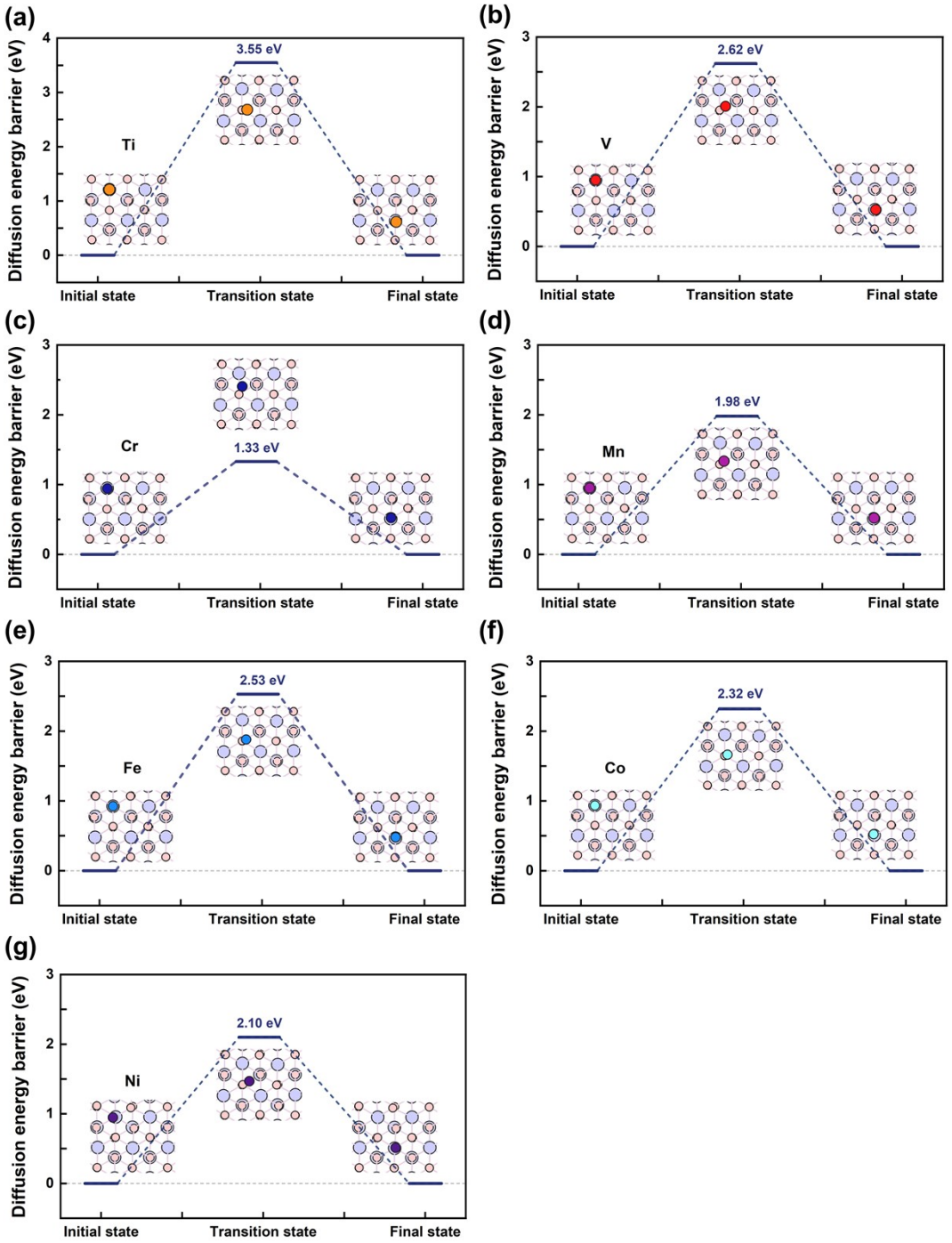

Fig. S4 Energy profile and corresponding structures for single TM atom diffusion on In_2Se_3 surface.

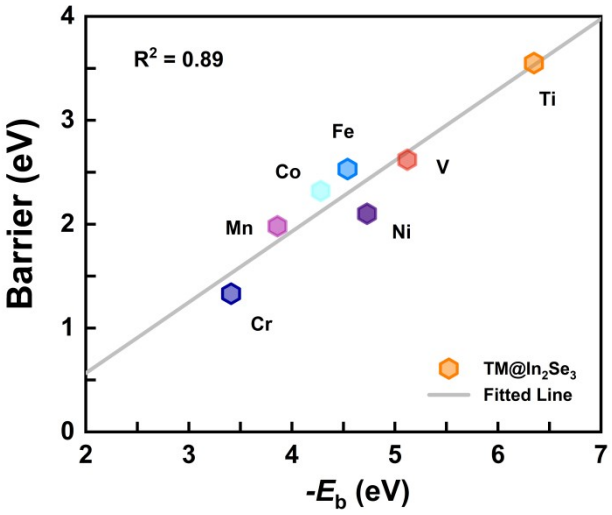

Fig. S5 Correlation between binding energies (E_b) and diffusion barriers (Barrier) for single TM atom absorbed on In_2Se_3.

