Supporting Information

C_2N-Supported Single Metal Ion Catalyst for HCOOH Dehydrogenation

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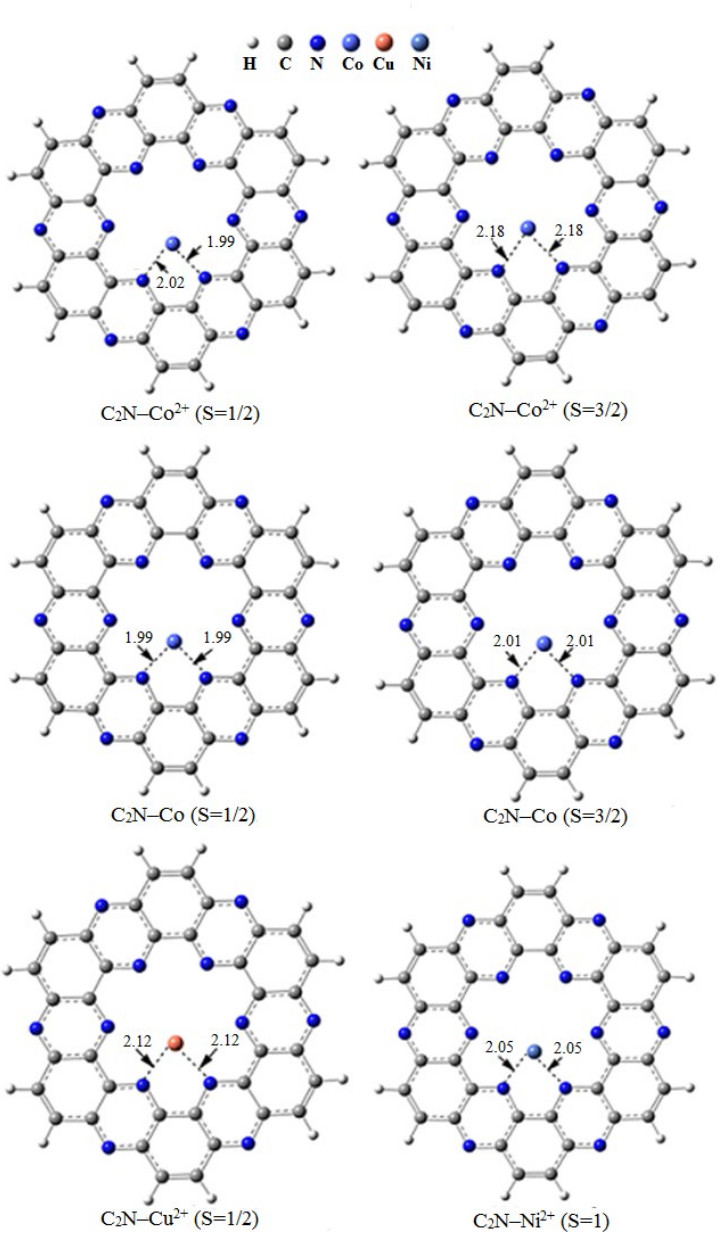

