

## Supporting Information

### **Adjusting the active sites of Cu and ZnO by coordination effect of H<sub>3</sub>BTC and its influence for enhanced RWGS reaction**

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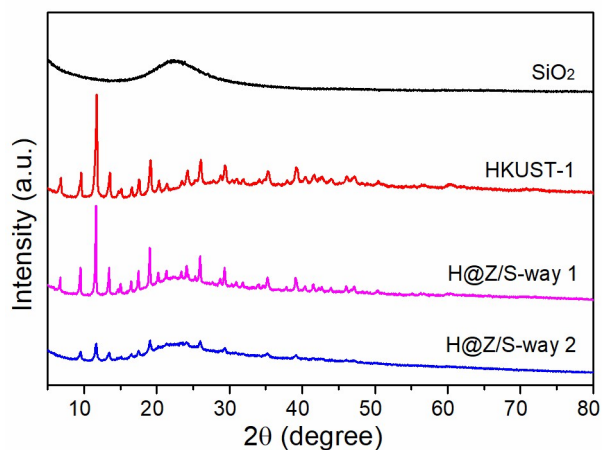


Figure S1. XRD patterns for materials prepared by different methods.

In order to explore a better method for synthesizing HKUST-1 on ZnO/SiO<sub>2</sub>, the following two preparation methods were adopted. The first way was the ZnO/SiO<sub>2</sub> powder containing divalent copper ions was added in the methanol solution containing H<sub>3</sub>BTC, then stirred for 3 h at room temperature and aged overnight. The second way was methanol solution containing H<sub>3</sub>BTC was gradually added to the SiO<sub>2</sub> powder containing the copper salt by manual stirring, and then dried at 60°C after allowed to stand for 1 h at room temperature. Finally, the samples prepared by the two options were centrifuged and washed several times with methanol, then dried at 60 °C for 24 h to obtain H@Z/S samples.

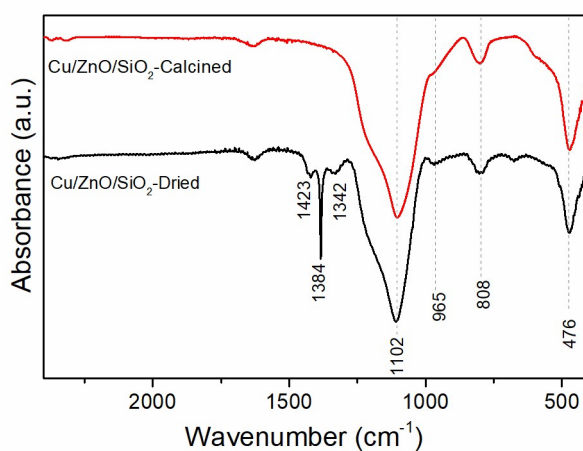


Figure S2. IR spectra of the Cu/ZnO/SiO<sub>2</sub> samples.

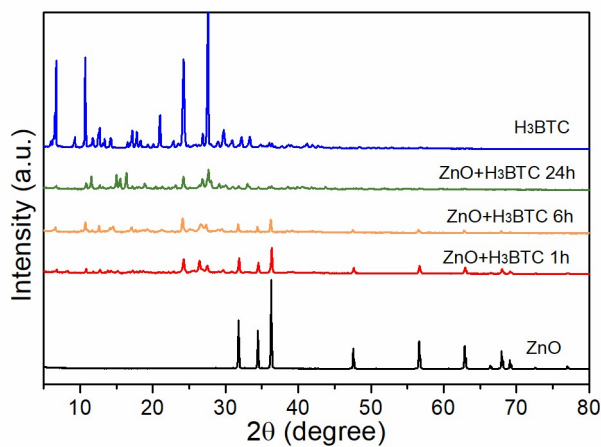


Figure S3. XRD patterns on the mechanism of ZnO etching by organic trimesic acid.

In order to prove that ZnO can be etched by H<sub>3</sub>BTC at room temperature, the ZnO particles were stirred in a methanol solution containing H<sub>3</sub>BTC for certain time, and then dried at 60 °C for 24 h. The resulting sample was called ZnO+H<sub>3</sub>BTC-T h.

