

Supporting Information
Carbonization of Ethylenediamine Co-impregnated
CoMo/Al₂O₃ Catalysts Sulfided by Organic Sulfiding Agent

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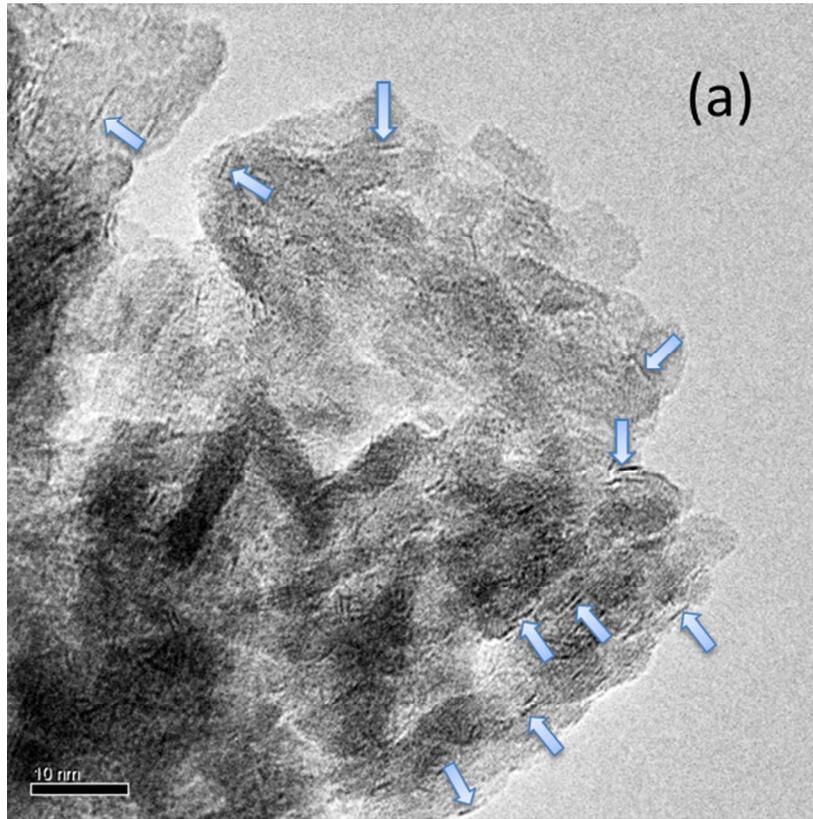
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