Figure S1. The atomic structures of different C_2N–TM^{x+} hybrid systems

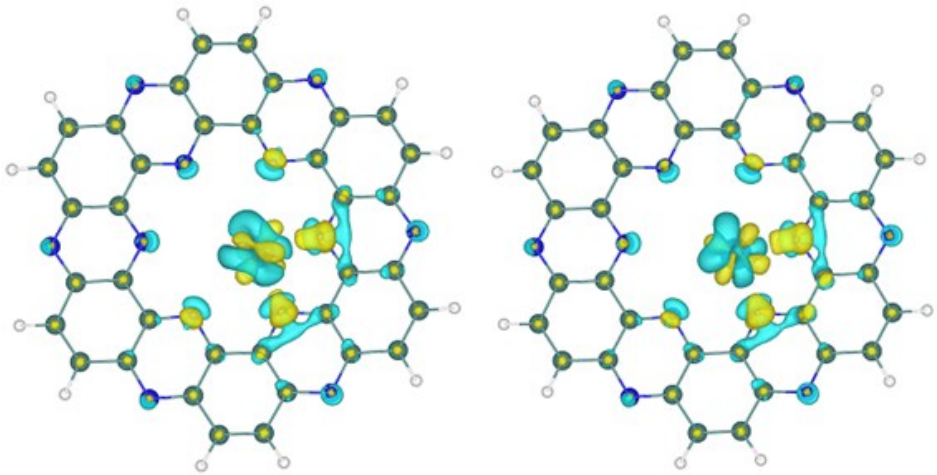

Figure S2. The electron density difference for C_2N–Co(S= 1/2 and 3/2) which reflect charge re-distribution due to the deposition of Co on C_2N.The unit of isosurface values is 0.006 e $Å^{-3}$.Yellow bubble represents electron accumulation and cyan bubble denotes electron depletion.

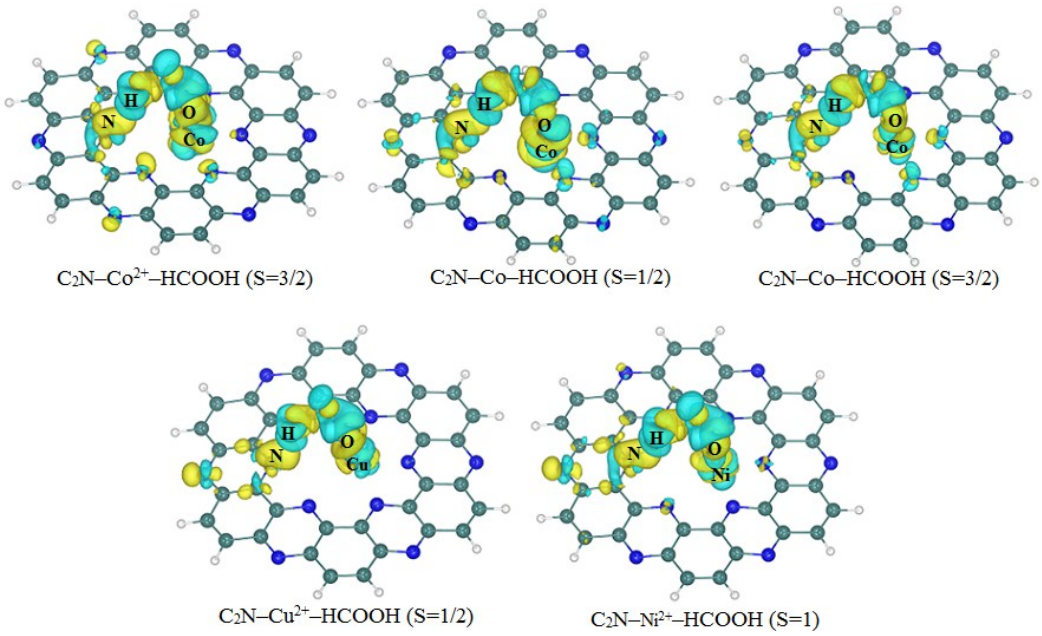

Figure S3.The electron density difference for HCOOH adsorbed on C_2N–Co^{2+}(S=3/2), C_2N–Co(S=1/2), C_2N–Co(S=3/2), C_2N–Cu^{2+} (S = 1/2) and C_2N–Ni^{2+}(S=1). The unit of isosurface values is 0.002 e $Å^{-3}$.Yellow bubble represents electron accumulation and cyan bubble denotes electron depletion.

