

Electronic Supplementary Information

Efficient and stable N-heterocyclic ketone-Cu complex catalysts for acetylene hydrochlorination: Promotion effect of ligands revealed by DFT calculation

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Table S1. Surface Cu Components of Catalysts (XPS Cu 2p)

Catalyst	Area Cu ²⁺ (%)	Area Cu ⁺ (%)	Area Cu ⁰ (%)
20%CuCl ₂ -fresh	52.5	43.7	3.7
20%CuCl ₂ -used	34.9	60.4	4.7
20%CuCl ₂ -10%2P-fresh	90.5	8.7	0.8
20%CuCl ₂ -10%2P-used	86.6	12.1	1.3
20%CuCl ₂ -10%NM2P-fresh	93.2	6.4	0.4
20%CuCl ₂ -10%NM2P-used	91.1	8.5	0.3

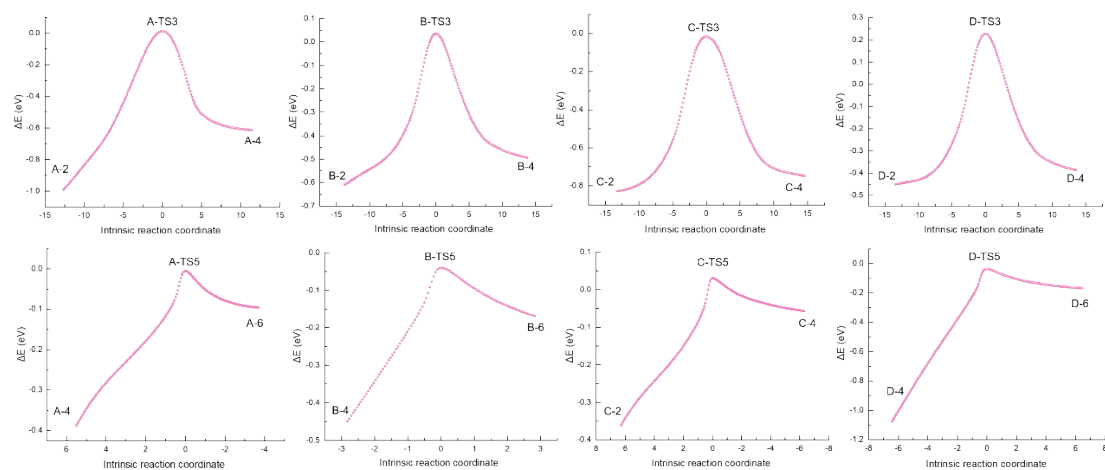


Figure S1. Intrinsic reaction coordinate (IRC) for TS3 and TS5 of acetylene hydrochlorination over the CuCl/AC site, CuCl₂-NM2P/AC site, CuCl₂-2P/AC site, and CuCl₂/AC site.