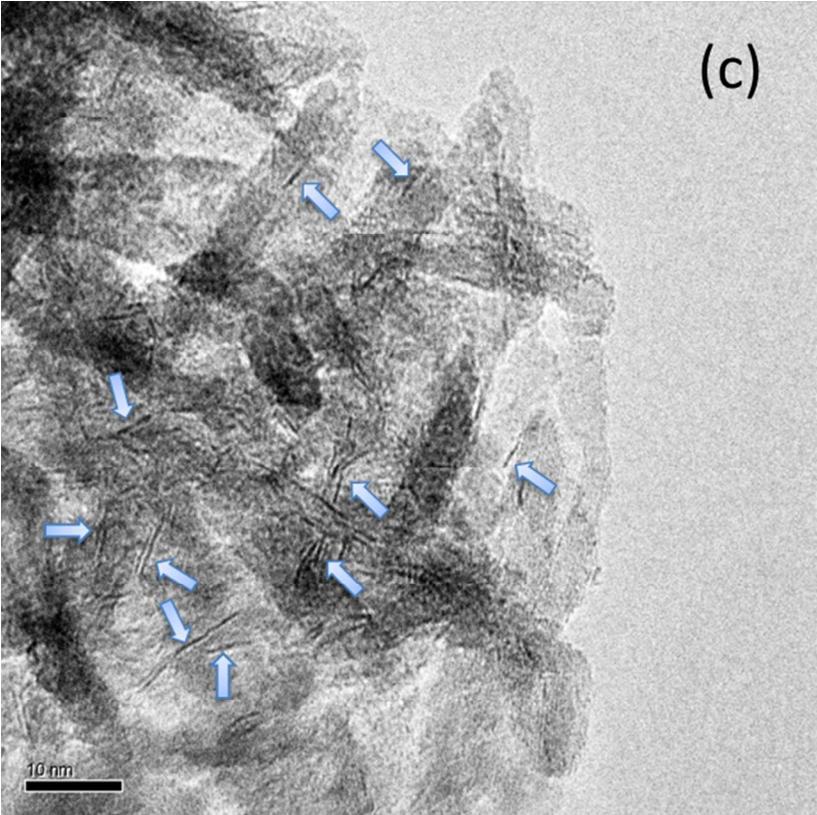
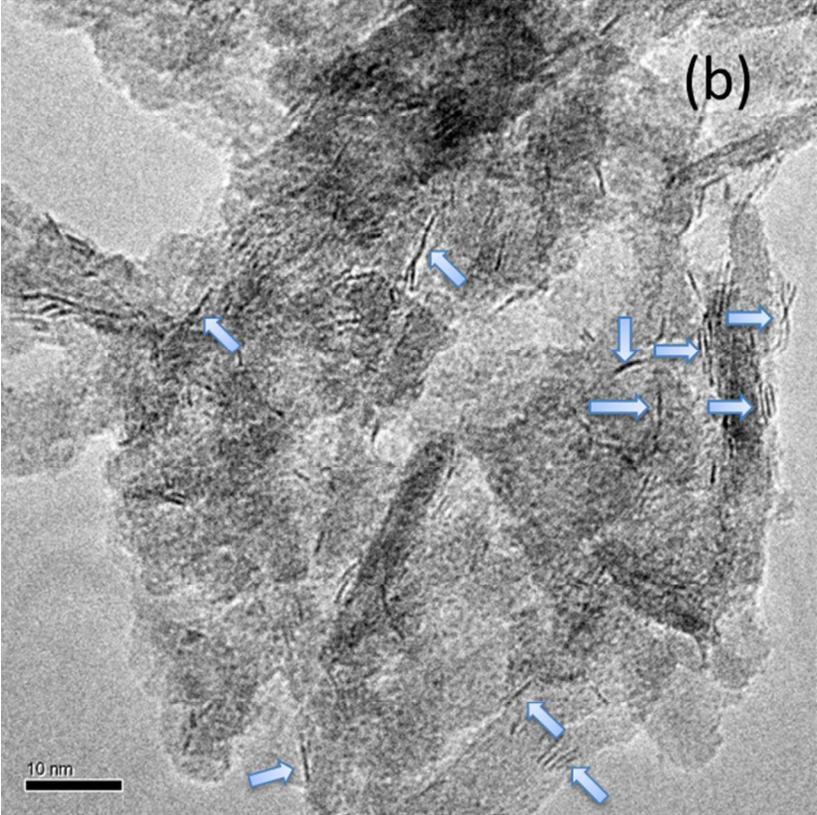
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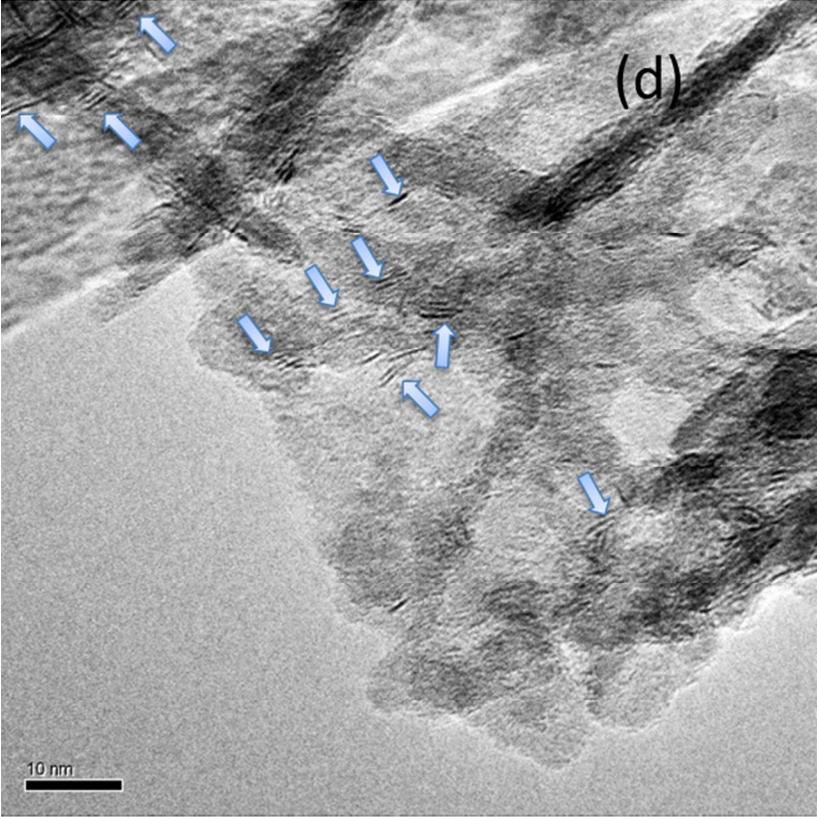
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A. Supplementary Figures







