Supporting Information

Enhanced Activity of CoMoS Catalysts towards Hydrodesulfurization and Hydrogen Evolution Reaction via NaBH$_4$ Assisted Formation

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S1 Chemicals

Cobaltous nitrate hexahydrate(Co(NO$_3$)$_2$·6H$_2$O), ammonium molybdate tetrahydrate ((NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O), tetranap and thiocarbamide (CH$_4$N$_2$S)were purchased from Shanghai Macklin Biochemical CO.,Ltd. Sodium borohydride(NaBH$_4$) and n-Heptane (C$_7$H$_{16}$) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Deionized water (H$_2$O) was received from Beijing University of Chemical Technology. All chemical reagents were commercially available and used as received without further purification.

S2 Electrochemical Measurements

The Tafel slope for HER was calculated as follows:

$\log j = b + aE$

j : the current density(mA/cm_2);

b: the intercept;

E: the electrode potential(mV);

a: the Tafel slope(mV/dec)

S3 Formulas for the calculation of CoMoS and MoS2 content

$$[CoMoS](\%) = \frac{A_{CoMoS}}{A_{CoMoS} + A_{MoS2} + A_{Co2+}} \times 100 \quad (1)$$

$$[MoS2](\%) = \frac{A_{MoS2}}{A_{CoMoS} + A_{MoS2} + A_{Co2+}} \times 100 \quad (2)$$

where Ax represents the peak area of species x.

S4 Computational Details

In this research , a 4 × 4 molybdenum disulfide cycle model was established, and a 15Å vacuum layer was constructed in the Z-axis direction. The plane wave pseudo-method based on density functional theory is used to simulate the MoS2 periodic model with VASP calculation software. In the simulation, the generalized gradient approximation PBE functional is used as the exchange correlation energy. Within the MoS2 cell, all atoms except the edge atoms are fixed, while the edge atoms are set to complete relaxation. Taking 10^{-5}eV as the energy convergence accuracy of A single atom, and the upper limit of the interatomic interaction force is set to 0.02 eV/Å, the Monkhorst-Pack automatic generation method is set as the K-point sampling of Brillouin region integration, and performs electronic autonomous calculation on the K-point grid of 2x2x1. The plane wave truncation energy is set to 400 eV. The climbing image nudged elastic band method were employed to find the transition state. Then, Co atoms were used to replace 50% Mo atoms at the S-edge edge of MoS2 model, and the difference between HDS and HER of 1T and 2H crystal was calculated and compared.

According to this calculation model, the variation of Gibbs free energy of each step (ΔG) can be calculated from the following equation:

ΔG = ΔE + ΔZPE − TΔS

Where ΔE is the difference of electronic energy in ground-state obtained from

self-consistent calculation; ΔZPE is the difference of zero point energy; T is the temperature (T=298.15 K); ΔS is the difference of entropy; The entropies and vibrational frequencies of molecules in the gas phase were taken from the NIST database

Figure Captions

Figure. S1. (a)N_2 adsorption-desorption isothermal curve and (b) the pore size distribution curve of Co-Mo-S(NaBH4) and Co-Mo-S catalysts.

Figure S2. CV curve and double-layer capacitance test diagram. (a) Co-Mo-S CV curve; (b) double-layer capacitance curve with Co-Mo -S; (c) CV curve of Co-Mo-S(NaBH4); (d) curve of double-layer capacitance of Co-Mo-S(NaBH$_4$)

Figure S3. The conversion of Co-Mo-S(NaBH$_4$) and Co-Mo-S catalysts to thiophene at different reaction time.

Figure S4. (a) TEM images of Co-Mo-S catalysts after HDS testing. (b) TEM images of Co-Mo-S(NaBH4) catalysts after HDS testing. (c)HRTEM images of Co-Mo-S catalysts after HDS testing. (d)HRTEM images of Co-Mo-S(NaBH4) catalysts after HDS testing.

Figure S5. XRD patterns of Co-Mo-S and Co-Mo-S(NaBH4) catalysts after HDS testing.

Figure S6. Mechanism diagram of thiophene hydrodesulfurization reaction

Figure S7. Calculated structures of the intermediates in the DDS pathway at the S edge

Figure S8. Calculated structures of the intermediates in the HYD pathway at the S edge.

