Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary Information: CH_4 and H_2S reforming to CH_3SH and H_2catalyzed by metal promoted Mo_6S_8 cluster: a first-principles micro-kinetic study

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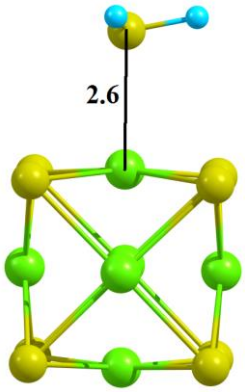
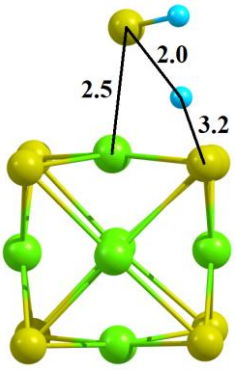
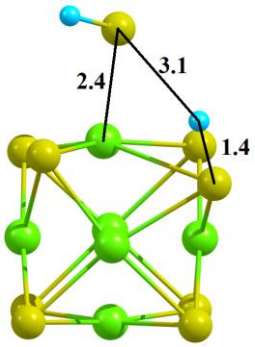
Figure S1. Structures adsorbed on Mo_6S_8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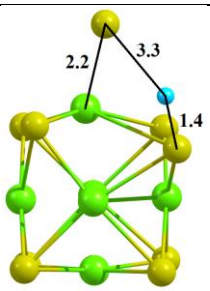	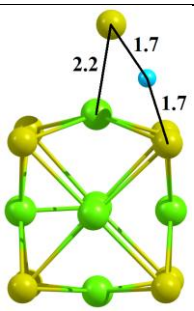	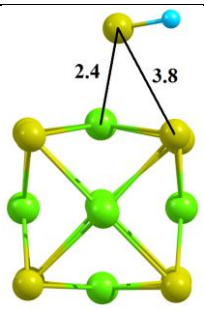
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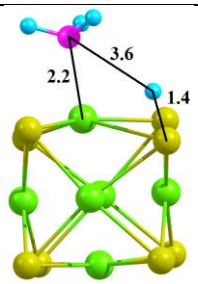	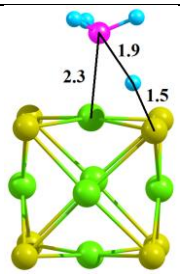	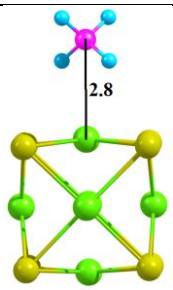
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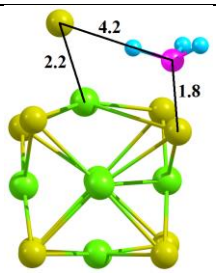	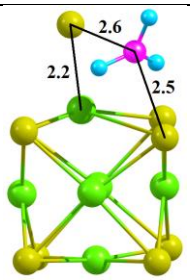	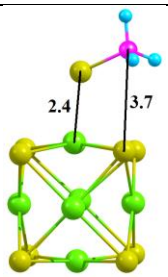
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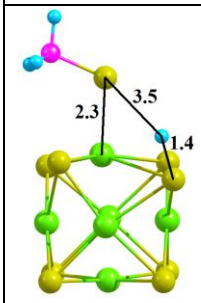	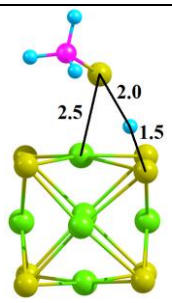	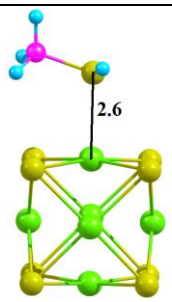
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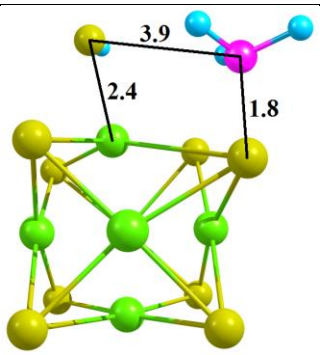	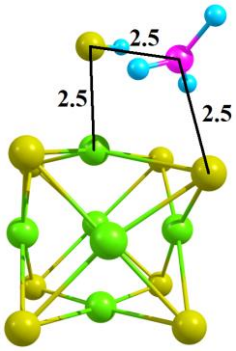	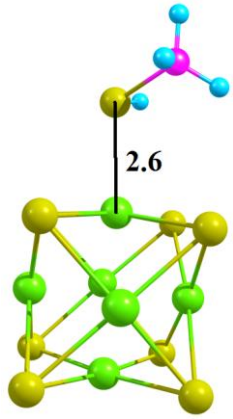
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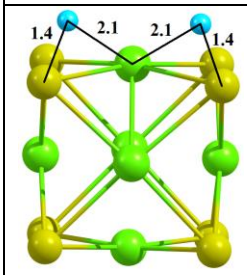	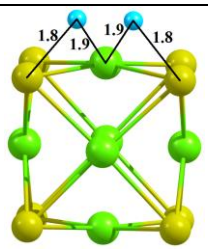	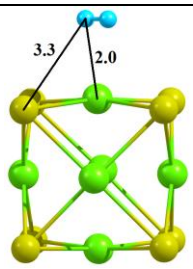
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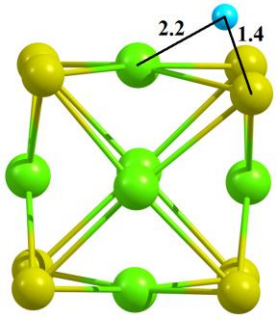
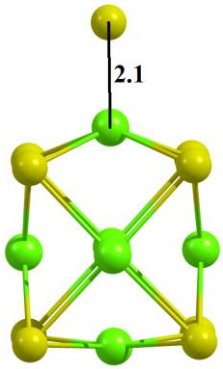
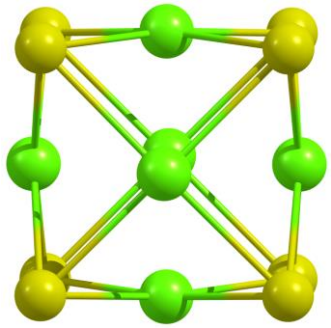
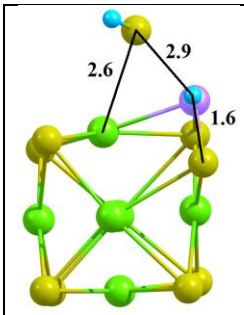
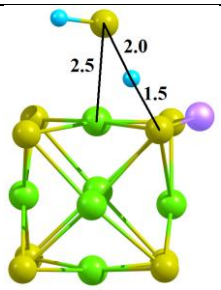
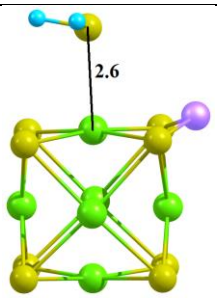
		