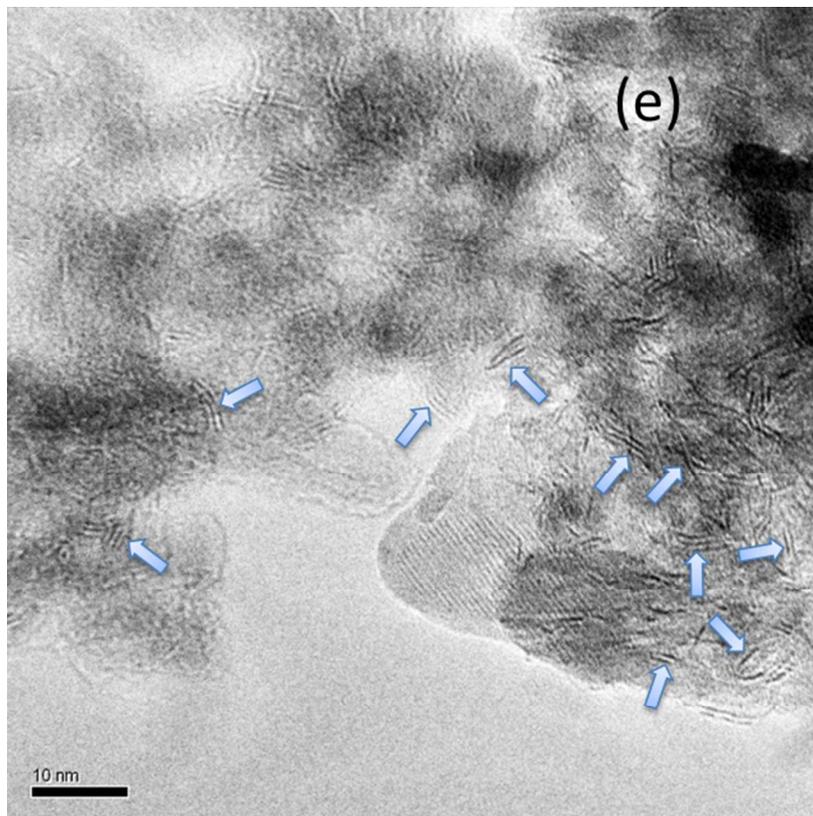


Figure S1. HRTEM images of spent catalysts

Sulfidation by thiophene: (a) CoMo; (b) CoMo(En1); (c) CoMo(En2)

Sulfidation by DMDS: (d) CoMo; (e) CoMo(En1). The arrows point to the (Co)MoS_x(C) slabs.