Figure S9. (a,d)The total density of states maps were calculated for the Co-doped 1t-MoS_2 and 2H-MoS_2 configurations, respectively; (b,e) Projected density of states maps of atomic orbitals of Mo and S elements;(c,f) Projected density of states maps of atomic orbitals of Co and S elements.

Table S1. pore parameters of the catalysts

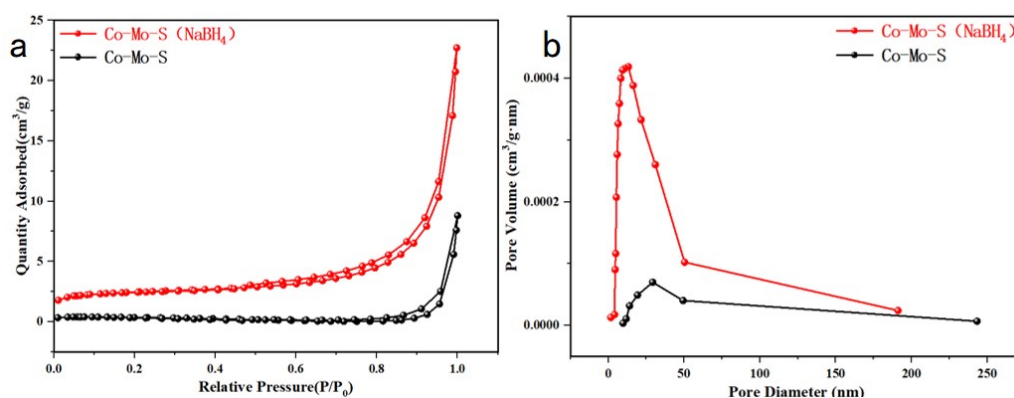**Table S2.** Content of Molybdenum Sulfide and CoMoS Active Phase in Catalyst

Figure. S1. (a)N_2 adsorption-desorption isothermal curve and (b) the pore size distribution curve of Co-Mo-S(NaBH$_4$) and Co-Mo-S catalysts.