Table S3 The binding energies (E_b in eV) and diffusion barrier (Barrier in eV) for single TM atom on In_2Se_3

TM	Ti	V	Cr	Mn	Fe	Co	Ni
E_b	-6.35	-5.12	-3.41	-3.86	-4.54	-4.28	-4.73
Barrier	3.55	2.62	1.33	1.98	2.53	2.32	2.10

Table S4 The average electrons transferred from the anchored TM atoms to the In_2Se_3 substrate (Q in e)

TM	Ti	V	Cr	Mn	Fe	Co	Ni
Q	0.88	0.62	0.54	0.63	0.47	0.30	0.03

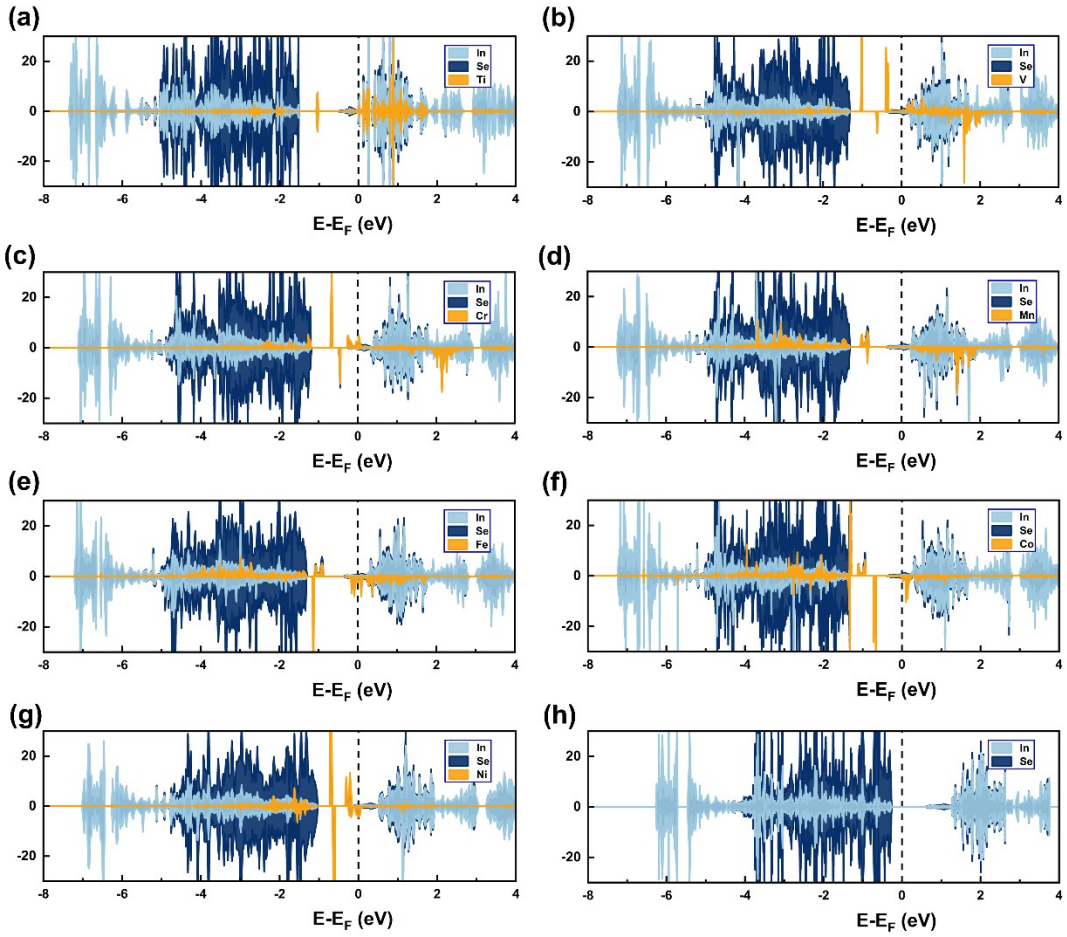

Fig. S6 Projected density of states (PDOS) of the TM@In_2Se_3. (a) Ti@In_2Se_3, (b) V@In_2Se_3, (c) Cr@In_2Se_3, (d) Mn@In_2Se_3, (e) Fe@In_2Se_3, (f) Co@In_2Se_3, (g) Ni@In_2Se_3, (h) In_2Se_3. The positive and negative values represent the spin-up and spin-down states, respectively. The Fermi level is set to 0 eV.