B. Extended DFT Results and Discussion

B.1. Carburization at S edge with 100% Mo atoms substituted by Co promoters

The formula for the carburization of the Co-Mo₈S_x periodic models are expressed in Eq S1, using atomic carbon and sulfur as references. The relative energy ΔE of the carburization is calculated by Eq S2. Negative value of ΔE represents the thermodynamically favored.



$$\Delta E = [E(\text{Co-Mo}_8\text{S}_{x-n}\text{C}_n) + nE(\text{S})] - [E(\text{Co-Mo}_8\text{S}_x) + nE(\text{C})] \quad (\text{S2})$$

Figure S2, S3 and S4 show the carburization process of S edge with 100%, 75% and 50% sulfur coverage respectively, where all the Mo atoms at S edge are substituted by Co atoms. It can be seen, except for the carburization process from 9 to 10 with a positive value of 0.24 eV, all other carburizations have the negative values of ΔE , illustrating that for 100% Co substituted S edge, the sulfur atoms are favored to be replaced by carbon atoms. Table 1S lists the influence of sulfur coverage on the carbon replacement. It shows that the average relative energy (av. ΔE) of carburization becomes more negative with increasing sulfur coverage. The absolute av. ΔE for 100% sulfur coverage is significantly higher than that of 75% sulfur coverage, meanwhile 75% sulfur coverage shows marginally higher absolute av. ΔE than 50% sulfur coverage. We deduce that the increase of sulfur coverage leads to the spatial repulsion between sulfur atoms increase. When the sulfur atoms are replaced by carbon atoms, the repulsive interactions are weakened owing to the smaller atomic volume of carbon atoms. Therefore, the carburization becomes more favorable for high sulfur coverage at S edge. Actually we have tried to explain this energetic difference between carburization and sulfidation using the bonding energies, but it is hardly to find the related experimental data for Mo-S bond. Further, based on the Pauling's rule for estimating bond energies,¹ The estimated Mo-S bond energy is around 433 kJ/mol. The Mo-C bond energy is 481±15.9 kJ/mol from the available experimental

data.² One can know that the estimated Mo-S bond energy is much lower than the Mo-C values. This gives a qualitative comparison that Mo-C bond is stronger than Mo-S bond, and therefore the formation of Mo-C bonds is energetically more favored than Mo-S bond.

Table S1. The influence of sulfur coverage at sulfur edge with 100% Mo atoms substituted by Co promoters on the reaction energy ΔE of carburization

Percentage of sulfur coverage	Number of substituted sulfur atoms	Total ΔE (eV)	Average ΔE^a (eV)
100%	4	-12.40	-3.10
75%	3	-4.46	-1.49
50%	2	-2.89	-1.45