H*	S*	*

Figure S2. Structures adsorbed on $NiMo_6S_8$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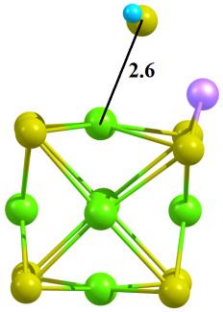
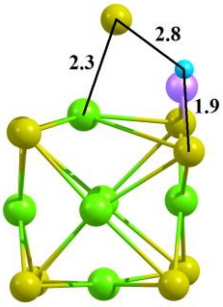
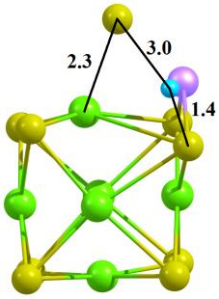
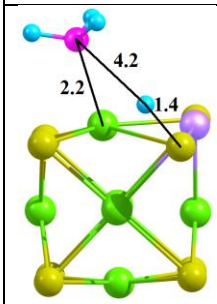
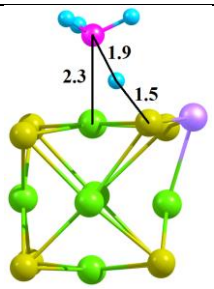
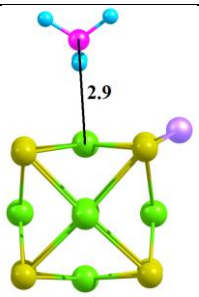
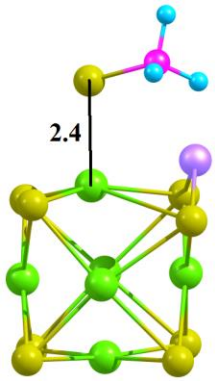
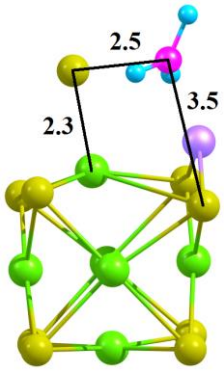
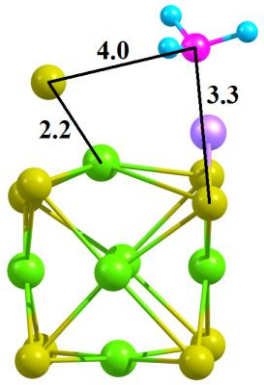
		
