Supporting Information for

Zeolite-Encapsulated Ultrasmall Cu/ZnO_x Nanoparticles for the Hydrogenation of CO_2 to Methanol

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Supporting Tables

Table S1. The experimental details including the composition of the initial solutions, and amount of added monomer stock solution.

MOF	Concentration of added metal stock solution		AV[b] (mL)	CV[c] (mL)
	Metals[a]	Ligands		
Cu-HKUST-1	$Cu(OAc)_2 \cdot H_2O$ (Ethanol/DMF=1/1, 15 mM)	BTC (DMF, 10 mM)	40	40
$CuZn_{(1/2)}$-HKUST-1	$Cu(OAc)_2 \cdot H_2O$ (Ethanol/DMF=1/1, 10 mM) $Zn(OAc)_2 \cdot H_2O$ (Ethanol/DMF=1/1, 20 mM)	BTC (DMF, 20 mM)	60	60
$CuZn_{(1/1)}$-HKUST-1	$Cu(OAc)_2 \cdot H_2O$ (Ethanol/DMF=1/1, 15 mM) $Zn(OAc)_2 \cdot H_2O$ (Ethanol/DMF=1/1, 15 mM)	BTC (DMF, 20 mM)	60	60
$CuZn_{(2/1)}$-HKUST-1	$Cu(OAc)_2 \cdot H_2O$ (Ethanol/DMF=1/1, 20 mM) $Zn(OAc)_2 \cdot H_2O$ (Ethanol/DMF=1/1, 10 mM)	BTC (DMF, 20 mM)	60	60

a. Ethanol and DMF are added in form of volume ratio, respectively.

b. Volume of added metal stock solution (mL).

c. Volume of reaction solution collected after the reaction period (mL).

Table S2. Structural parameters of various catalysts.

Catalyst	Cu loading[a] (wt.%)	Zn loading[a] (wt.%)	Cu/Zn wt.%/ wt.%	S_{BET}[b] ($m^2 \cdot g^{-1}$)	S_{Micro}[b] ($m^2 \cdot g^{-1}$)	V_{Total}[b] ($cm^3 \cdot g^{-1}$)[c]
ZSM-5	--	--	--	355	266	0.12
Cu/ZnO_x/Na-ZSM-5	3.7	2.8	1.32	214	158	0.07
Cu@Na-ZSM-5	4.5	--	--	205	145	0.06
Cu/ZnO_x(0.48)@Na-ZSM-5	2.2	4.6	0.48	198	166	0.08
Cu/ZnO_x(1.38)@Na-ZSM-5	3.2	2.2	1.38	218	143	0.08
Cu/ZnO_x(2.23)@Na-ZSM-5	4.8	2.15	2.23	223	160	0.05

a. Calculated from the results of ICP-OES.

b. S_{BET} (total surface area), S_{Micro} (micropore surface area), and V_{Total} (total volume) were calculated using BET equation ($0.05 < P/P_0 < 0.3$) of the adsorption isotherm.

Supporting Figures

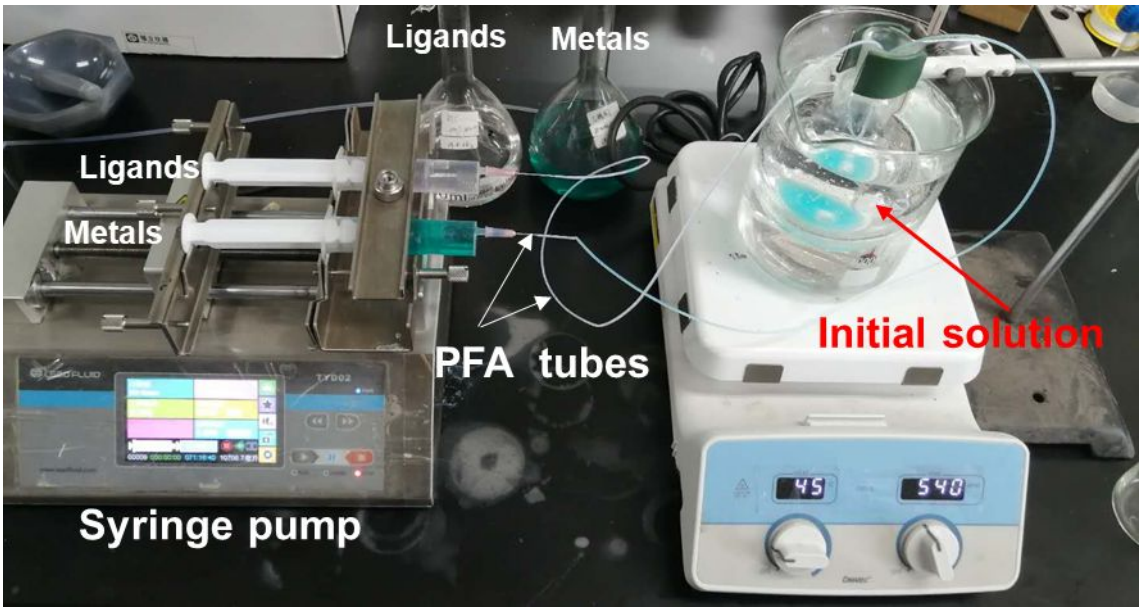

Figure S1. Photograph of a typical reactor for the synthesis of nano-HKUST-1 in this work.