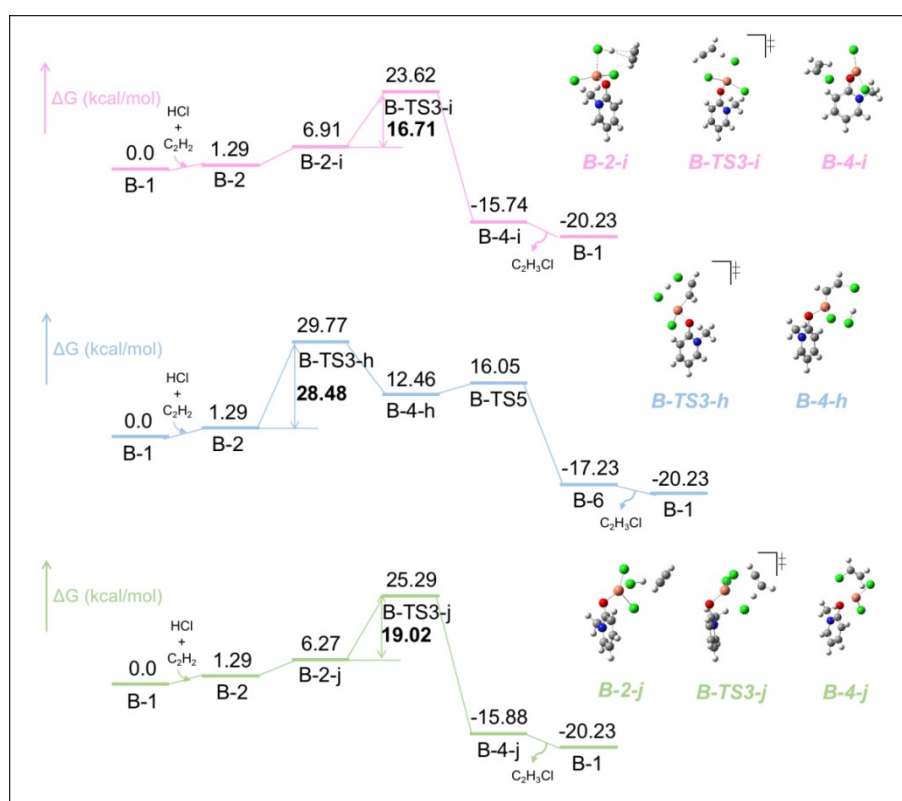


Figure S2. Energy profiles of acetylene hydrochlorination of HCl and C₂H₂ with the CuCl₂-NM2P/AC catalyst along other possible pathways.

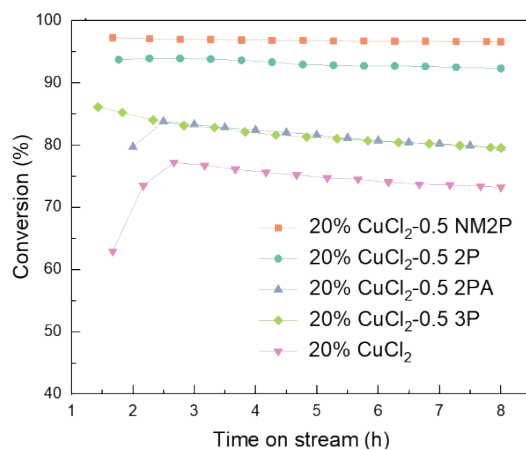


Figure S3. Acetylene conversion in acetylene hydrochlorination over different catalysts including CuCl₂-0.5 NM2P/AC, CuCl₂-0.5 2P/AC, CuCl₂-0.5 2PA/AC, CuCl₂-0.5 3P/AC and CuCl₂/AC. Reaction conditions: T = 180 °C, GHSV(C₂H₂) = 160 h⁻¹, V(HCl)/V(C₂H₂) = 1.2.

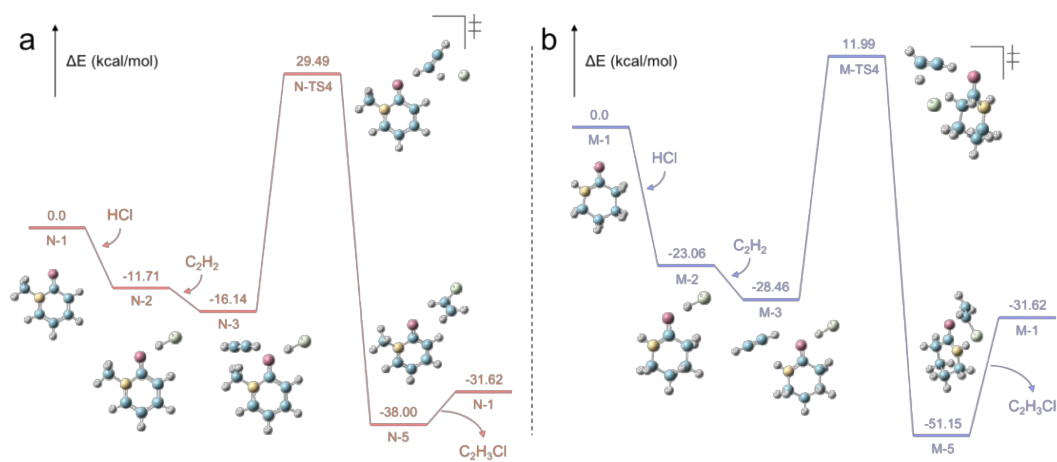


Figure S4. Energy profile of acetylene hydrochlorination of HCl and C₂H₂ with the N-methyl-2-pyridone or 2-piperidone catalyst.