H_S_TS-m [*,SH*]	H_S_TS-ts	H_S_TS-p [S*,H*]
		
CH3_H_TS-m [H*,CH3*]	CH3_H_TS-ts	CH3_H_TS-p [*,CH4*]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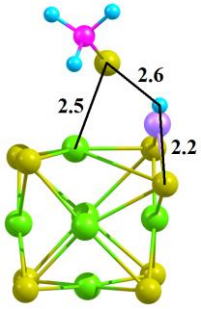	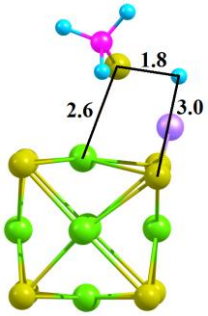	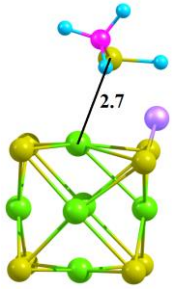
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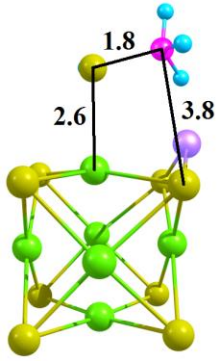
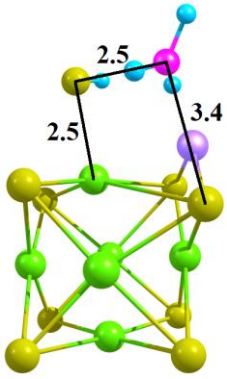
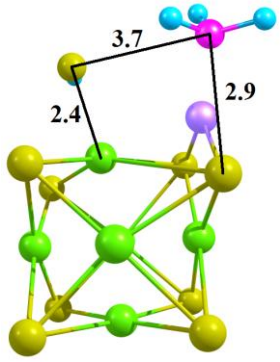
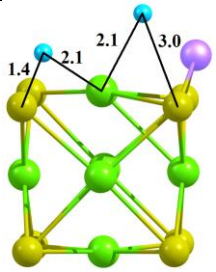
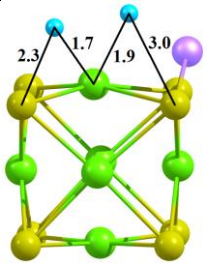
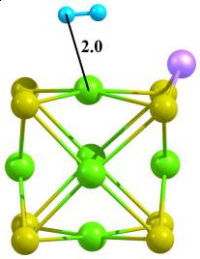
		
CH3_SH_TS-m [*,CH3SH*]	CH3_SH_TS-ts	CH3_SH_TS-p [CH3*,SH*]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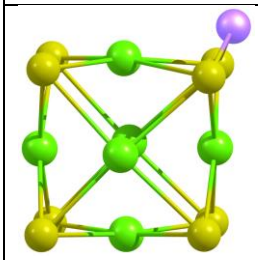
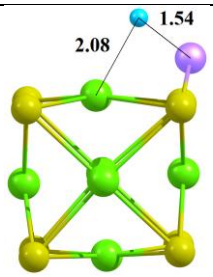
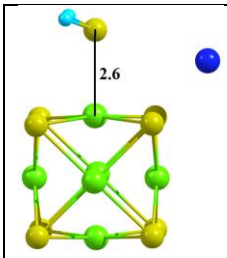
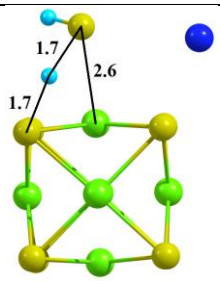
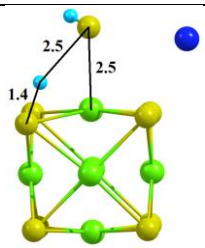
		