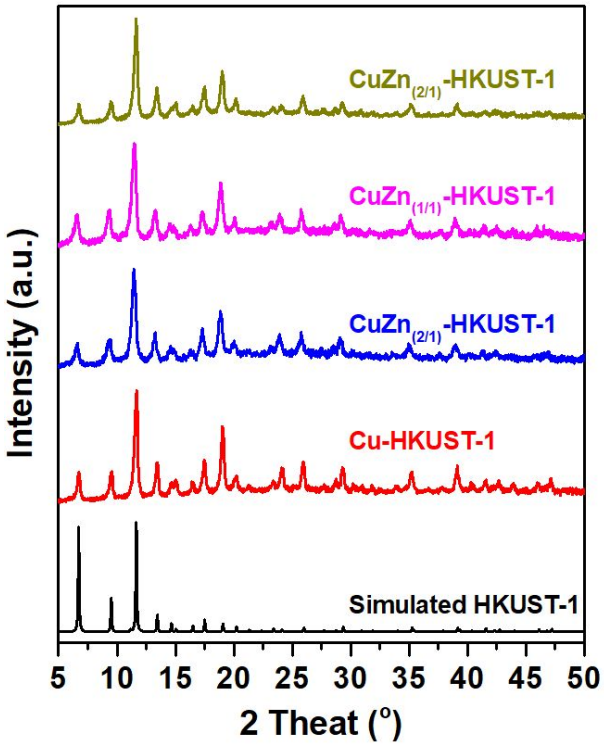

Figure S2. XRD patterns of Cu-HKUST-1, $CuZn_{(1/2)}$-HKUST-1, $CuZn_{(1/1)}$-HKUST-1, and $CuZn_{(2/1)}$-HKUST-1 NPs.