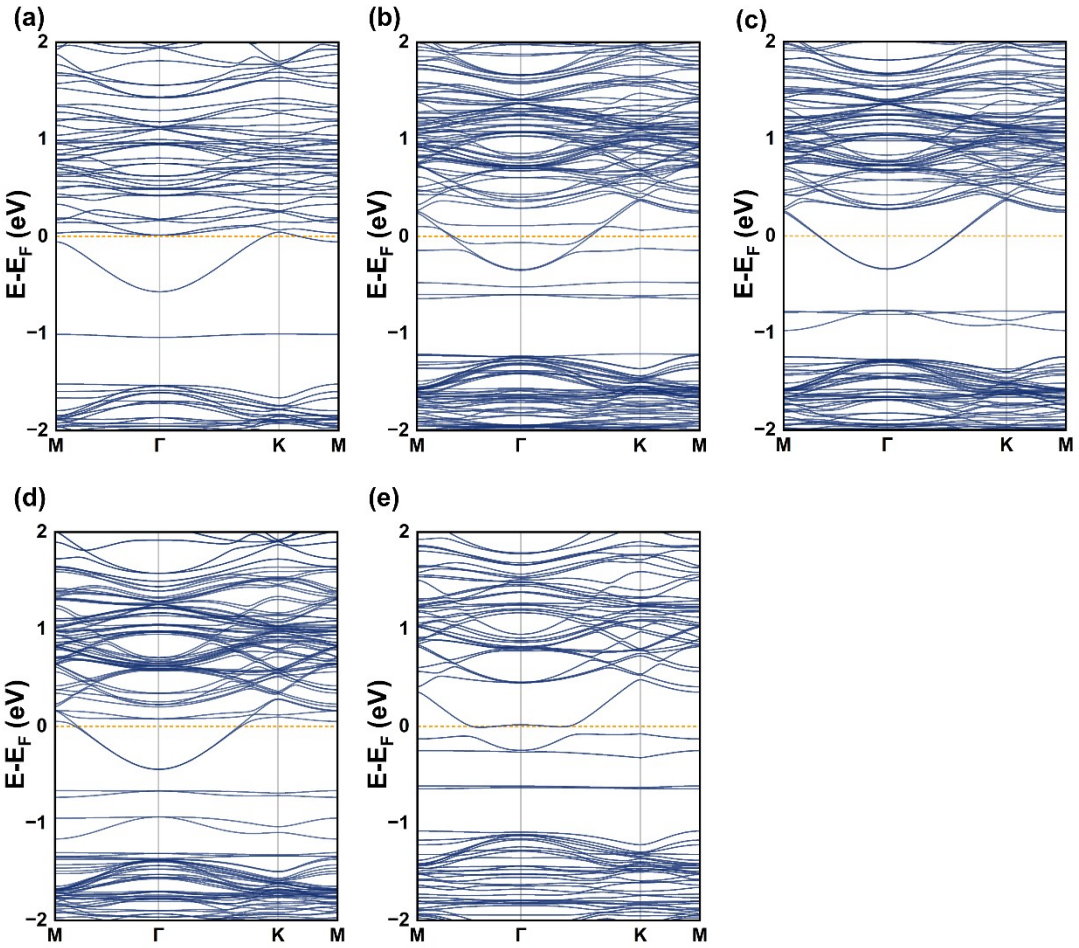

Fig. S7 Electronic band structures of TM@In_2Se_3. (a)-(e) Represent for Ti@In_2Se_3, Cr@In_2Se_3, Mn@In_2Se_3, Co@In_2Se_3 and Ni@In_2Se_3, respectively.