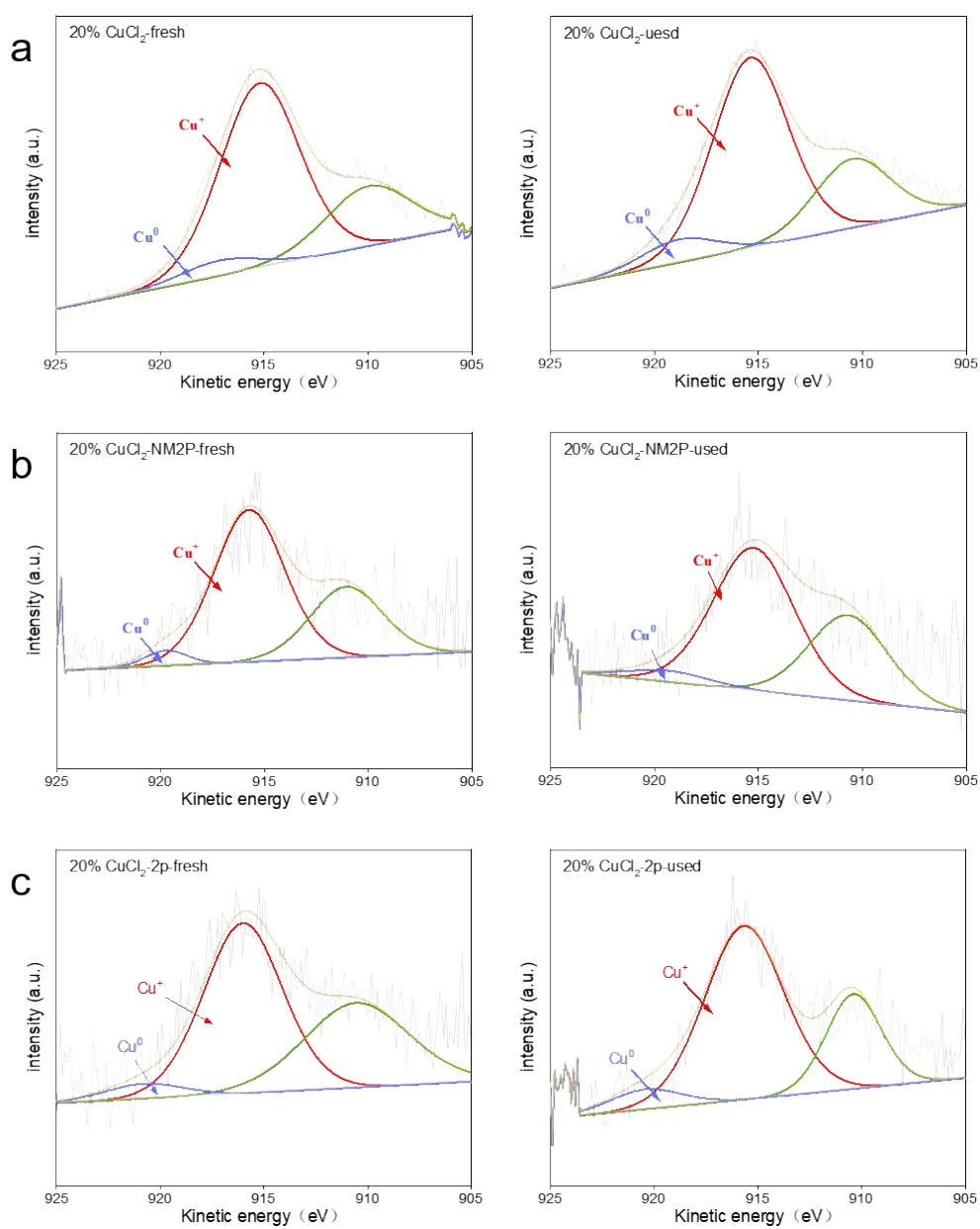


Figure S5. Cu LMM Auger spectra of fresh catalysts and used catalysts (a) CuCl₂/AC, (b) CuCl₂-NM2P/AC and (c) CuCl₂-2P/AC.

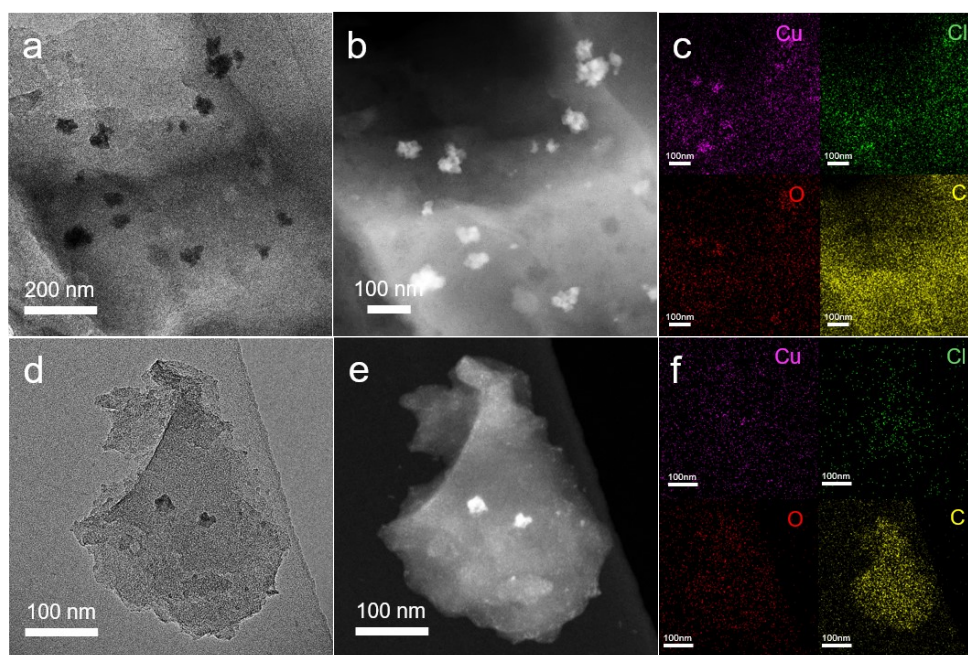


Figure S6. TEM images of used catalysts: (a) 20%CuCl₂/AC, (d) 20%CuCl₂-NM2P/AC, and HAADF-STEM image of used catalysts: (b) 20%CuCl₂/AC, (e) 20%CuCl₂-NM2P/AC, and EDS elemental maps of used catalysts: (c) 20%CuCl₂/AC, (f) 20%CuCl₂-NM2P/AC.