^a The average relative energy of one sulfur atom substituted by carbon atom

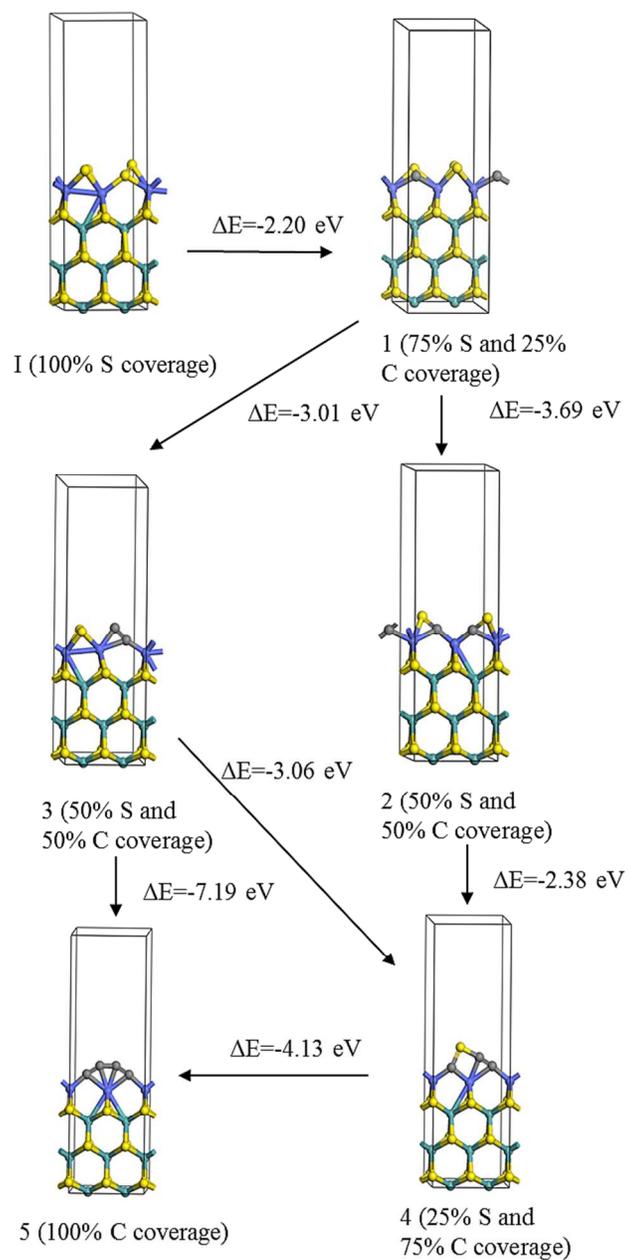


Figure S2. Carburization on S edge with 100% sulfur coverage and 100 % Mo atoms substituted by Co promoters

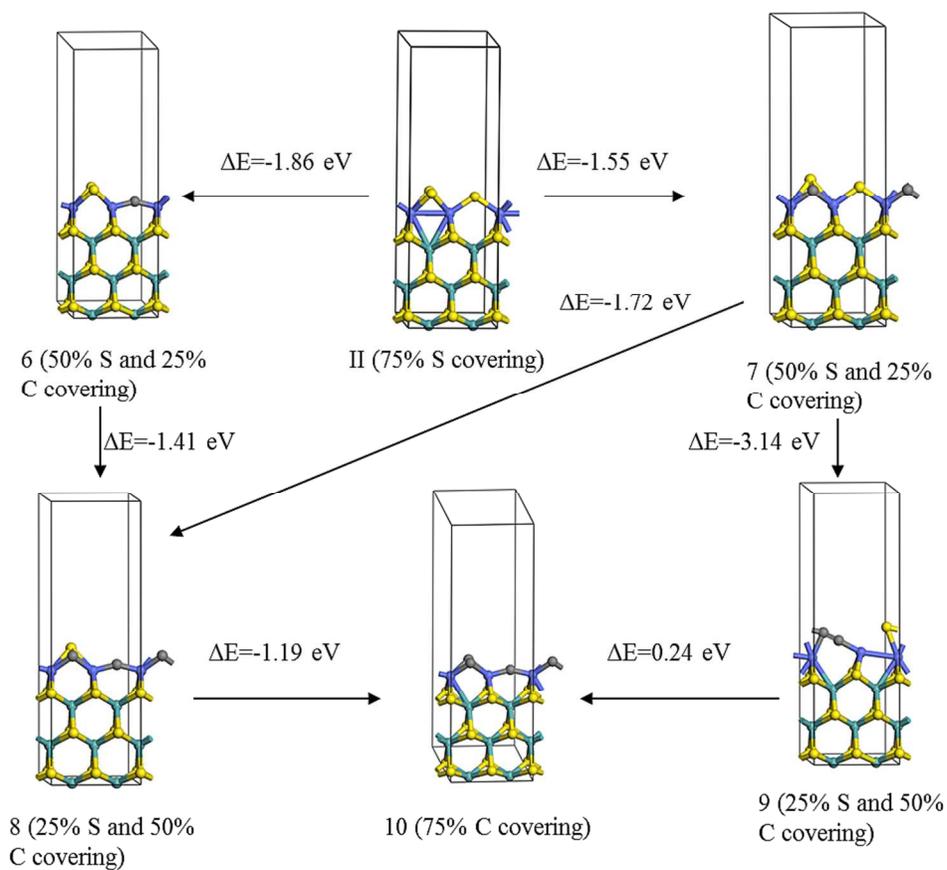


Figure S3. Carburization on S edge with 75% sulfur coverage and 100 % Mo atoms substituted by Co promoters.