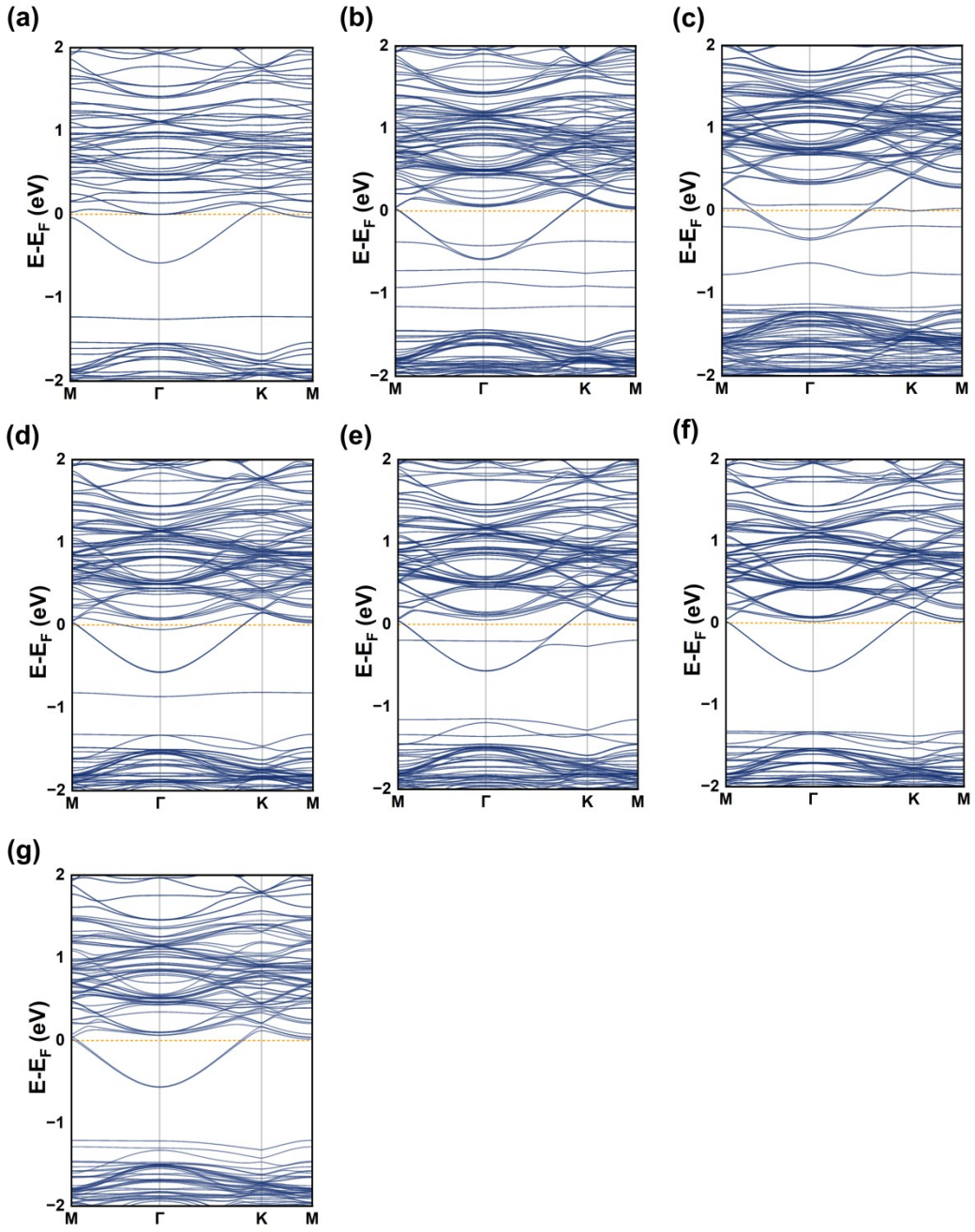

Fig. S8 Electronic band structures of TM@In_2Se_3 calculated by DFT+U. (a)-(g) Represent for Ti@In_2Se_3, V@In_2Se_3, Cr@In_2Se_3, Mn@In_2Se_3, Fe@In_2Se_3, Co@In_2Se_3 and Ni@In_2Se_3, respectively.

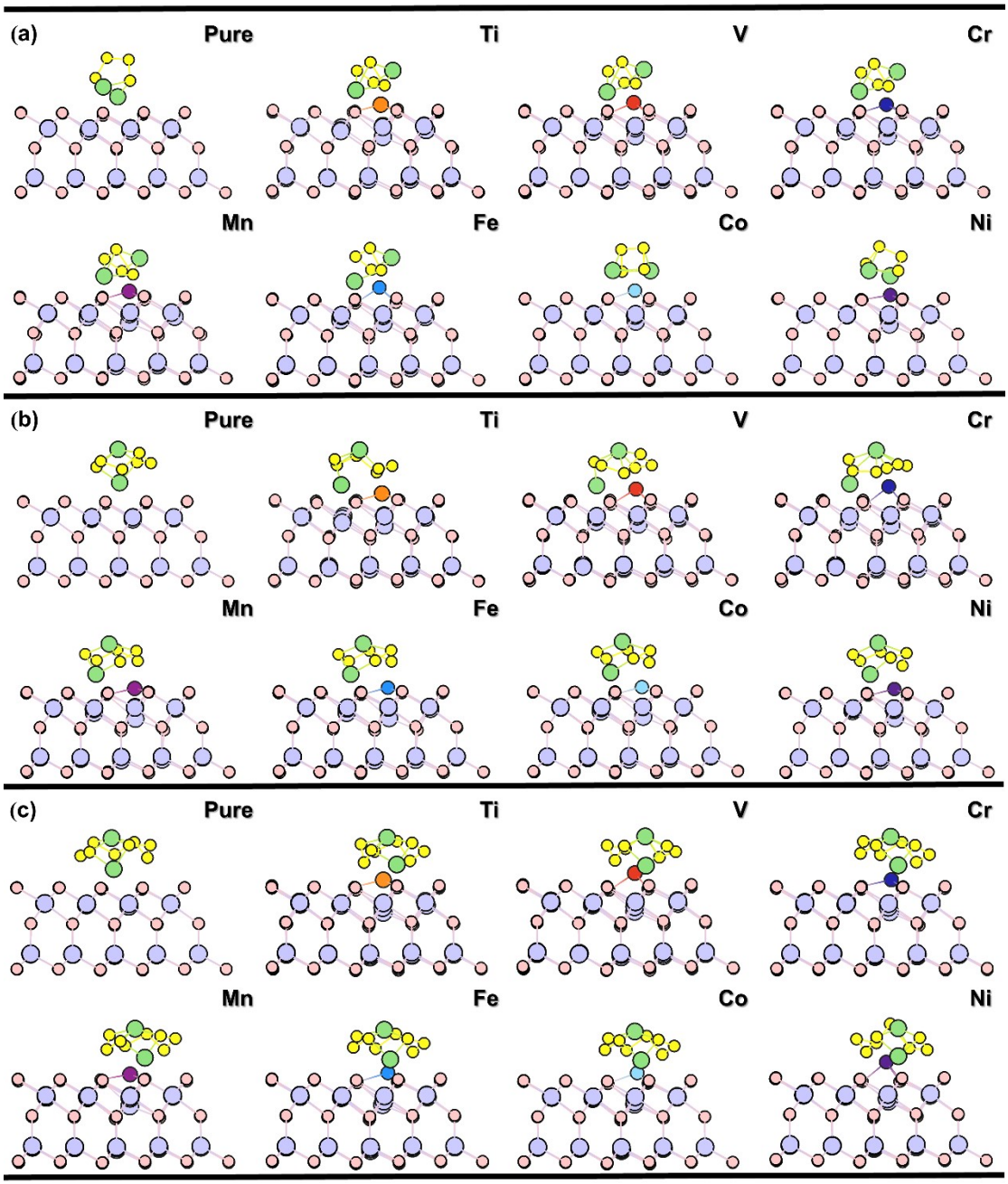

Fig. S9 Optimized adsorption structures: (a) Li_2S_4 adsorbs on In_2Se_3 and TM@In_2Se_3, (b) Li_2S_6 adsorbs on In_2Se_3 and TM@In_2Se_3, (c) Li_2S_8 adsorbs on In_2Se_3 and TM@In_2Se_3 (color code: pink, Se; purple, In; yellow, S; green, Li; other colors, TM)