Fig.S1 shows the N2 adsorption-desorption isotherms curve and pore size distribution of Co-Mo-S catalysts and Co-Mo-S (NaBH4) catalyst. As can be seen from Fig.S1a, they all exhibit type IV isotherms and H1 hysteresis loop, which proves that both the Co-Mo-S catalyst and the Co-Mo-S (NaBH4) catalyst have mesoporous structures, indicating that the incorporation of sodium borohydride does not change the mesoporous structure of the catalyst material. The specific surface areas, pore volumes and pore diameters of the support and catalysts were obtained by N2 sorption measurement and the results are summarized in Table S1. Fig.S1b shows that the pore size distribution peaks of the two catalysts are slightly different, and the center of the pore size of the catalyst modified by sodium borohydride is slightly reduced. Comparison of the catalyst before and after modification shows that the specific surface area of the catalyst modified by sodium borohydride is increased.Increasing the specific surface area can increase the contact between the reactants thiophene and the catalyst, thus facilitating the HDS reaction, which is one of the reasons for the improvement of Co-Mo-S (NaBH4) catalyst performance.
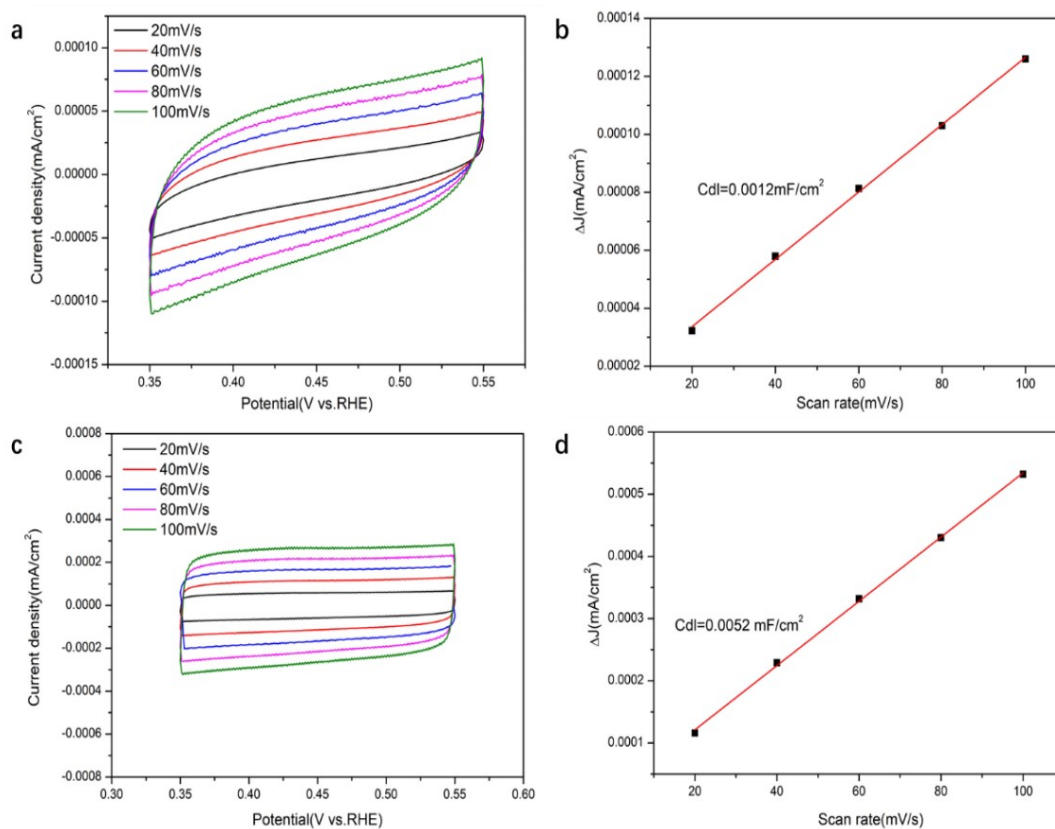
Figure S2. CV curve and double-layer capacitance test diagram. (a) Co-Mo-S CV curve; (b) double-layer capacitance curve with Co-Mo -S; (c) CV curve of Co-Mo-S(NaBH4); (d) curve of double-layer capacitance of Co-Mo-S(NaBH$_4$)
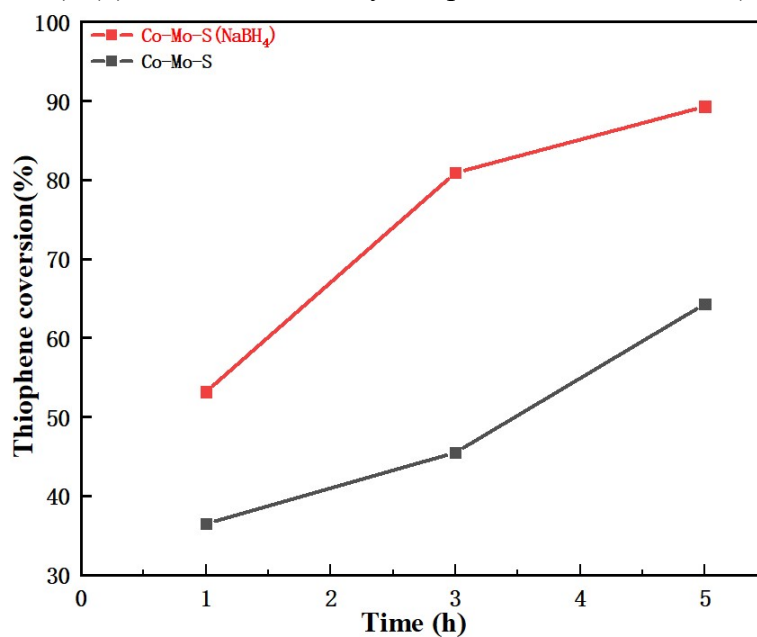

Figure S3. The conversion of Co-Mo-S(NaBH$_4$) and Co-Mo-S catalysts to thiophene at different reaction time.