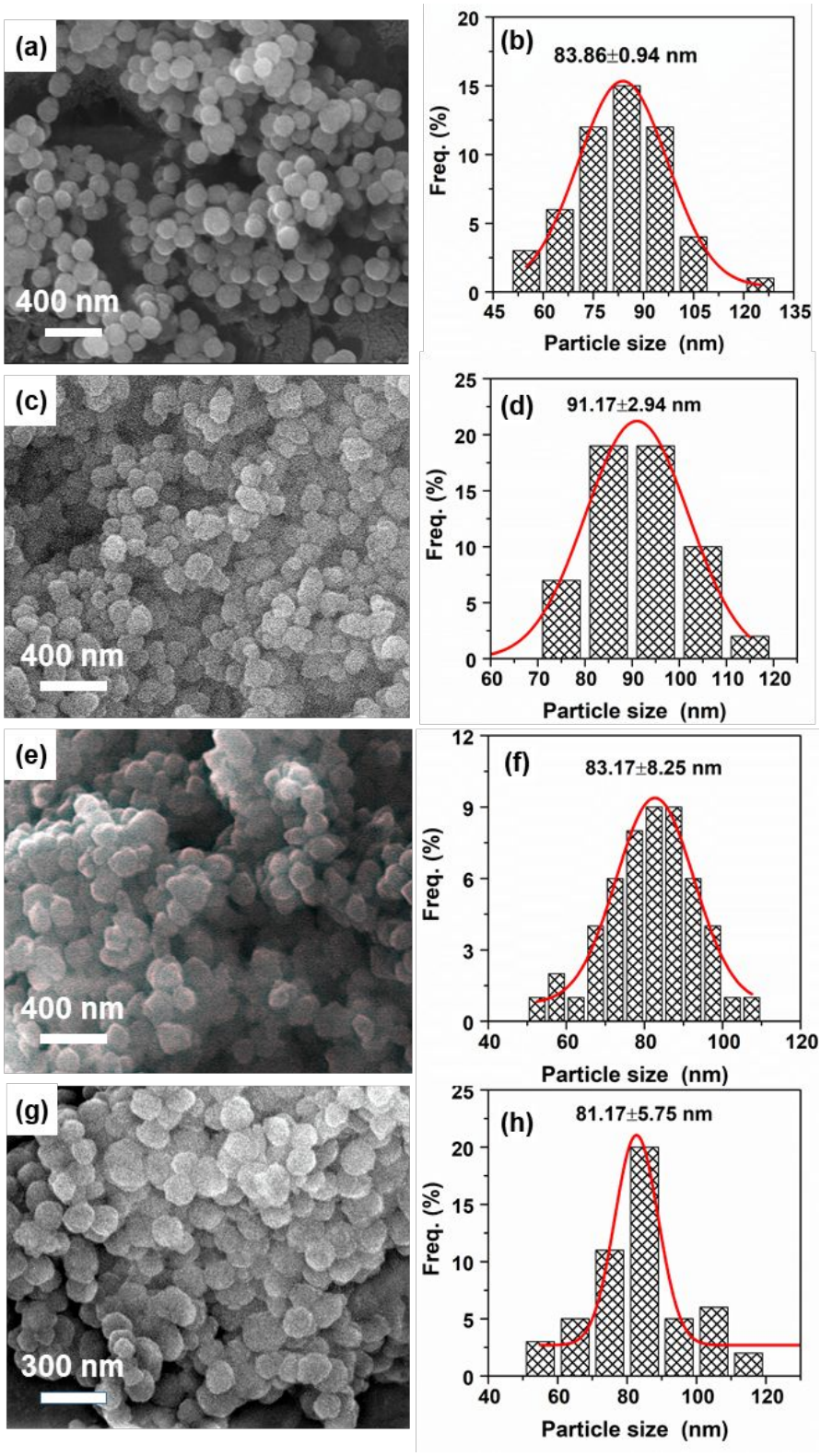

Figure S3. SEM images of (a) Cu-HKUST-1, (c) $CuZn_{(1/2)}$-HKUST-1, (e) $CuZn_{(1/1)}$-HKUST-1, and (g) $CuZn_{(2/1)}$-HKUST-1 NPs. The corresponding size distribution histograms of (b) Cu-HKUST-1, (d) $CuZn_{(1/2)}$-HKUST-1, (f) $CuZn_{(1/1)}$-HKUST-1, and (h) $CuZn_{(2/1)}$-HKUST-1 NPs obtained from SEM analysis.

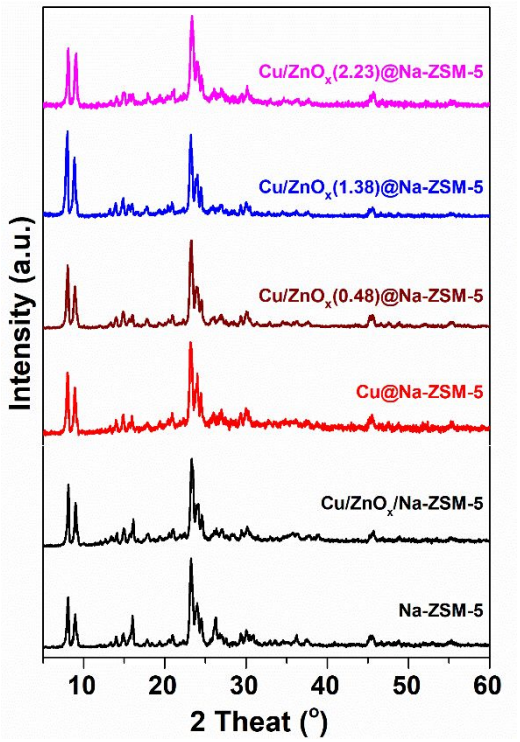

Figure S4. XRD patterns of Na-ZSM-5, Cu/ZnO_x/Na-ZSM-5, Cu@Na-ZSM-5, and Cu/ZnO_x@Na-ZSM-5 samples with different mass ratios of Cu/Zn. All samples exhibit XRD peaks associated with typical MFI zeolite structure. In addition, it is difficult to observe the peaks related to Cu or ZnO_x crystals, indicating the high dispersion of the Cu/ZnO_x species.

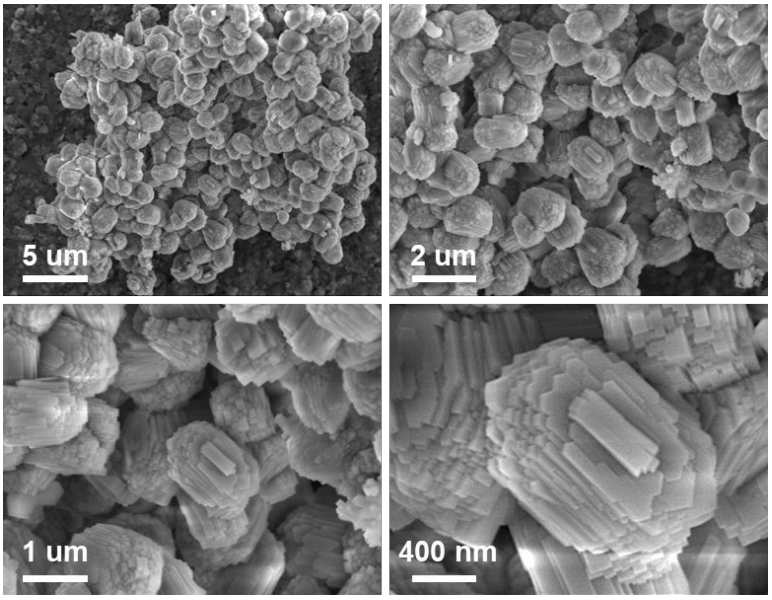

Figure S5. SEM images of obtained Na-ZSM-5 sample.