Table S5 Adsorption energies for Li_2S_n on TM@In_2Se_3

E_{ads} (eV) / Catalyst	Li_2S	Li_2S_2	Li_2S_4	Li_2S_6	Li_2S_8	S_8
In_2Se_3	-3.3	-2.33	-1.69	-1.71	-2.19	-1.46
Ti@In_2Se_3	-4.26	-3.81	-2.91	-2.85	-3.13	-1.93
V@In_2Se_3	-4.36	-3.93	-3.12	-3.29	-3.64	-2.44
Cr@In_2Se_3	-4.19	-3.86	-2.81	-2.82	-3.13	-1.94
Mn@In_2Se_3	-3.74	-3.2	-2.32	-2.39	-2.79	-1.84
Fe@In_2Se_3	-3.53	-2.89	-2.23	-2.27	-2.63	-1.74
Co@In_2Se_3	-3.59	-3.19	-2.34	-2.37	-2.81	-1.89
Ni@In_2Se_3	-3.38	-2.87	-2.39	-2.29	-2.8	-1.81

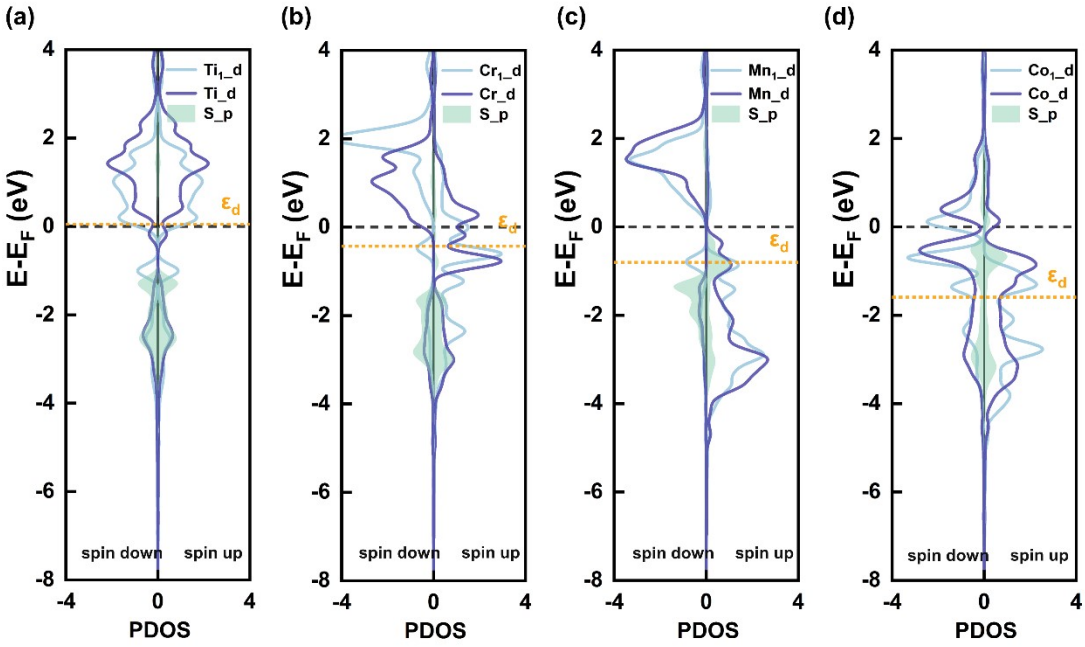

Fig. S10 (a)-(d) Projected density of states (PDOS) for Li_2S adsorbed on Ti@In_2Se_3, Cr@In_2Se_3, Mn@In_2Se_3, and Co@In_2Se_3, respectively.