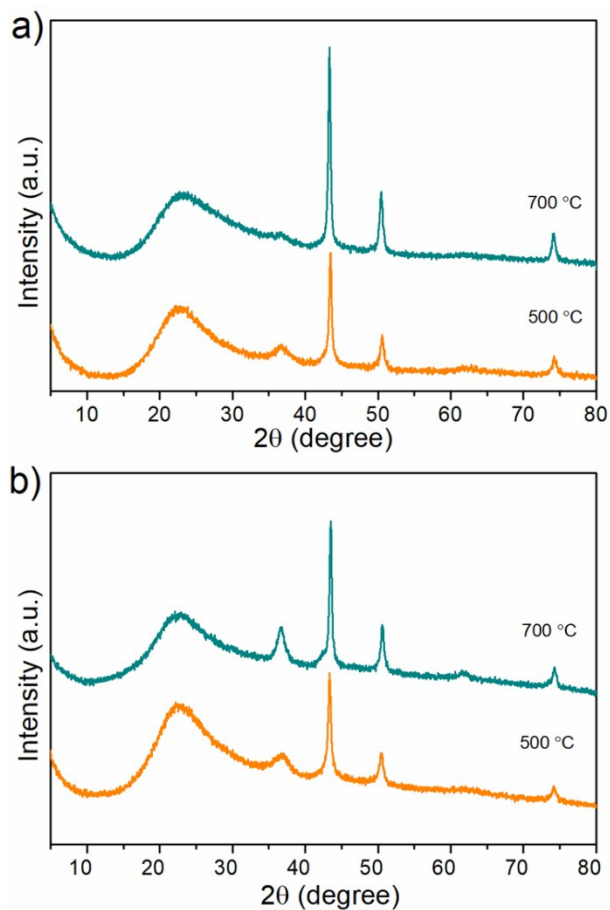


Figure S4. XRD patterns of H<sub>2</sub>O@SiO<sub>2</sub> at different calcination temperatures. a) before reaction, b) after reaction.

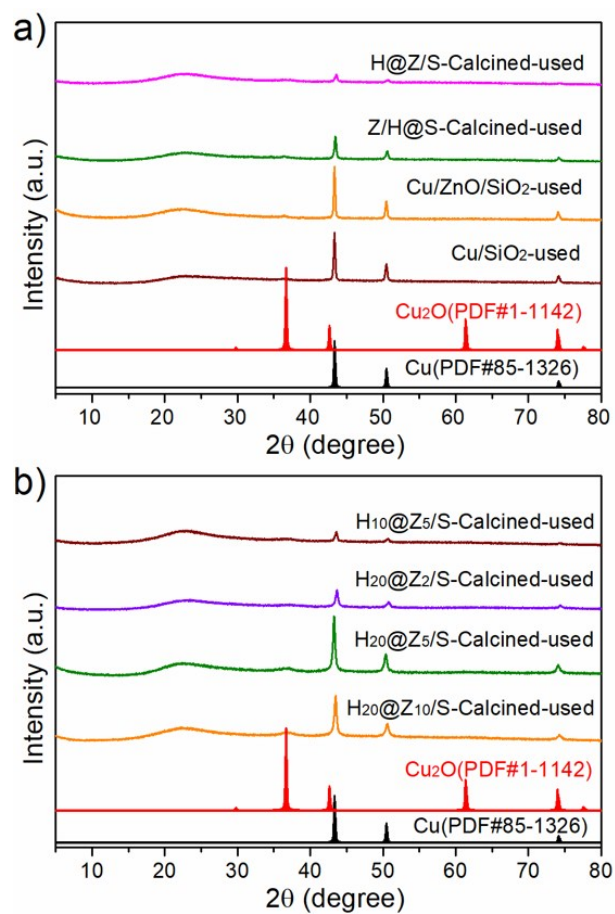


Figure S5. XRD patterns of a) different components and b) different ratio of calcined catalysts. a) Copper and zinc loadings are 10% and 5% respectively.