*	H*	

Figure S3. Structures adsorbed on KMo_6S_8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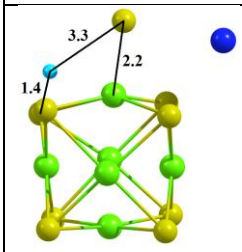
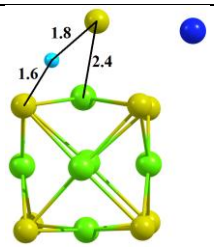
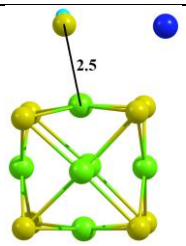
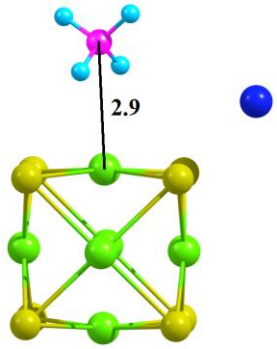
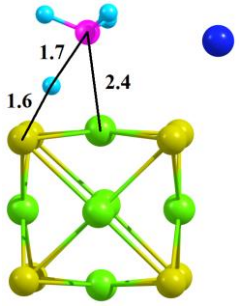
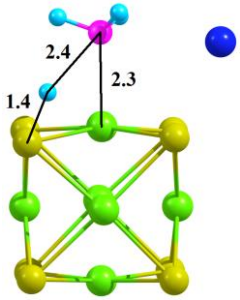
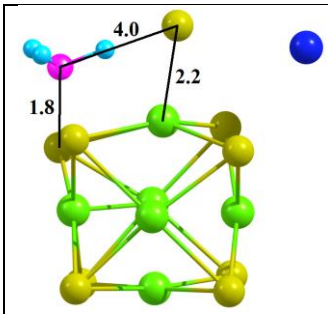
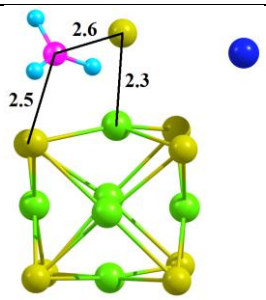
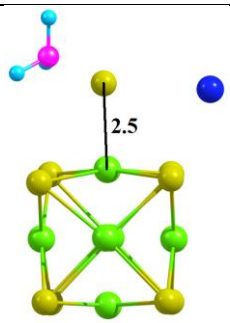
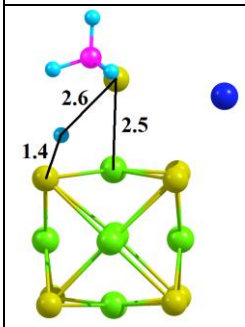
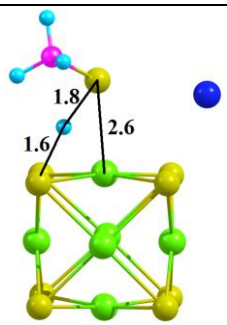
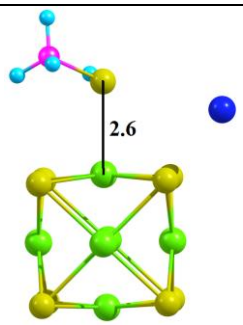
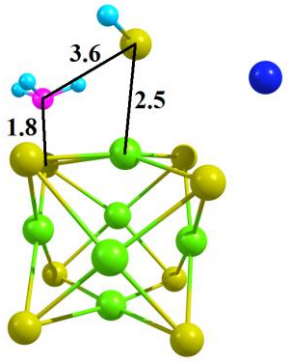
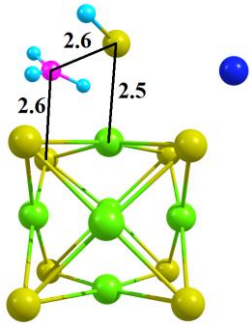
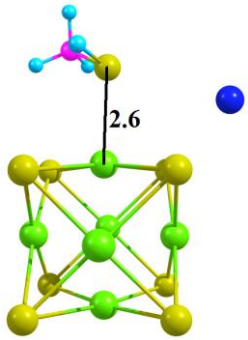
		