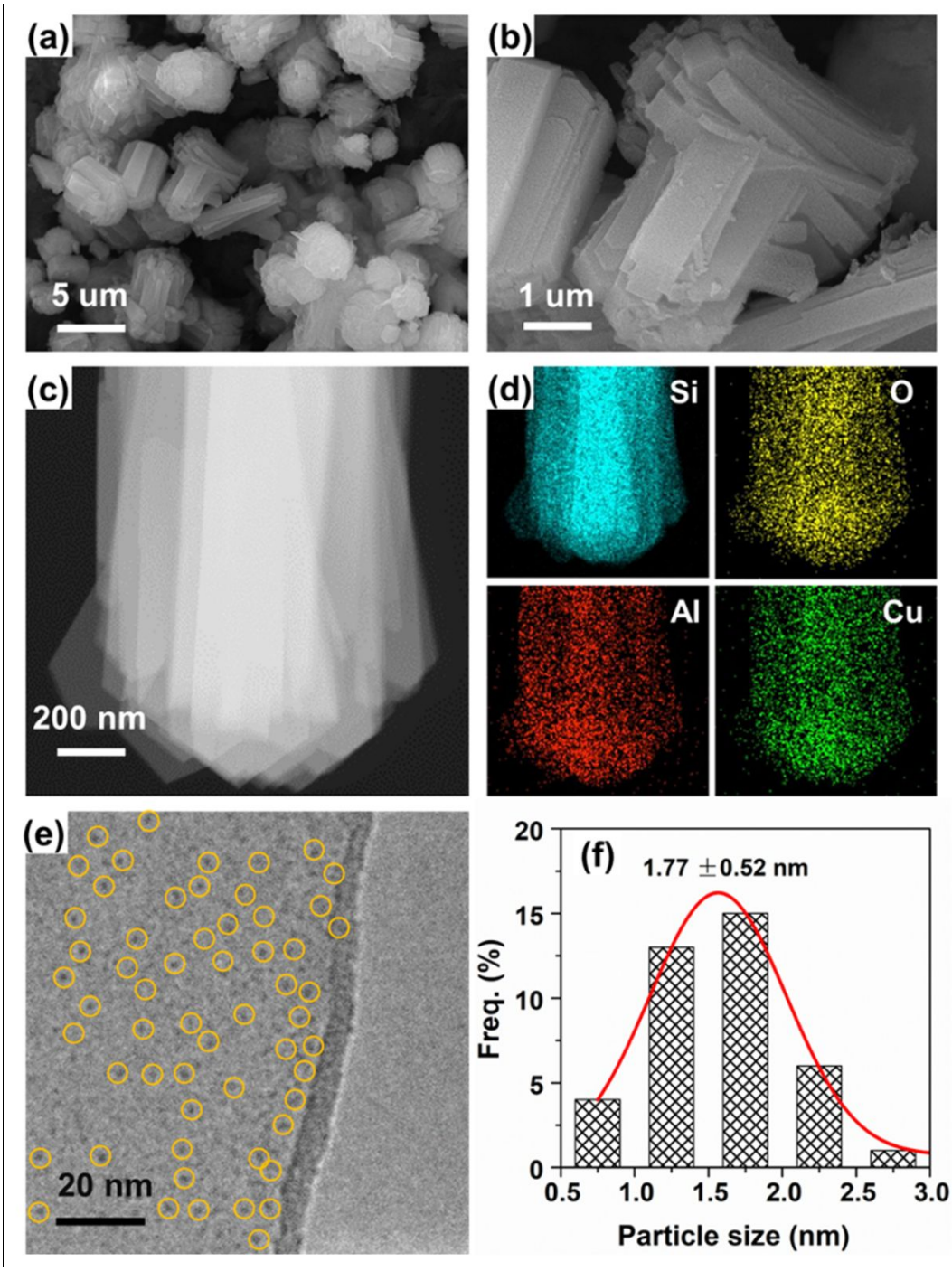

Figure S6. (a,b) SEM images of Cu@Na-ZSM-5 sample; (c,d) TEM images and corresponding element mapping images of Cu@Na-ZSM-5; (e) high-resolution TEM image of Cu@Na-ZSM-5 and (f) corresponding size distribution of Cu NPs.