Figure S4. (a) TEM images of Co-Mo-S catalysts after HDS testing. (b) TEM images of Co-Mo-S(NaBH4) catalysts after HDS testing. (c)HRTEM images of Co-Mo-S catalysts after HDS testing. (d)HRTEM images of Co-Mo-S(NaBH4) catalysts after HDS testing.
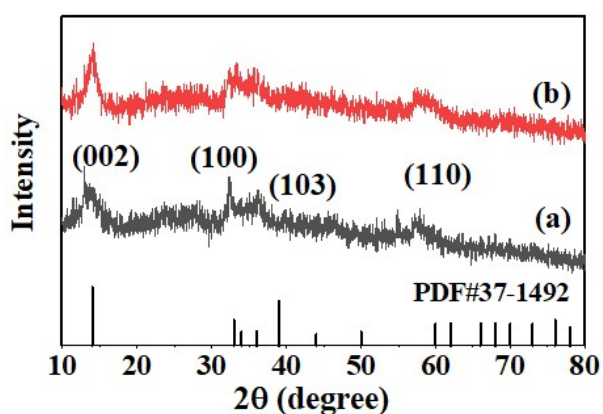

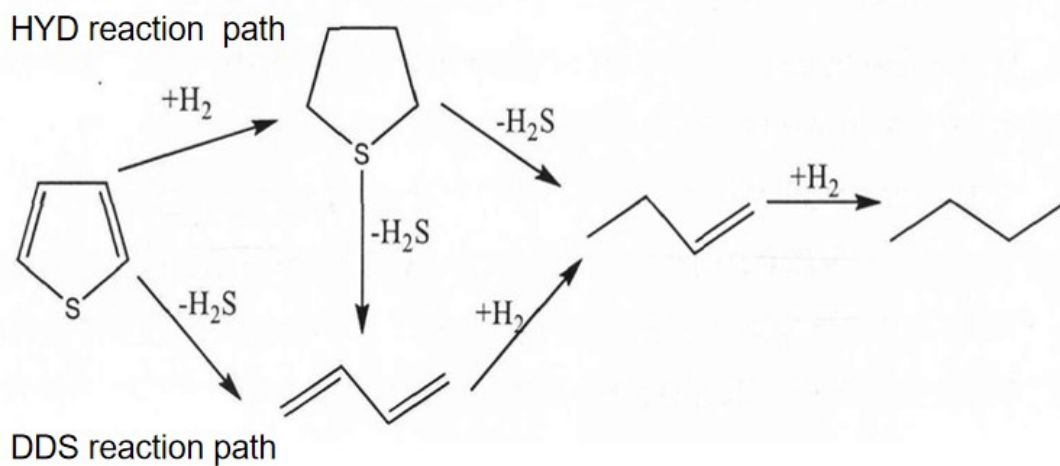**Figure S5.** XRD patterns of Co-Mo-S and Co-Mo-S(NaBH4) catalysts after HDS testing.