H_S_TS-m [H*,S*]	H_S_TS-ts	H_S_TS-p [*,SH*]
		
CH3_H_TS-m [*,CH4*]	CH3_H_TS-ts	CH3_H_TS-p [H*,CH3*]

		
CH3_S_TS-m [CH3*,S*]	CH3_S_TS-ts	CH3_S_TS-p [*,CH3S*]
		
CH3S_H_TS-m [H*,CH3S*]	CH3S_H_TS-ts	CH3S_H_TS-p [*,CH3SH*]
		
CH3_SH-TS-m [CH3*,SH*]	CH3_SH-TS-ts	CH3_SH-TS-p [*,CH3SH*]

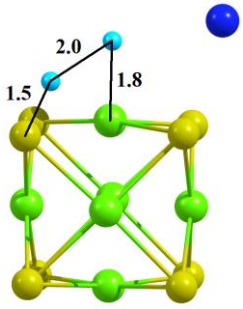
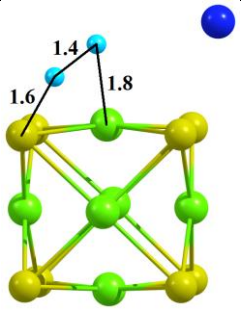
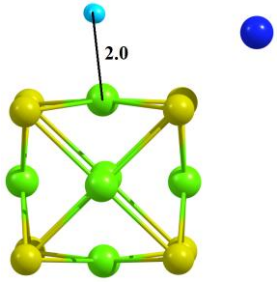
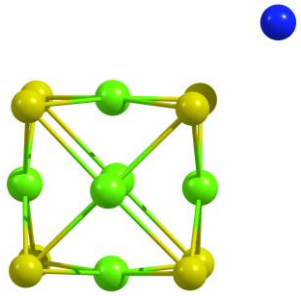
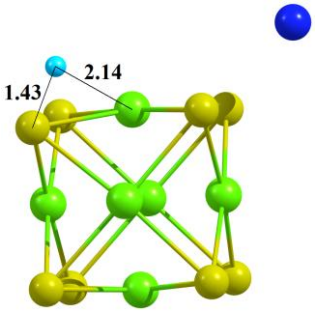
		
H_H_TS-m [H*,H*]	H_H_TS-ts	H_H_TS-p [*,H2*]
		
*	*H	

Figure S4. Gibbs free energy landscapes for the bare, K- and Ni-promoted Mo_6S_8 clusters as evaluated at 1200 K. Two parallel pathways are shown, a more direct pathway from [CH_3*,*] and [*,SH*], and a longer, stepwise pathway through splitting SH and forming CH_3S which is then hydrogenated (lighter shade).