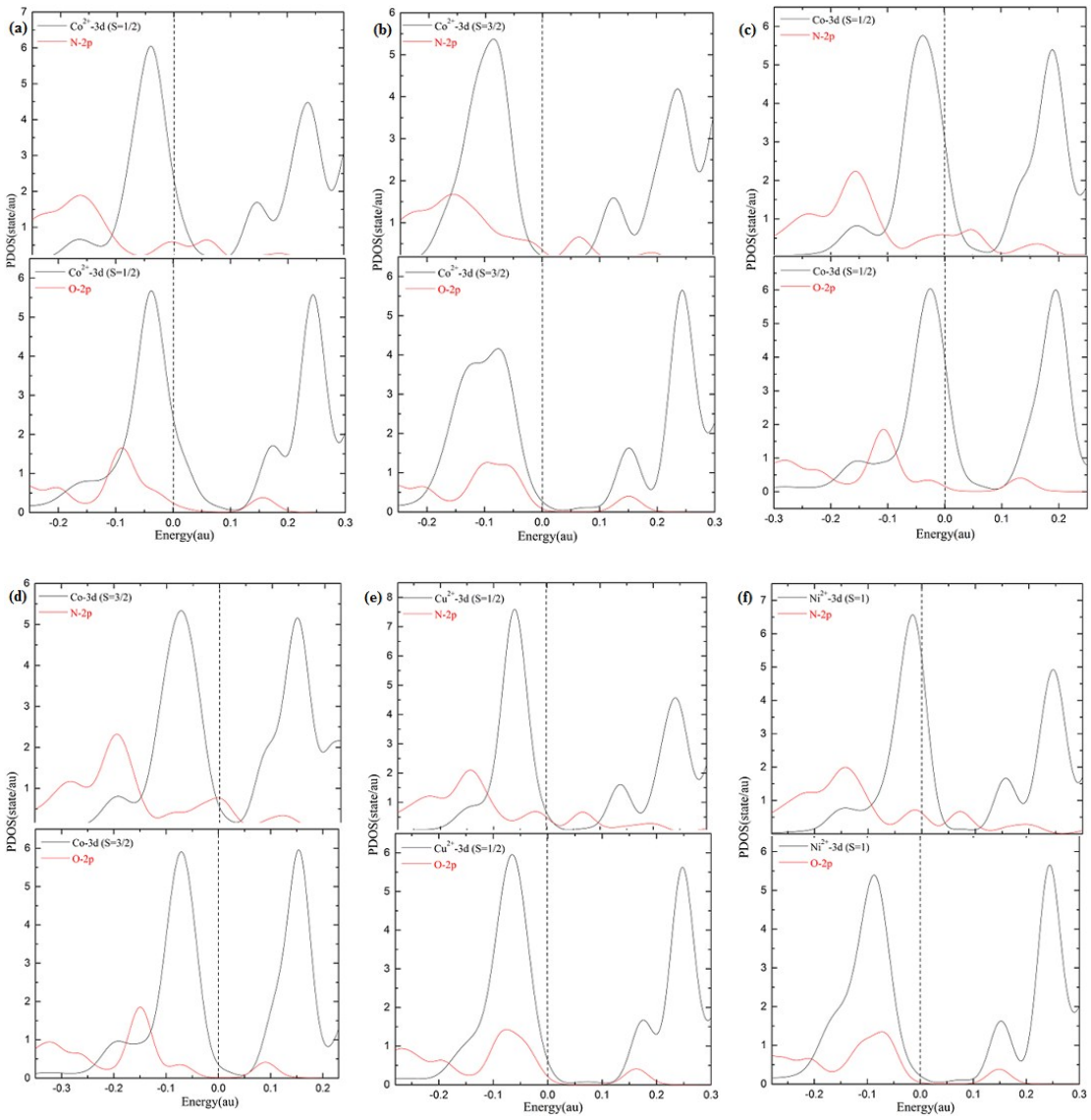

Figure S4. The PDOS of pre and post HCOOH adsorption on C_2N–TM^{x+}.