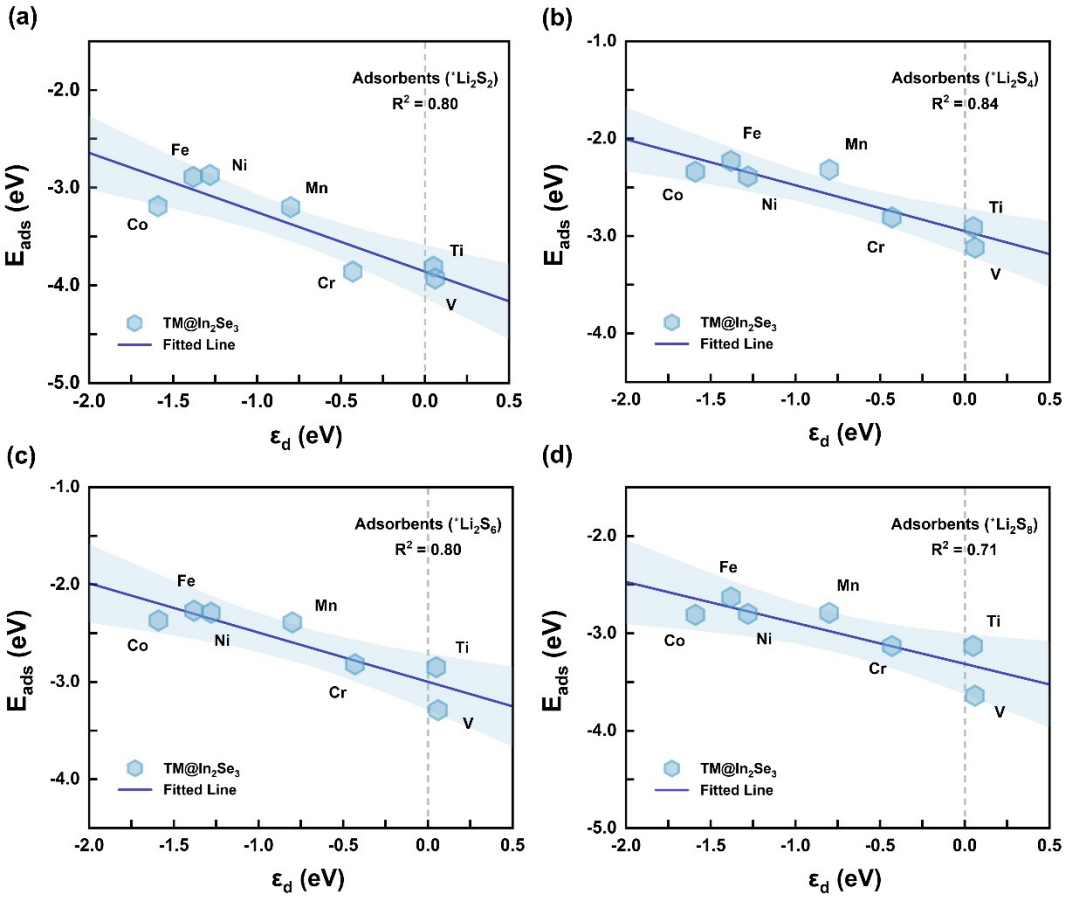

Fig. S11 (a)-(d) The correlation between ε_d of the adsorbed TM atoms and E_{ads} for Li_2S_2, Li_2S_4, Li_2S_6, and Li_2S_8 adsorption.

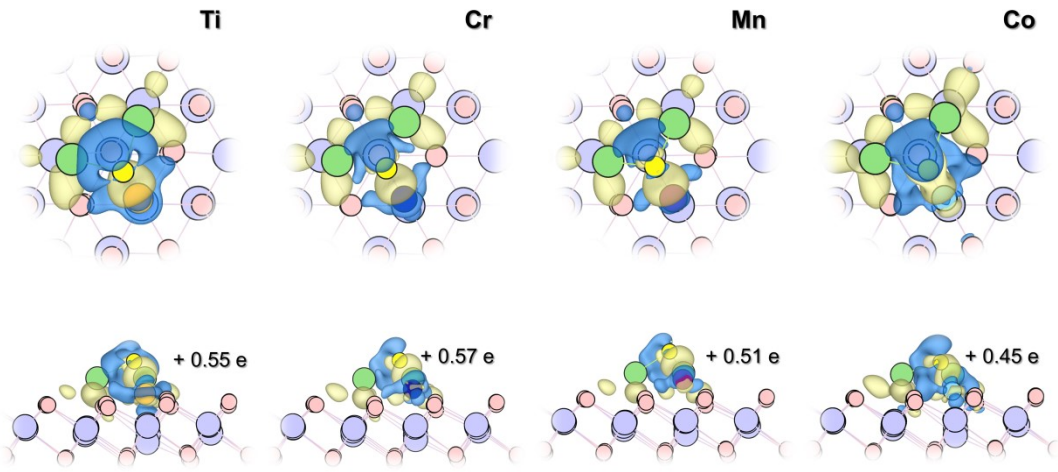

Fig. S12 Top view and side view of charge density differences for Li_2S adsorbed on $Ti@In_2Se_3$, $Cr@In_2Se_3$, $Mn@In_2Se_3$, and $Co@In_2Se_3$. Yellow and blue states represent the charge accumulation and loss, respectively. The isosurface is set to be 0.003 e/bohr^3. The amount of charge accumulated on S of the adsorbed Li_2S is presented.

Table S6 The average Li-S bond length ($d_{Li\text{-}S}$ in Å) and S-S bond length ($d_{S\text{-}S}$ in Å) for Li_2S_2 absorbed on In_2Se_3 and TM@In_2Se_3

TM	Pure	Ti	V	Cr	Mn	Fe	Co	Ni
$d_{Li\text{-}S}$	2.39	2.48	2.48	2.49	2.52	2.51	2.50	2.51
$d_{S\text{-}S}$	2.05	2.09	2.08	2.06	2.05	2.04	2.03	2.03