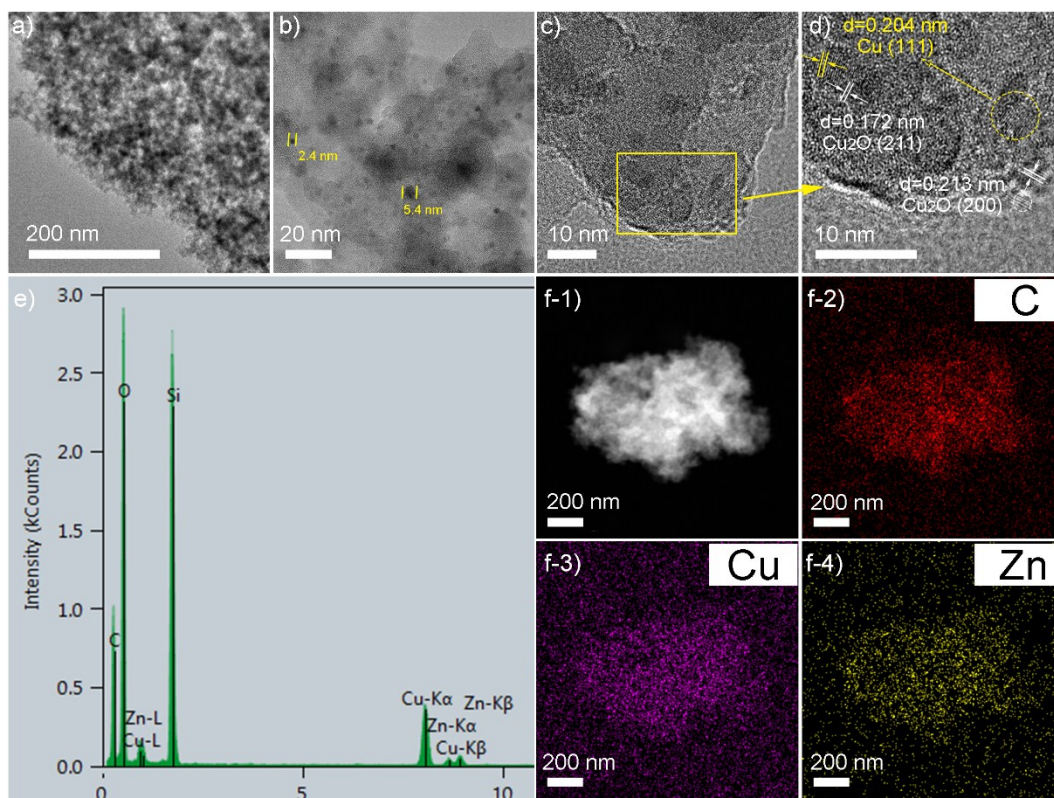


Figure S6. a-d) TEM images, f-1~f-4) elemental mapping and e) EDS of the calcined  $H_{10}@Z_5/S$  catalyst.

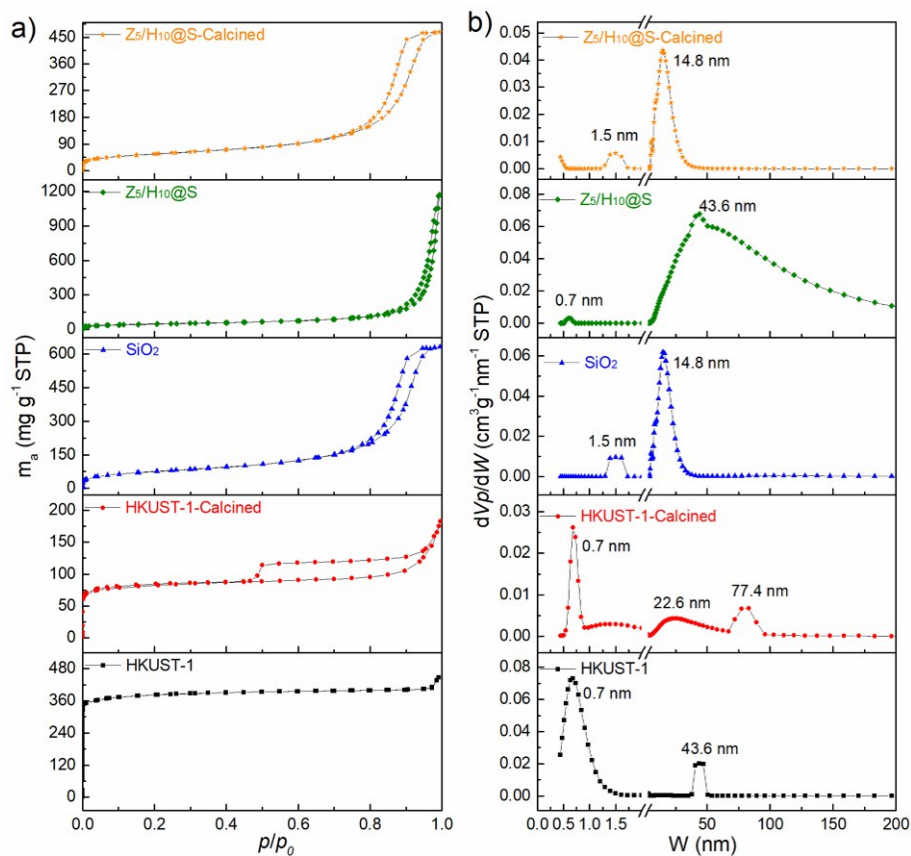


Figure S7. The adsorption/desorption isotherm and pore size distribution curves of different catalysts.