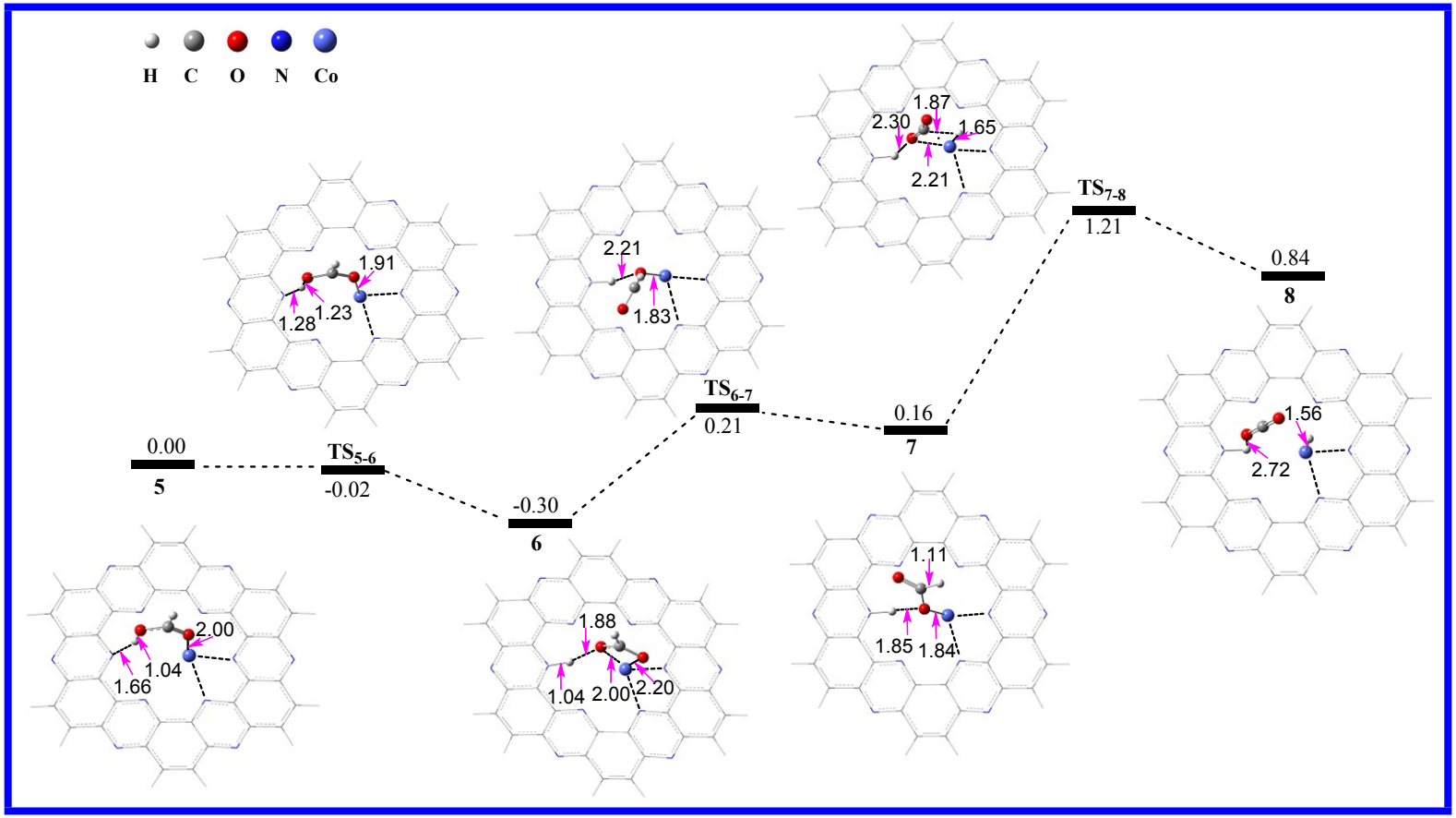

Figure S5. Calculated potential energy profile of the HCOOH dehydrogenation reaction on C_2N–Co^{2+} (S=3/2) with the optimized geometries of intermediates and transition states involved in the reaction. The relative free energies are given in eV.The distances are in Å.