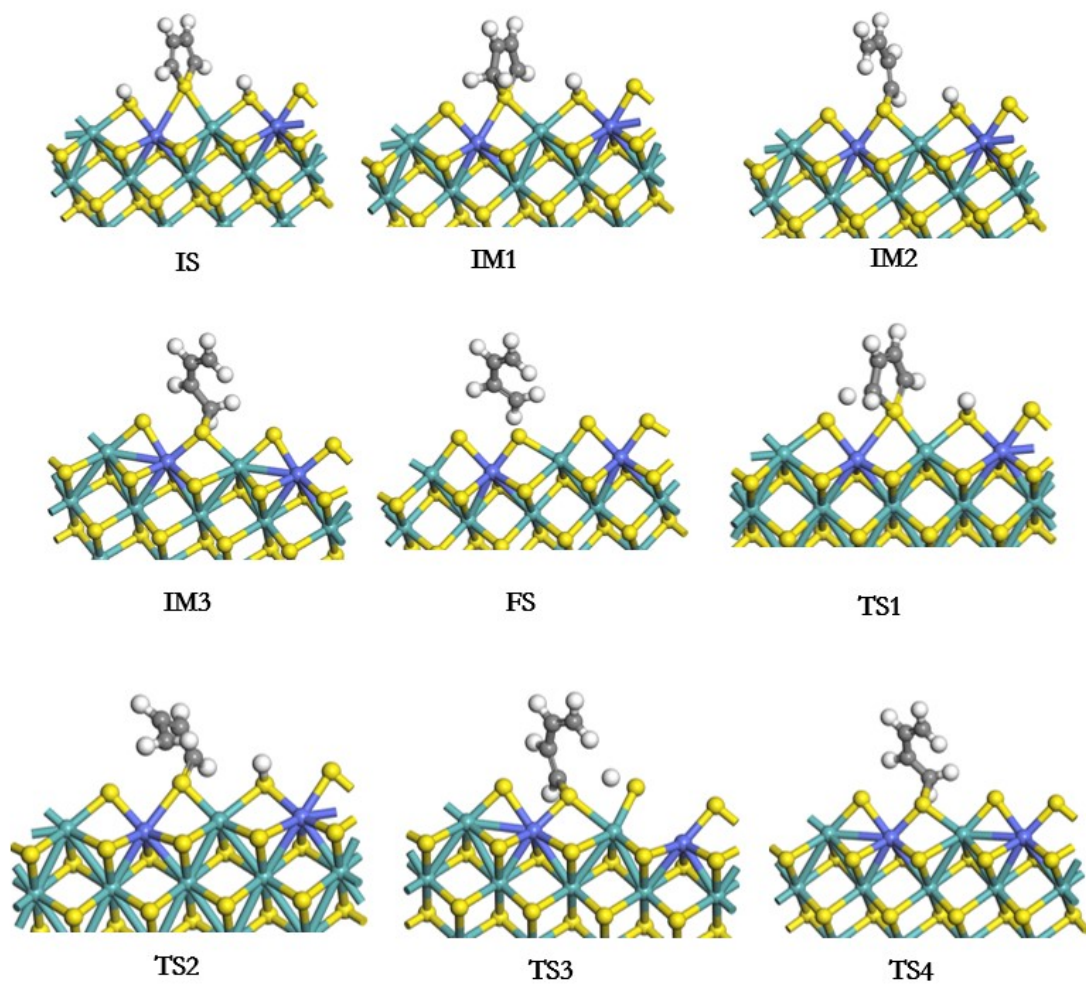**Figure S6.** Mechanism diagram of thiophene hydrodesulfurization reaction

Figure S7. Calculated structures of the intermediates in the DDS pathway at the S edge
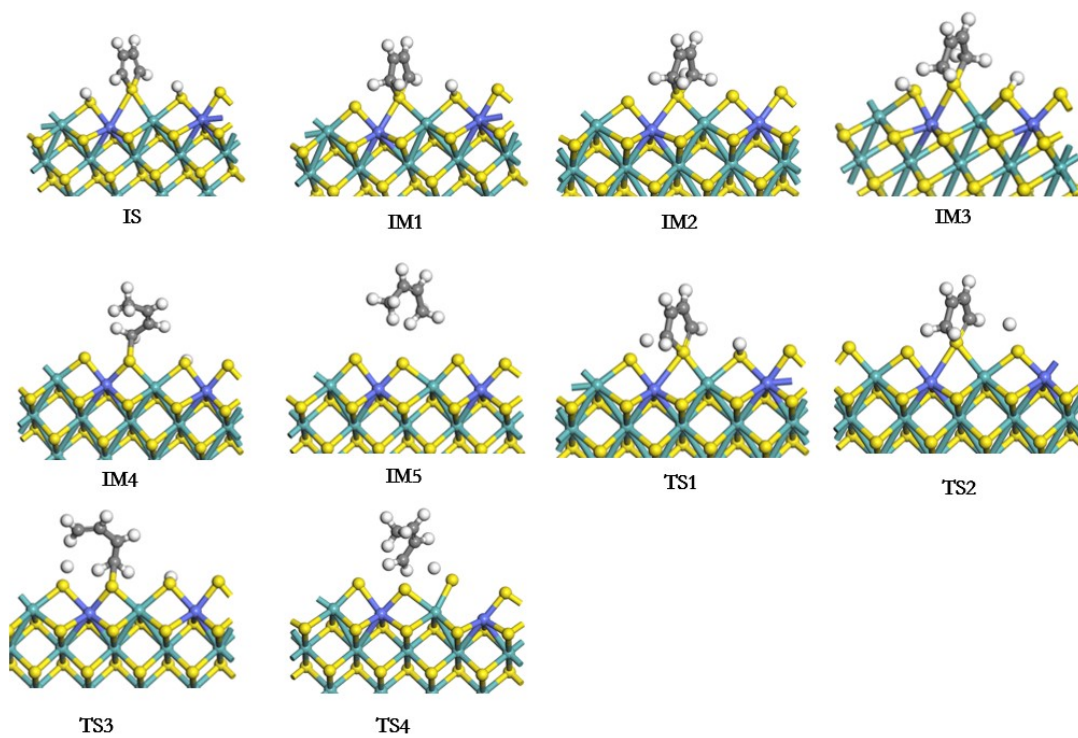
IS   IM1   IM2   IM3