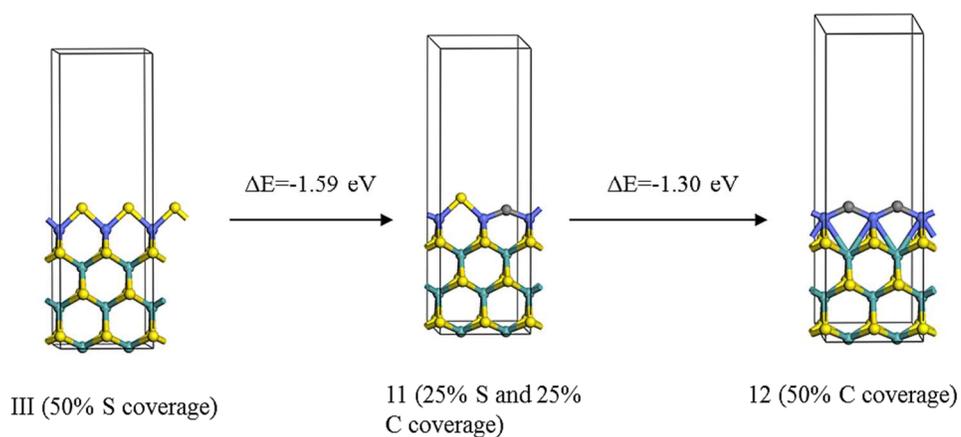


Figure S4. Carburization on S edge with 50% sulfur coverage and 100 % Mo atoms substituted by Co promoters

B.2. Carburization at S and Mo edges with 50% Mo atoms substituted by Co promoters

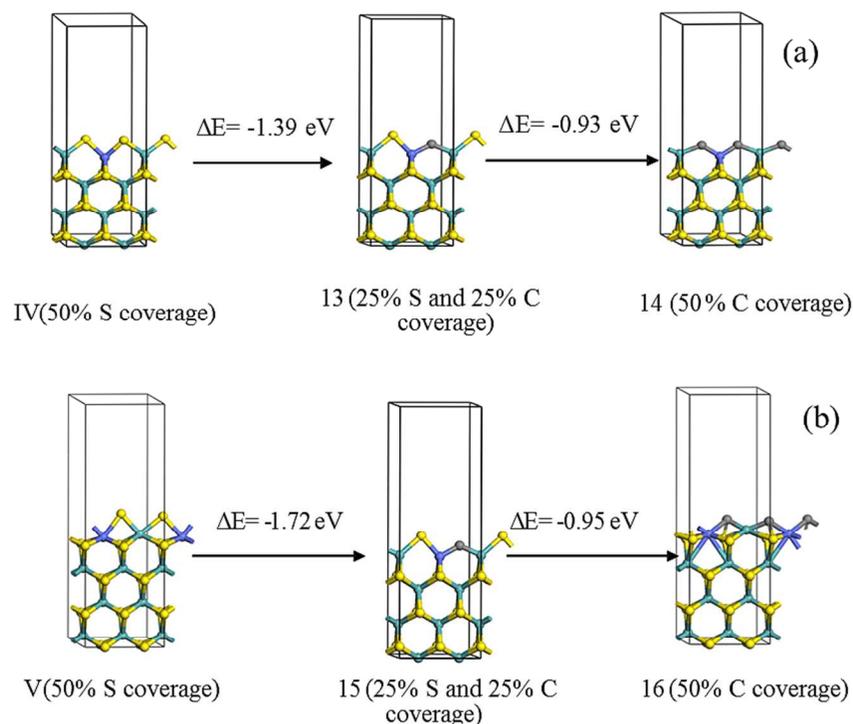


Figure S5. Carburization on S and Mo edge with 50% sulfur coverage and 50% Mo atoms substituted by Co promoters; (a) S edge, (b) Mo edge.

For comparing the carburization differences between S edge and Mo edge, the carburization process are investigated on S and Mo edges both with 50% sulfur coverage and 50% Mo atoms substituted by Co promoters. Figure S5 lists the reaction energies for the carburizations. The av. ΔE at Mo edge is more negative than at S edge, indicating that carburization at Mo edge is more favored. However the difference of av. ΔE is only -0.18 eV. In this situation, the carburization is expected to present simultaneously on the Mo and S edge. Compared with the S edge with 100% Mo atoms substituted by Co atoms (Figure S4), the total substituted S edge is easier to be carburized than the partly

substituted S edge, suggesting that the Co-promoter facilitates the carburization.