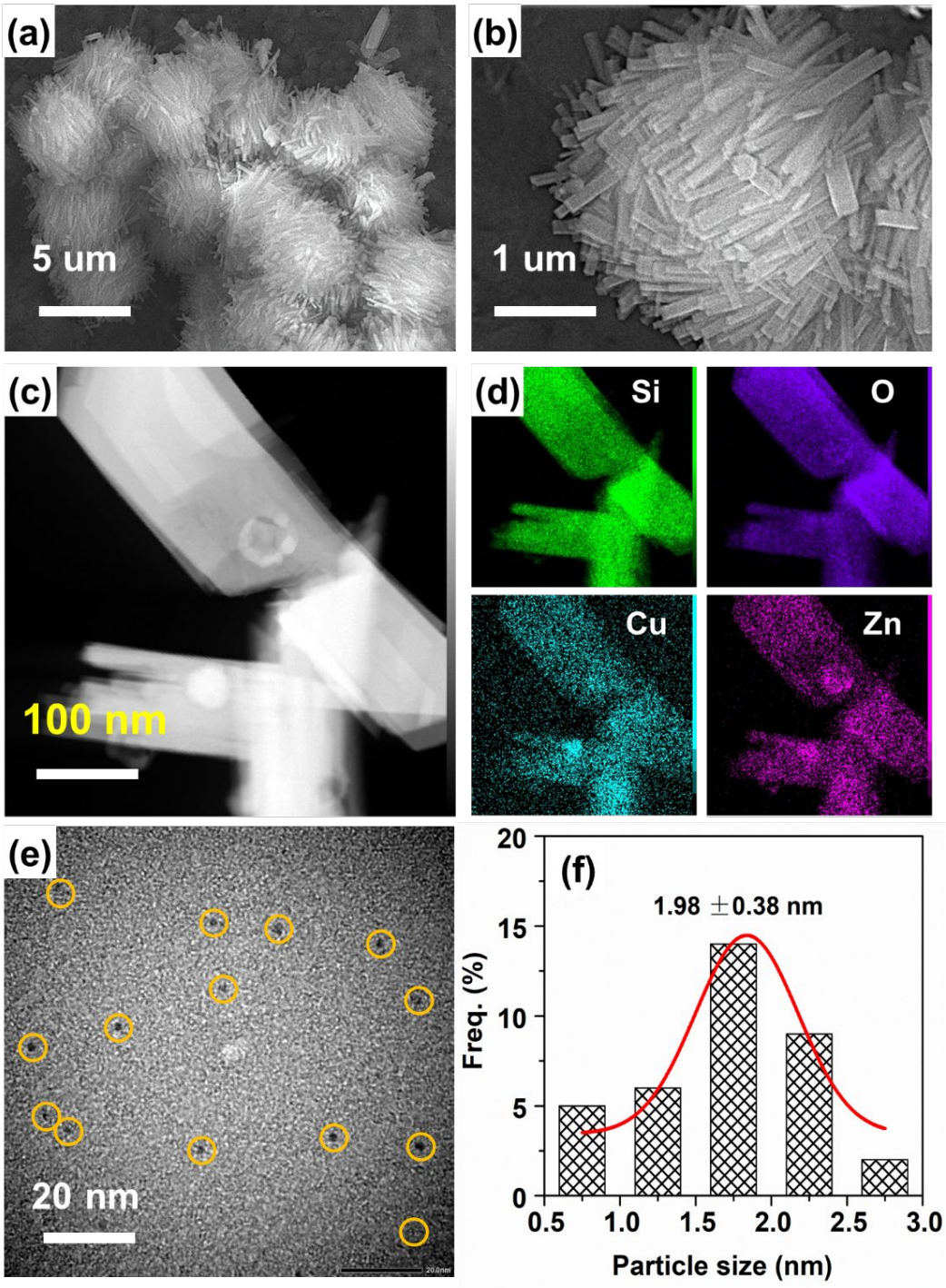

Figure S7. (a,b) SEM images of Cu/ZnO_x(0.48)@Na-ZSM-5 sample; (c,d) TEM images and corresponding element mapping analyses images of Cu/ZnO_x(0.48)@Na-ZSM-5; (e) high-resolution TEM image of Cu/ZnO_x(0.48)@Na-ZSM-5 and (f) corresponding size distribution of Cu/ZnO_x NPs.