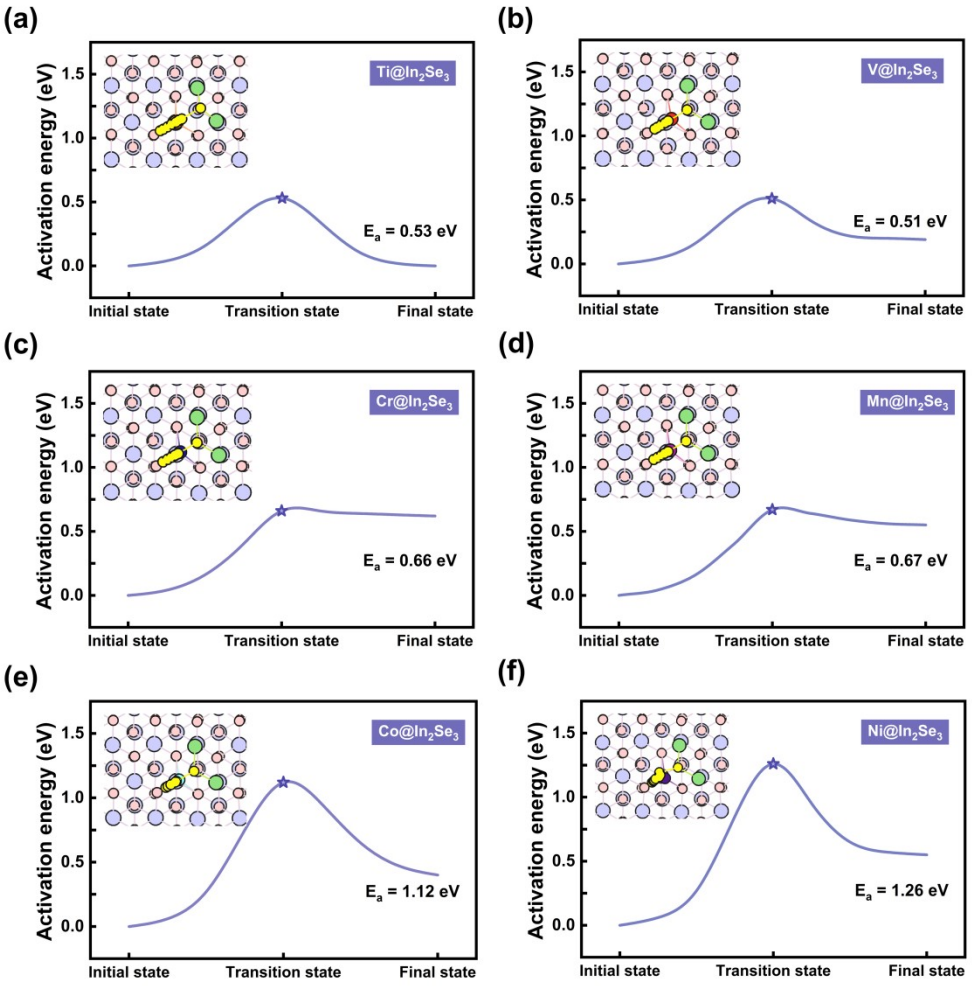

Fig. S13 (a)-(f) Energy profiles and corresponding structures for Li_2S_2 dissociation on $Ti@In_2Se_3$, $V@In_2Se_3$, $Cr@In_2Se_3$, $Mn@In_2Se_3$, $Co@In_2Se_3$, and $Ni@In_2Se_3$.

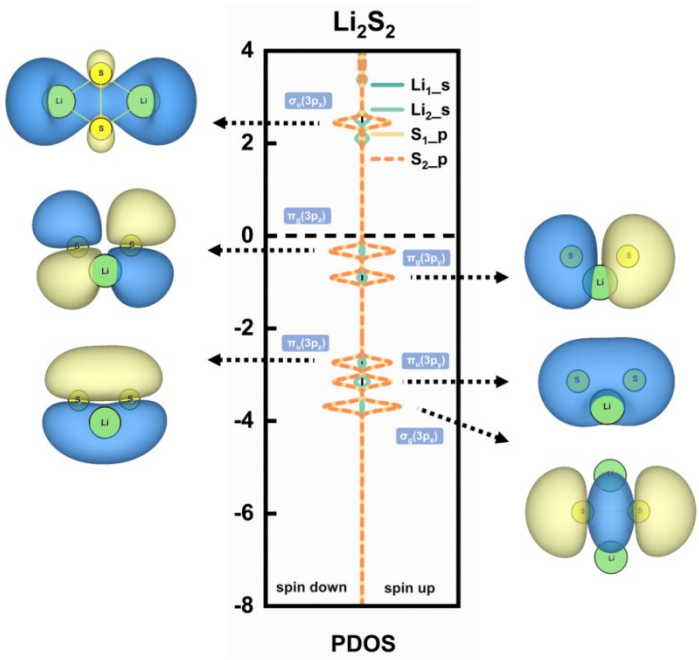

Fig. S14 Molecular orbitals of gas-phase Li_2S_2.