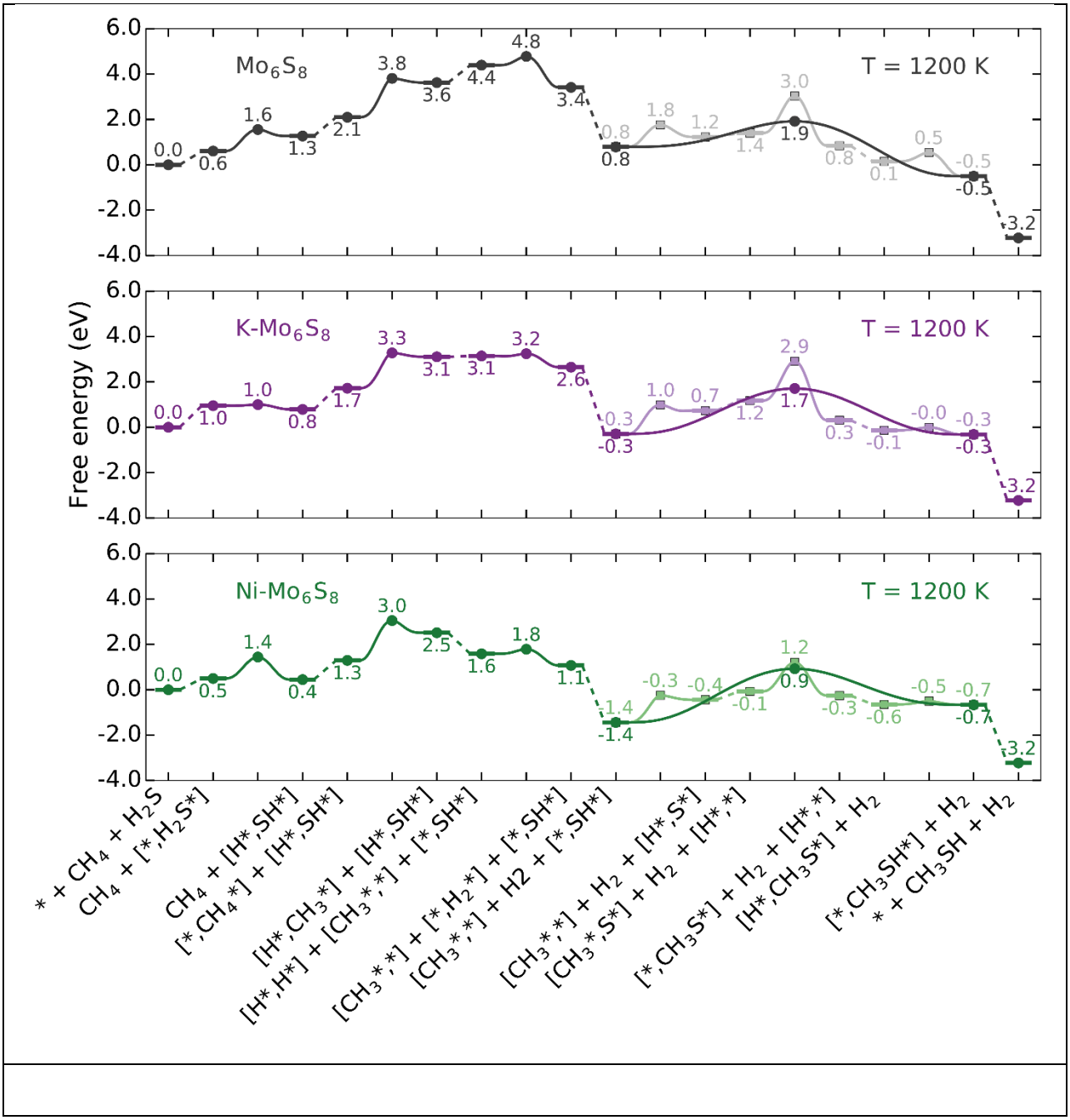


Figure S5. The coverage of various reaction intermediates on the bare (grey), K-promoted (purple) and Ni-promoted (green) Mo_6S_8 clusters as a function of temperature.