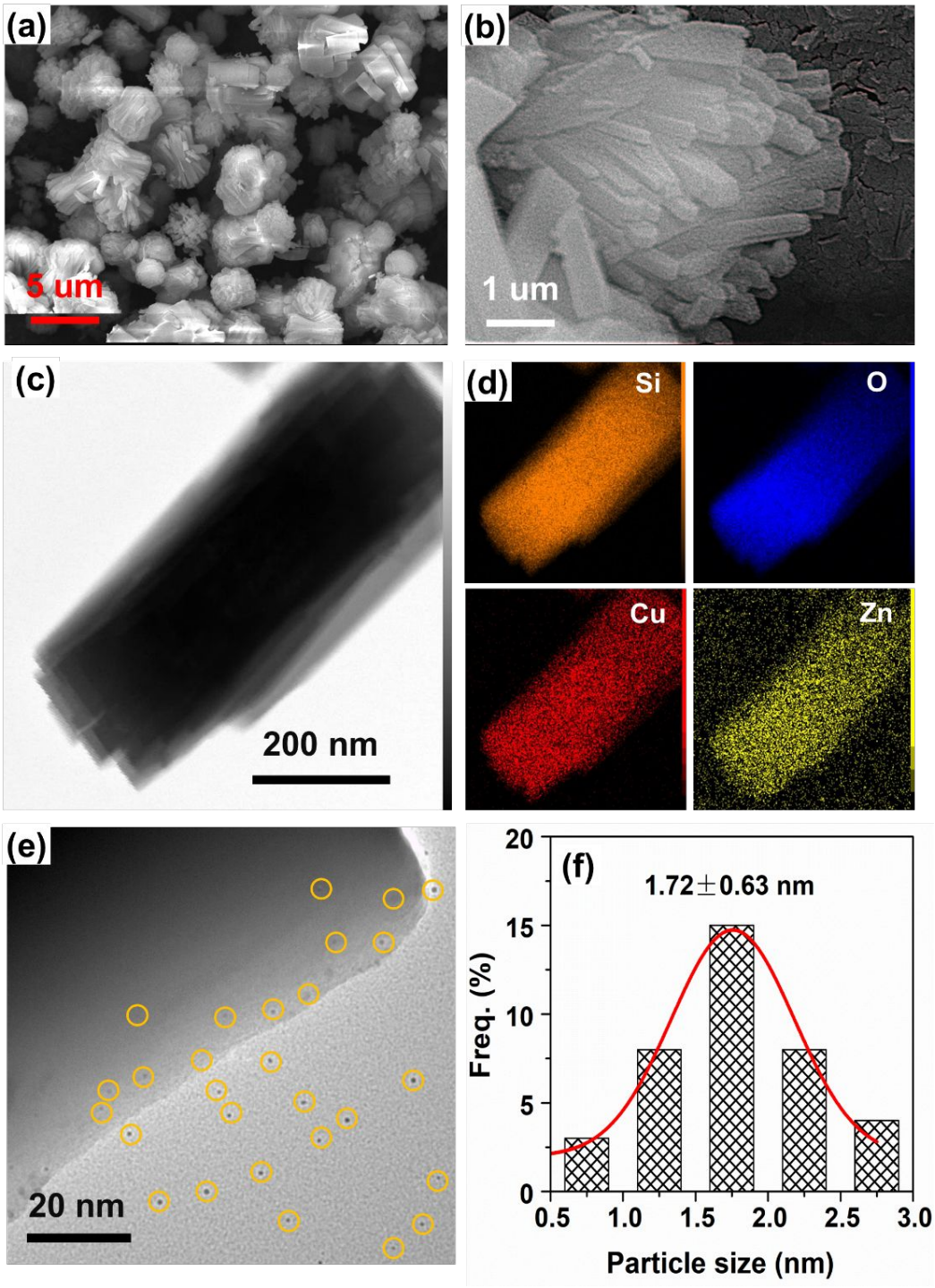

Figure S8. (a,b) SEM images of $Cu/ZnO_x(2.23)$@Na-ZSM-5 sample; (c,d) TEM images and corresponding element mapping analyses images of $Cu/ZnO_x(2.23)$@Na-ZSM-5; (e) high-resolution TEM image of $Cu/ZnO_x(2.23)$@Na-ZSM-5 and (f) corresponding size distribution of Cu/ZnO_x NPs.