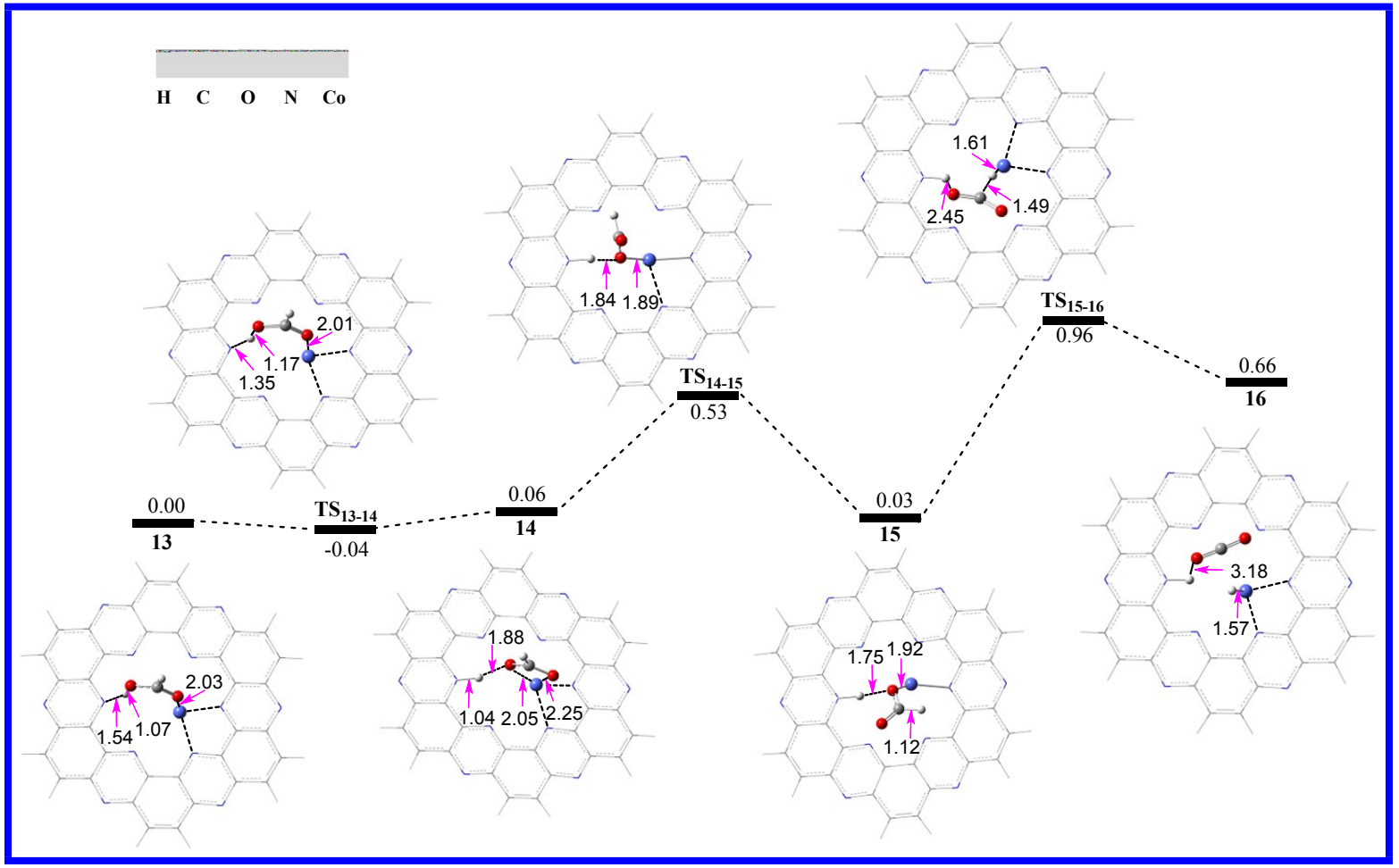

Figure S6. Calculatedpotential energy profile of the HCOOH dehydrogenation reaction on C_2N–Co (S=3/2)with the optimized geometries of intermediates and transition states involved in the reaction. The relative free energies are given in eV.The distances are in Å.