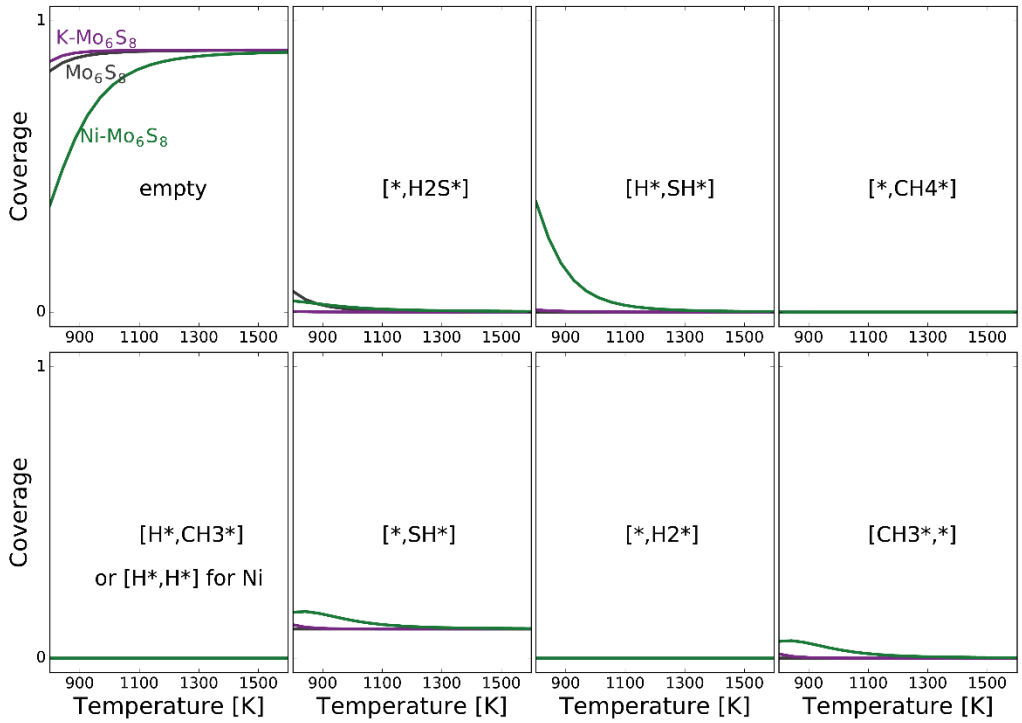


Figure S6. Bader charges for the K- and Ni-promoted clusters as well as the unpromoted cluster. Compared to the Bader charge for the isolated atoms, 8.86 for Kand 9.95 for Ni, this demonstrates that the promoter atoms transfer charge to the clusters.

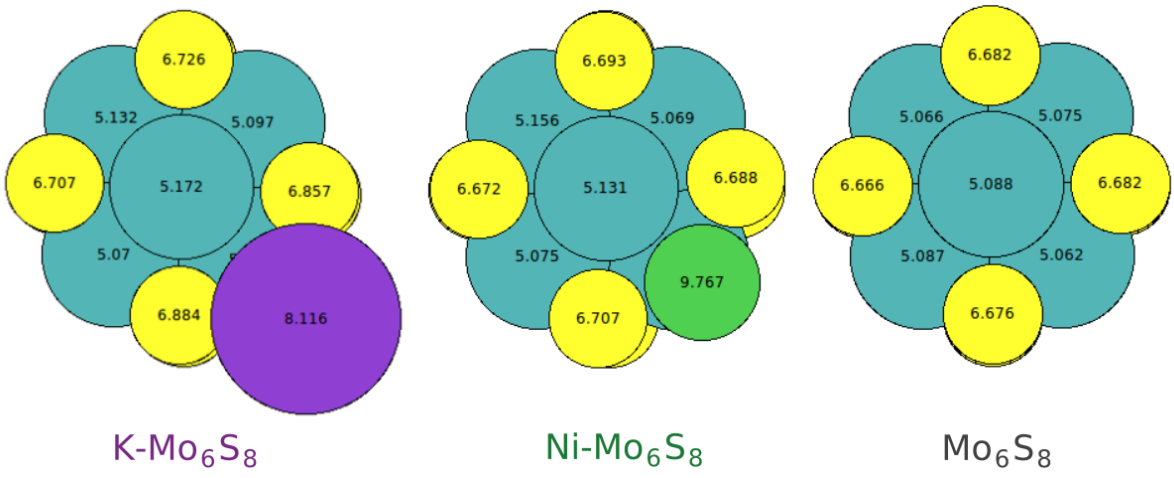


Figure S7. Charge density difference between the promoted cluster and the promoter atom isolated for K- and Ni-Mo_6S_8. Blue meaning reduced charge (more positive) and yellow an increased charge (more negative). Clearly both K and Ni donate charge to the cluster, which is distributed equally over the cluster atoms. The isosurfaces demonstrate that the electron transferred from K has an s-character while the electron transferred from Ni has a d-character.