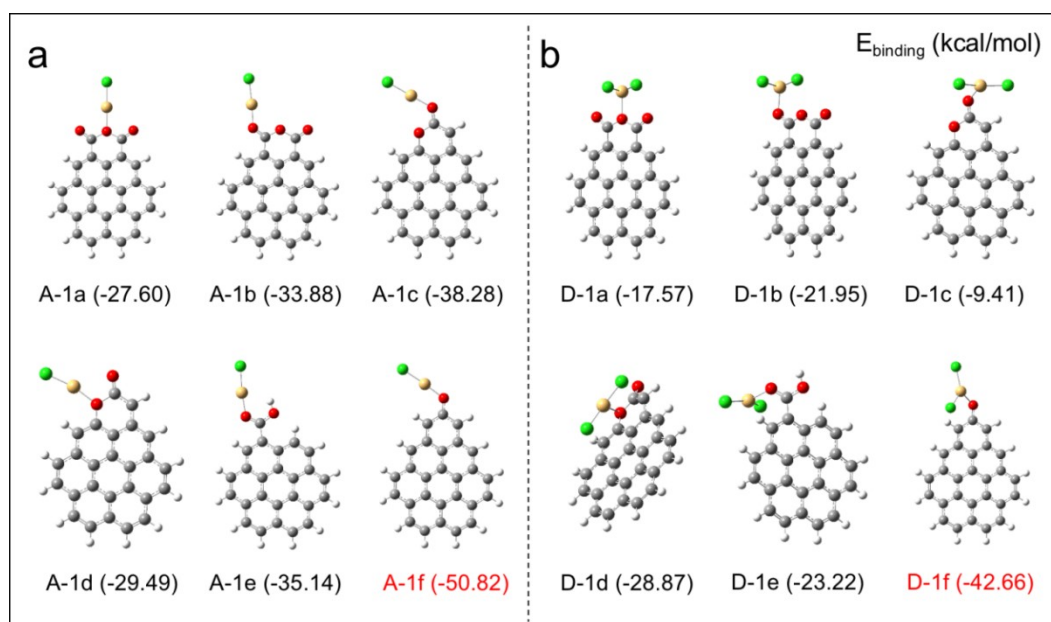


Figure S7. Optimized geometries of A-1n Cu(I)/AC and D-1n Cu(II)/AC.

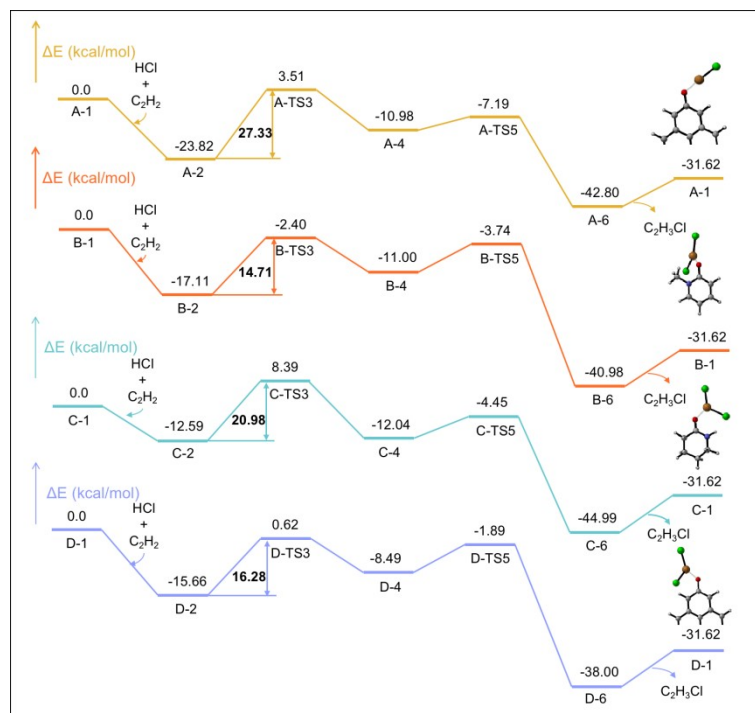


Figure S8. DFT calculations on the reaction mechanism. The system energy profile of the acetylene hydrochlorination of HCl and C₂H₂ with the catalysts CuCl/AC, CuCl₂-NM2P/AC, CuCl₂-2P/AC and CuCl₂/AC.