IM4   IM5   TS1   TS2

TS3   TS4

Figure S8. Calculated structures of the intermediates in the HYD pathway at the S edge.
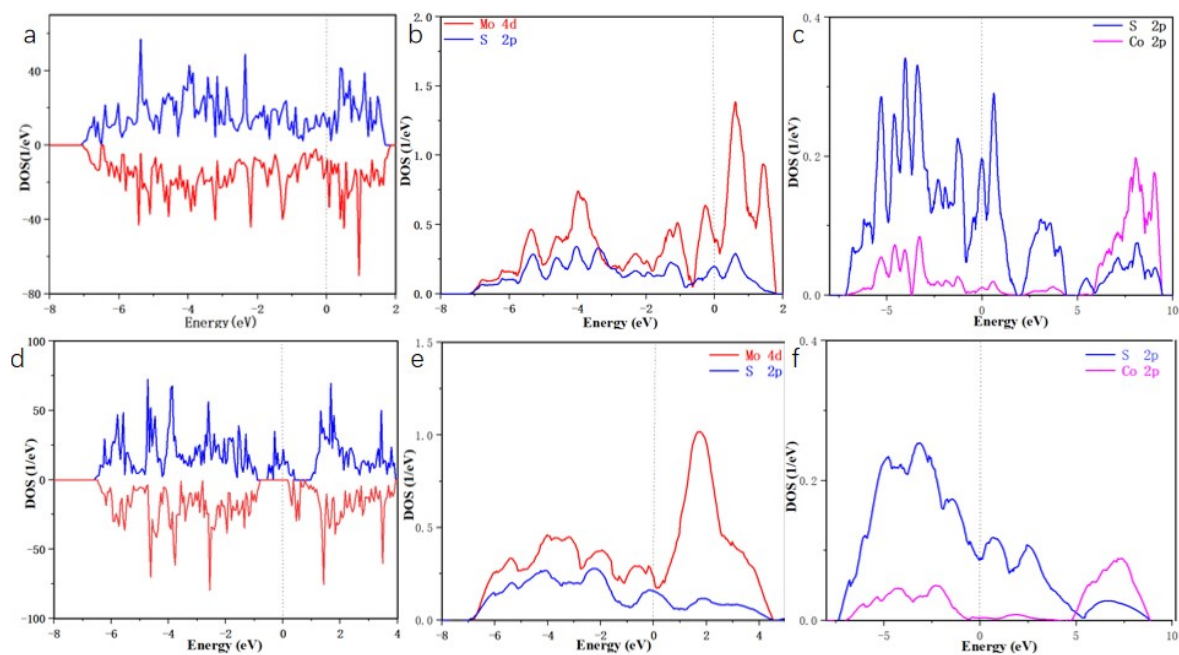
Figure S9. (a,d)The total density of states maps were calculated for the Co-doped 1t-MoS$_2$ and 2H-MoS$_2$ configurations, respectively; (b,e) Projected density of states maps of atomic orbitals of Mo and S elements;(c,f) Projected density of states maps of atomic orbitals of Co and S elements.

Table S1. pore parameters of the catalysts

Catalysts	SBET(m²/g)	Vmeso(cm³/g)	D(nm)
Co-Mo-S	1.214	0.0118	38.73
Co-Mo-S(NaBH₄)	8.668	0.0352	16.22

Table S2. Content of Molybdenum Sulfide and CoMoS Active Phase in Catalyst

Catalysts	C_{MoS2}（wt %）	C_{CoMoS} (wt %)
Co-Mo-S	33.3	22
Co-Mo-S(NaBH₄)	40.4	19

(The content was calculated based on XPS data, and the calculation method is listed in S3.)