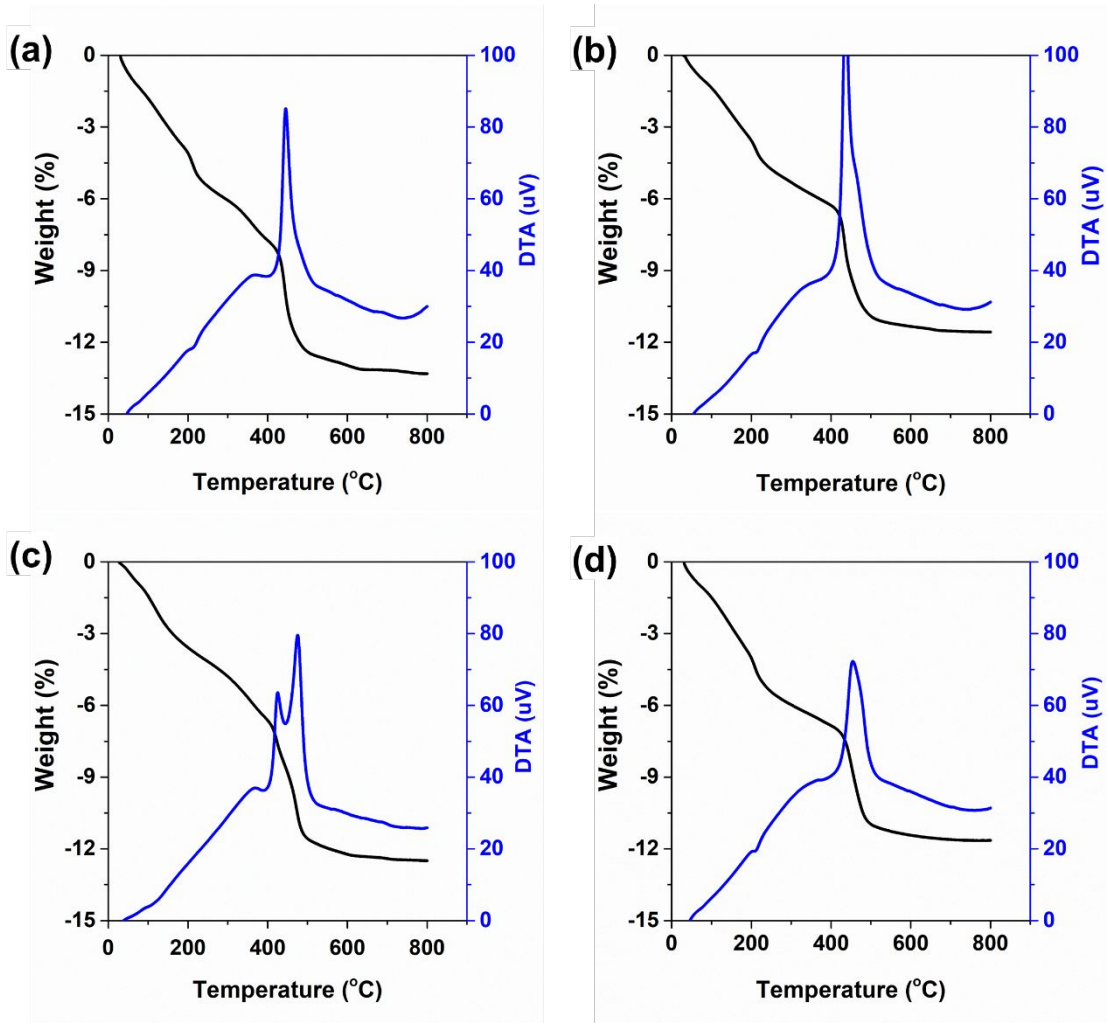

Figure S9. TGA (black) and DTA (blue) of (a) raw-Cu@Na-ZSM-5, (b) raw-Cu/ZnO_x(0.48)@Na-ZSM-5, (c) raw-Cu/ZnO_x(1.38)@Na-ZSM-5, (d) raw-Cu/ZnO_x(2.23)@Na-ZSM-5 measured from 30 to 800 °C in air at a heating rate of 10 °C·min^{-1}.

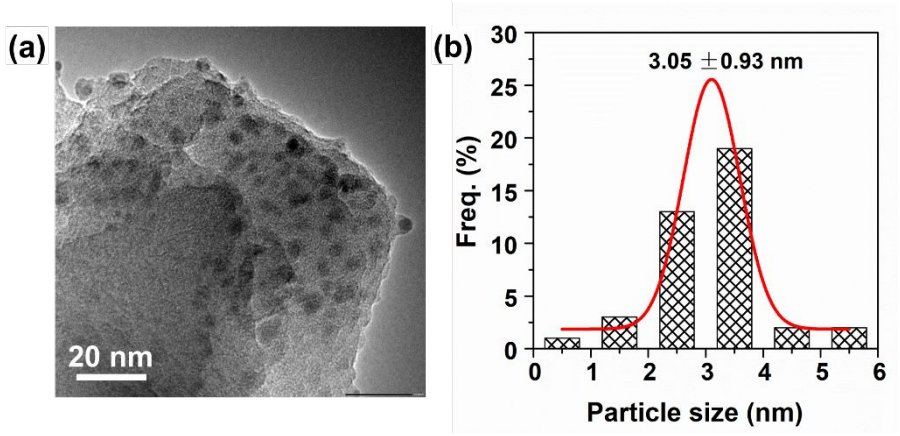

Figure S10. (a) High-resolution TEM image of Cu/ZnO_x/Na-ZSM-5 and (b) corresponding size distribution of Cu/ZnO_x NPs.