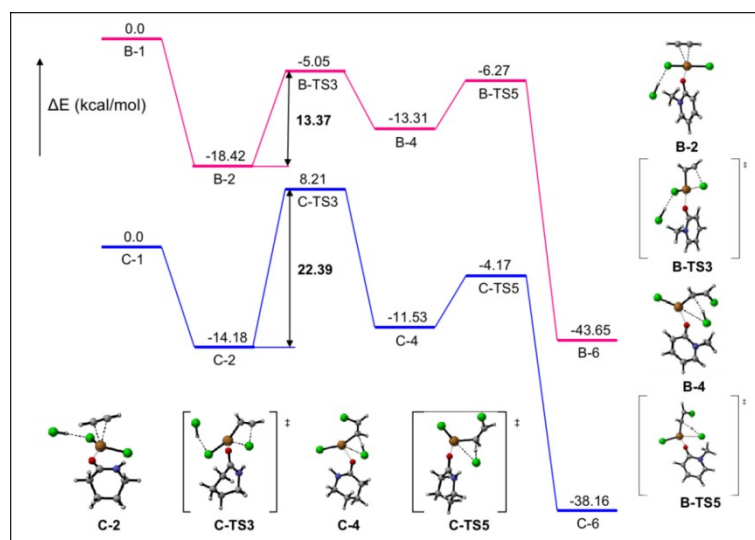


Figure S9. DFT calculations on the reaction mechanism using the M06 method. Energy profile of the acetylene hydrochlorination of HCl and C₂H₂ with the catalysts CuCl₂-NM2P/AC and CuCl₂-2P/AC and optimized geometries of intermediates and transition

states.

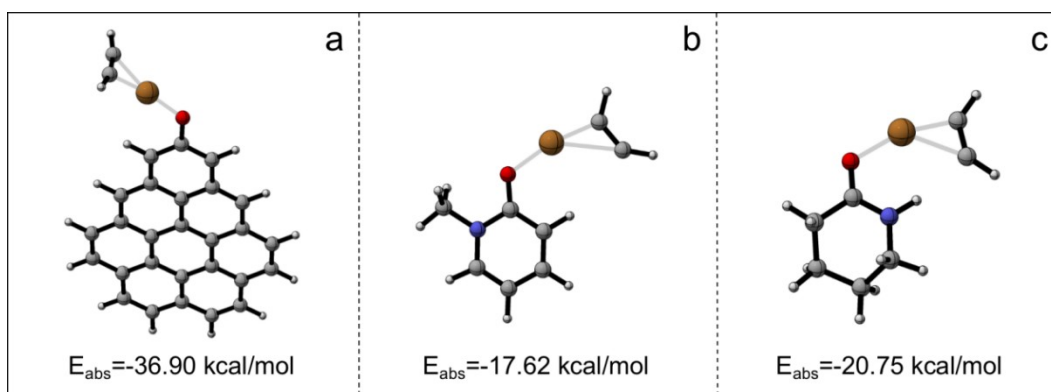


Figure S10. Adsorption configurations and energies of C_2H_2 and HCl on Cu^0 complexes.

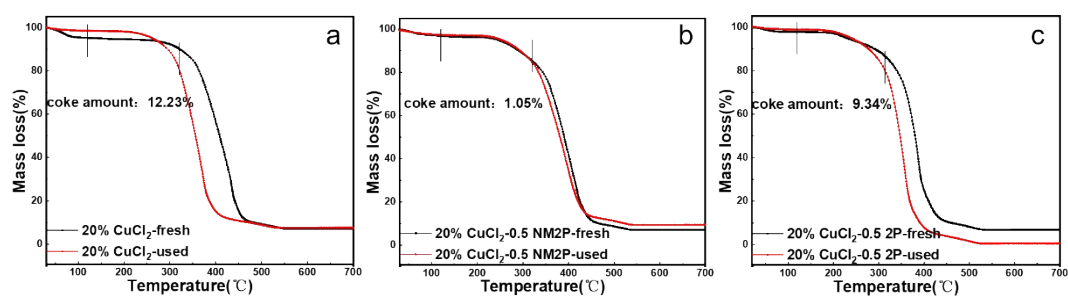


Figure S11. TGA curves of fresh and used catalysts (a) $CuCl_2/AC$ and (b) $CuCl_2$ -NM2P/AC and (c) $CuCl_2$ -2P/AC.