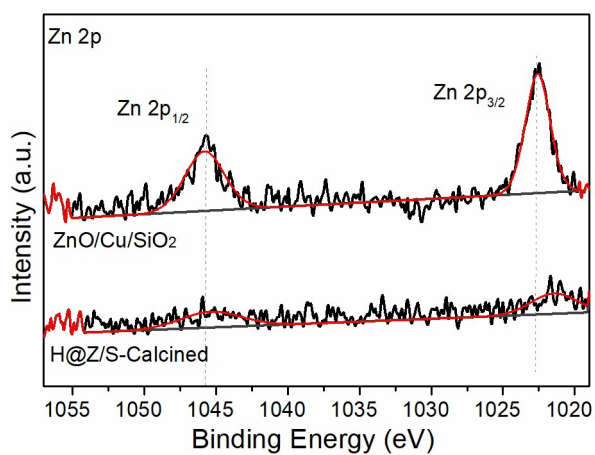


Figure S8. Zn 2p XPS spectra of calcined samples. Copper and zinc loadings are 10% and 5% respectively.

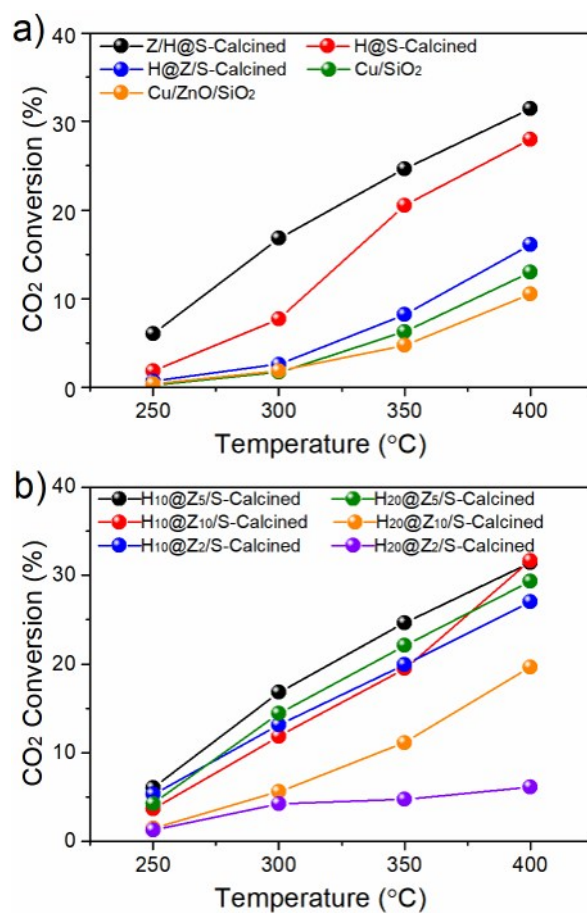


Figure S9. a) Different components and b) different ratio effect on the CO<sub>2</sub> hydrogenation performances (P=3.0MPa, GHSV = 3000 h<sup>-1</sup>, CO<sub>2</sub>:H<sub>2</sub> = 1:3). (a) Copper and zinc oxide loadings are 10% and 5% respectively.



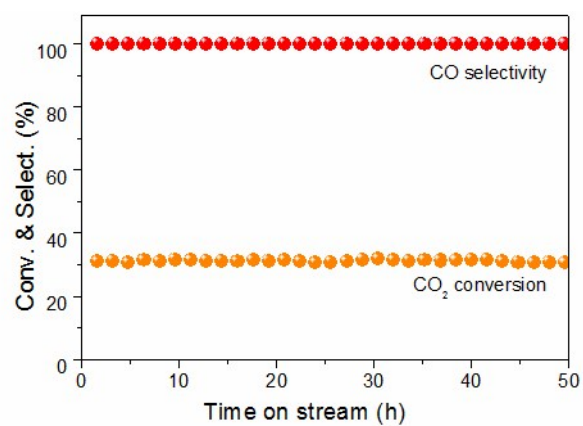


Figure S10. The catalysis stability of the H<sub>10</sub>@Z<sub>5</sub>/S catalyst (P = 3.0 MPa, T = 400 °C, GHSV = 3000 h<sup>-1</sup>, CO<sub>2</sub>:H<sub>2</sub> = 1:3).