B.3. The carburization at Mo edge without Co substitution

The carburization at no-substituted Mo edge with 0-50% sulfur coverage is also investigated. The reactions are shown in Eq S3 and S5. The relative energies change of sulfidation and CUS formation are calculated according to Eq S4 and S6 respectively. Figure S6 shows the sulfidation, CUS formation and carburization at no-substituted Mo edge; the addition of S atom (VI to VIII) to bared Mo edge releases the energy of 2.94 eV, and the CUS formation (VII to VIII) consumes the energy of 0.83 eV.



$$\Delta E = [E(\text{MoS}_{x+n}) + nE(\text{H}_2)] - [E(\text{MoS}_x) + nE(\text{H}_2\text{S})] \quad (\text{S4})$$



$$\Delta E = [E(\text{MoS}_{x-n}) + nE(\text{H}_2\text{S})] - [E(\text{MoS}_x) + nE(\text{H}_2)] \quad (\text{S6})$$

As for 50% sulfur coverage, the ΔE of first S atom substituted by C atom is -0.69 eV, and the ΔE increases to -1.03 eV for second carbon substitution. The result indicates that partly carbon substituted Mo edge is easier to be carburized, which is consistent with carburization at the sulfur edge with 100% Co substitution. For 25% sulfur coverage, the ΔE of S atom substituted by C atom is -0.77 eV. However the ΔE increases to -3.71 eV when carburization appears on the naked Mo edge (VII to 19), indicating that to directly deposit carbon atoms is a more favored process.

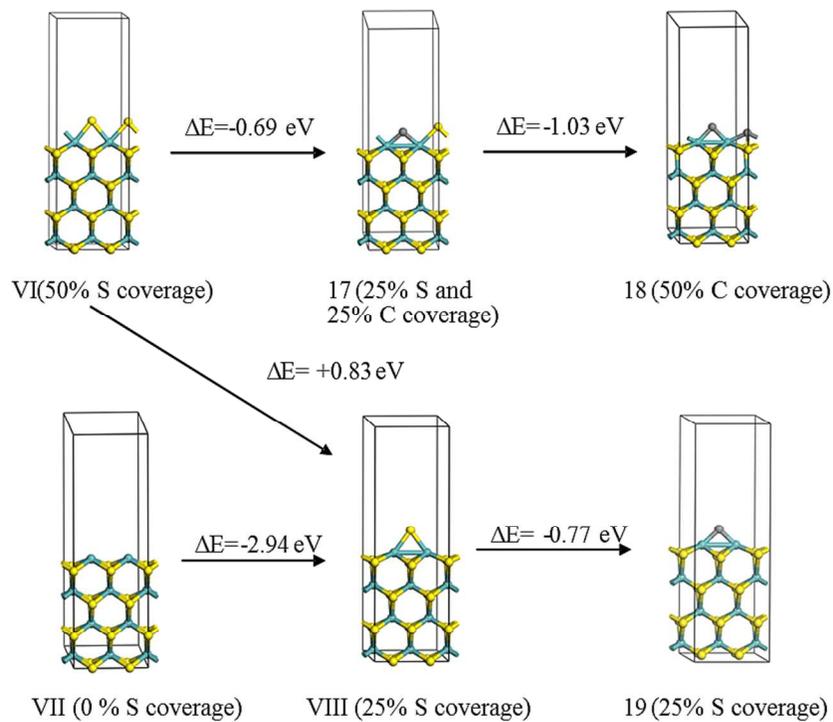


Figure S6. Carburization on Mo edge with different sulfur coverage.

C. Supplementary references

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- (1) Pauling, L. *The Nature of the Chemical bond and the Structure of Molecules and Crystals*; Cornell University Press, 1960; p 92.
 - (2) Lide, D. R. *Handbook of Chemistry and Physics*, 84th ed.; CRC Press, 2004, P9-56.