Electronic Supplementary Information

Density Functional Theory Study of Thiophene Desulfurization and Conversion of Desulfurization Product on Ni(111) Surface and Ni₅₅ Cluster: Implication for the Mechanism of Reactive Adsorption Desulfurization over Ni/ZnO Catalysts

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Figure S1. The upright adsorptions on Ni(111) and Ni₅₅, and the flat adsorption at the vertex site of Ni₅₅.



Figure S2. Conversion pathway of thiophene from the bridge-hcp to the cross-bridge site on Ni(111).



Figure S3. Conversion pathway of thiophene from the bridge to the hollow site on Ni_{55} .



Figure S4. Hydrogenation pathways of thiophene from the cross-bridge site on Ni(111). The energy reference corresponds to the total energy of the initial-state configuration (cross-bridge adsorbed thiophene in this case) plus two atomic H adsorbed at infinitely separated sites on the substrate. The atomic H's adsorbed at infinitely separated sites on the substrate are omitted for simplicity.



Figure S5. Hydrogenation pathways of thiophene from the thiolate-fcc configuration on Ni(111). Parameters follow the same notation as in Figure S4.



Figure S6. Hydrogenation pathways of thiophene from the bridge and hollow configurations on Ni_{55} . Parameters follow the same notation as in Figure S4.



Figure S7. Desulfurization pathway of thiophene from the bridge configuration on Ni_{38} . Parameters follow the same notation as in Figure S4.



Figure S8. Hydrogenation pathways of thiophene from the bridge configuration on Ni_{38} . Parameters follow the same notation as in Figure S4.



Figure S9. Projected crystal orbital Hamilton population (pCOHP) between the relevant adatoms (C^2 , S) and Ni substrate. Cyan stands for bonding contributions, while red stands for antibonding contributions. The embedded value is the integrated COHP (ICOHP), given in absolute value.