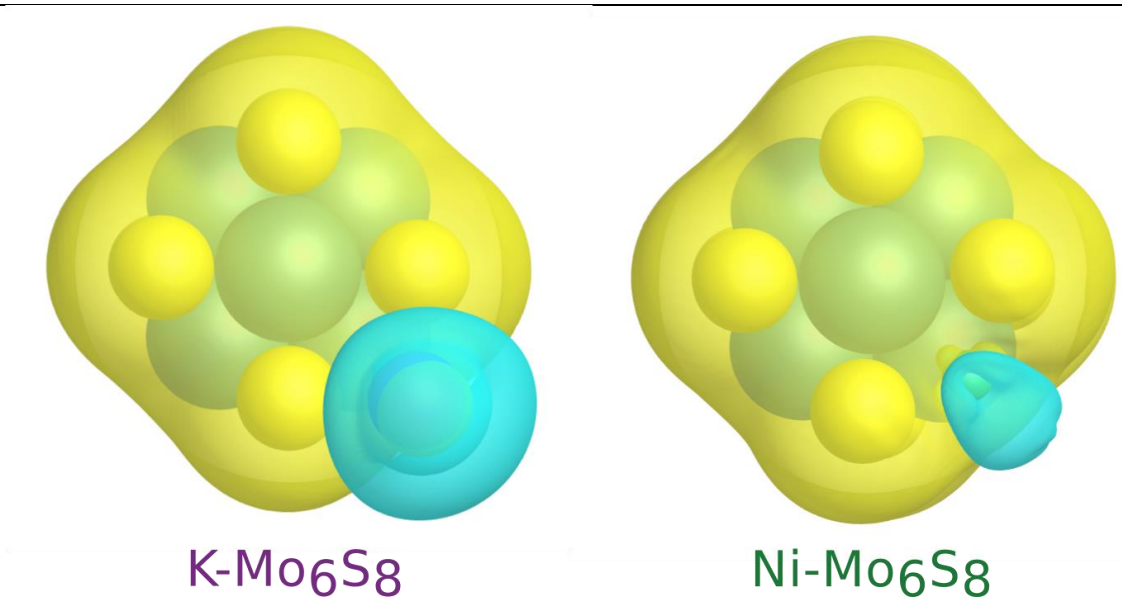


Figure S8. The turn-over frequency as a function of the partial pressure of the products (CH3SH and H2) at T=1200 K. This demonstrates that the pressure of the products must be low (as is shown in figure 3 in the article) and that the TOF does not change significantly when choosing a higher pressure. The red point marks the pressure used otherwise

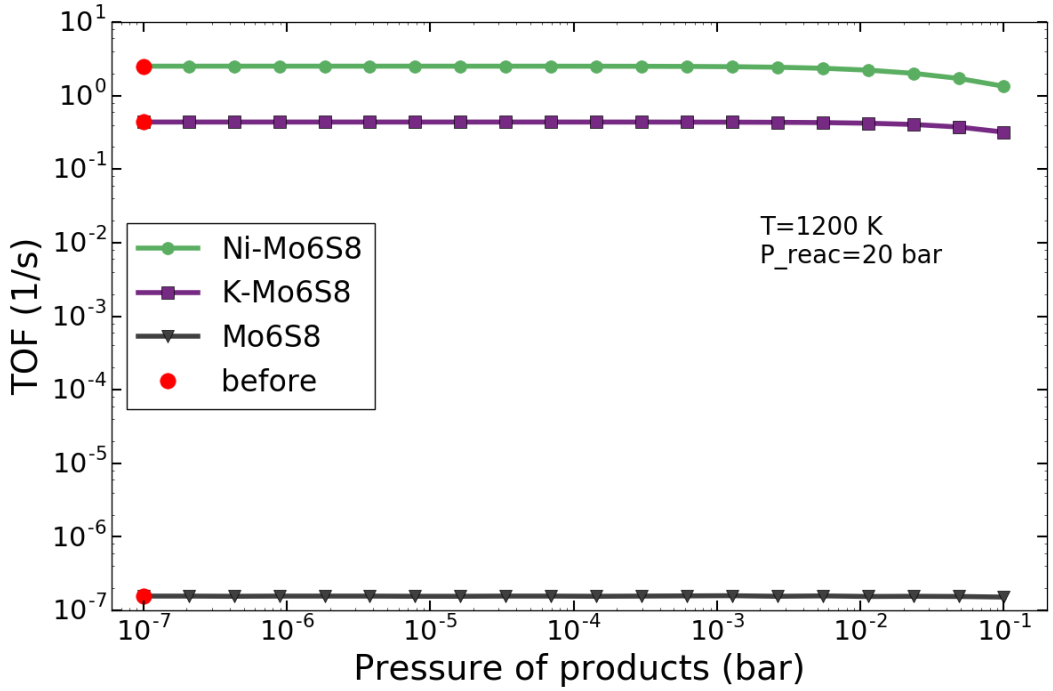


Figure S9. The turn-over frequency as a function of the partial pressure of the reactants (CH4 and H2S) at T=1200 K. This demonstrates that the pressure of the changes the TOF at significantly lower pressures than what is used in the article, but with the same shift for all clusters. The red point marks the pressure used otherwise.