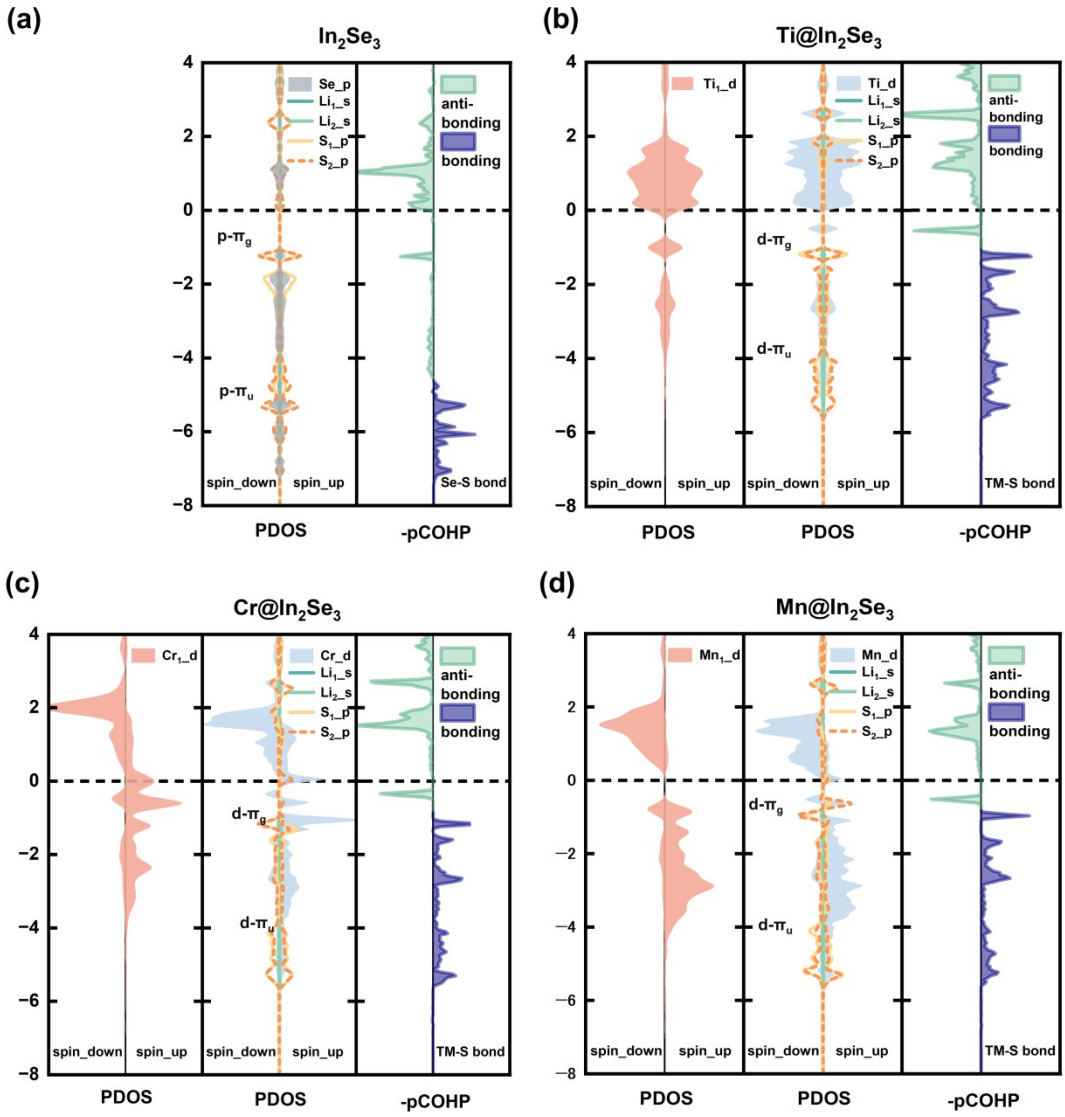

Fig. S15 Projected density of states (PDOS) and projected crystal orbital Hamilton population (pCOHP) for Li_2S_2 adsorbed on (a) In_2Se_3, (b) Ti@In_2Se_3, (c) Cr@In_2Se_3, (d) Mn@In_2Se_3.

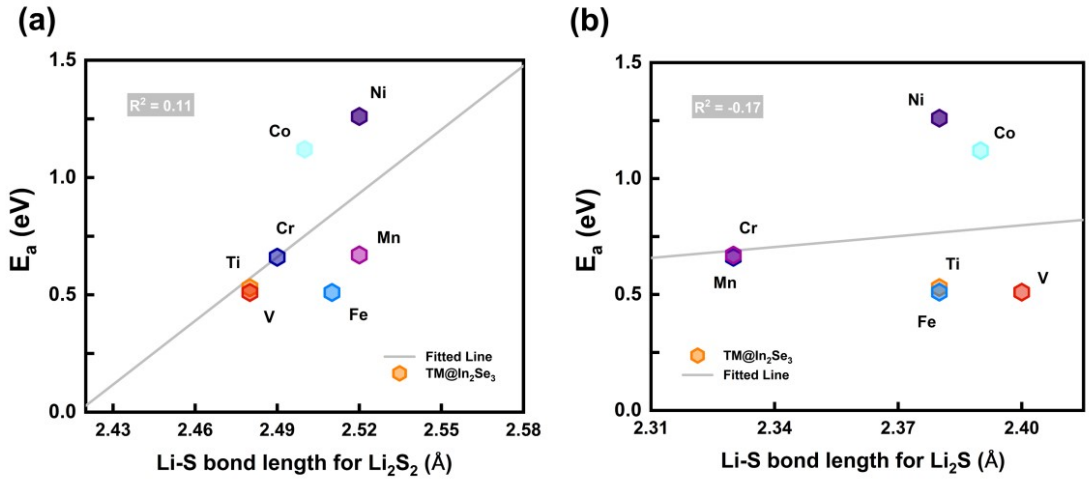

Fig. S16 Correlation between activation energy and Li-S bond length for (a) the adsorbed Li_2S_2 and the adsorbed Li_2S.