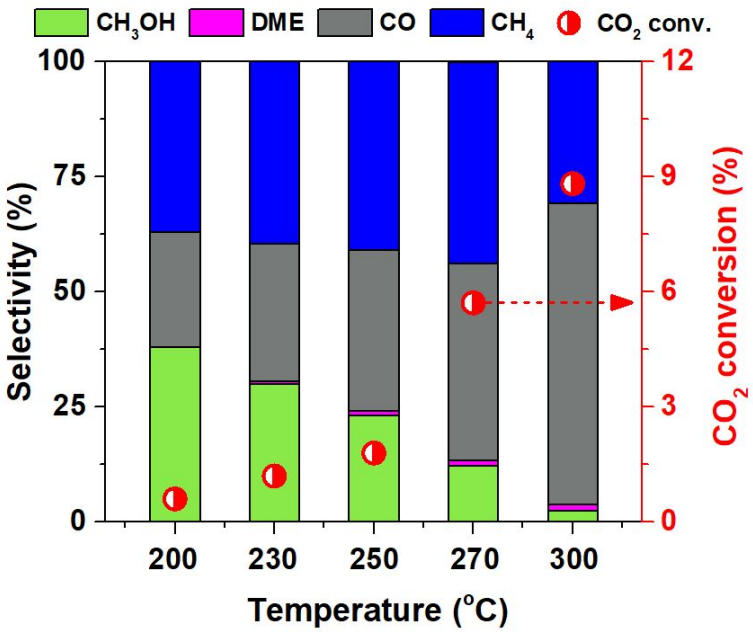

Figure S11. Dependences of the CO_2 conversion and product selectivity on temperature over $Cu/ZnO_x/Na\text{-}ZSM\text{-}5$ catalyst. Reaction conditions: 0.5 g of catalyst, 3.0 MPa, $H_2/CO_2/N_2$ = 71.5/23.5/5.0, and GHSV = 6,000 $mL \cdot g^{-1} \cdot h^{-1}$.

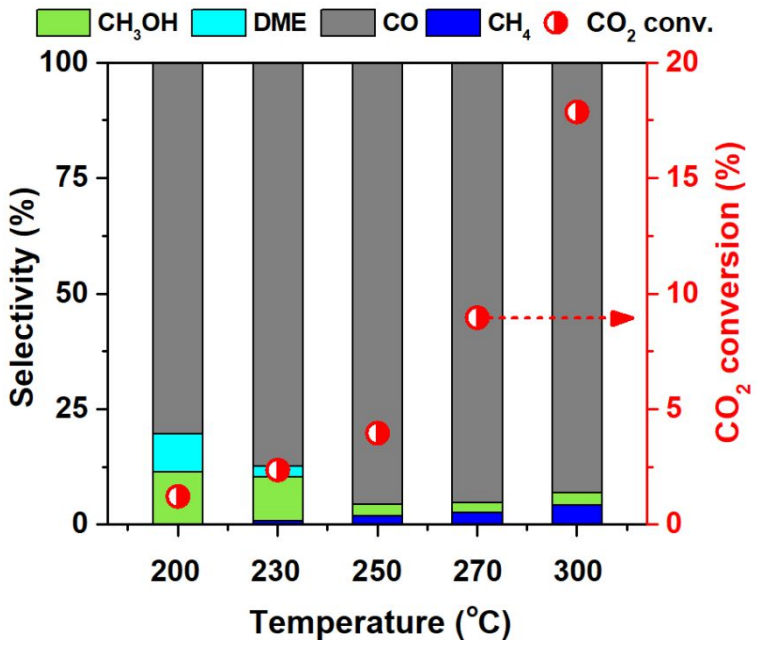

Figure S12. Dependences of the CO_2 conversion and product selectivity on temperature over Cu@Na-ZSM-5 catalyst. Reaction conditions: 0.5 g of catalyst, 3.0 MPa, $H_2/CO_2/N_2$ = 71.5/23.5/5.0, and GHSV = 6,000 $mL \cdot g^{-1} \cdot h^{-1}$.

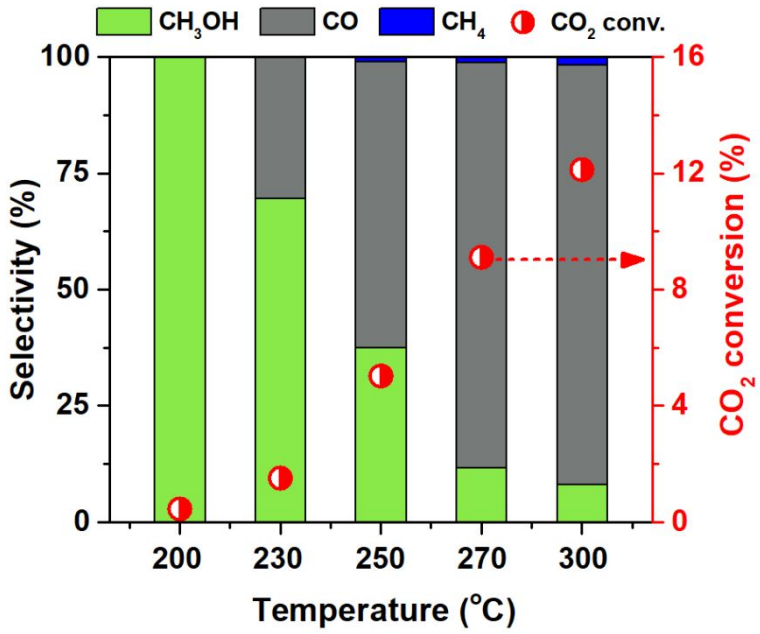

Figure S13. Dependences of the CO_2 conversion and product selectivity on temperature over $Cu/ZnO_x(2.23)$@Na-ZSM-5 catalyst. Reaction conditions: 0.5 g of catalyst, 3.0 MPa, $H_2/CO_2/N_2$ = 71.5/23.5/5.0, and GHSV = 6,000 $mL \cdot g^{-1} \cdot h^{-1}$.

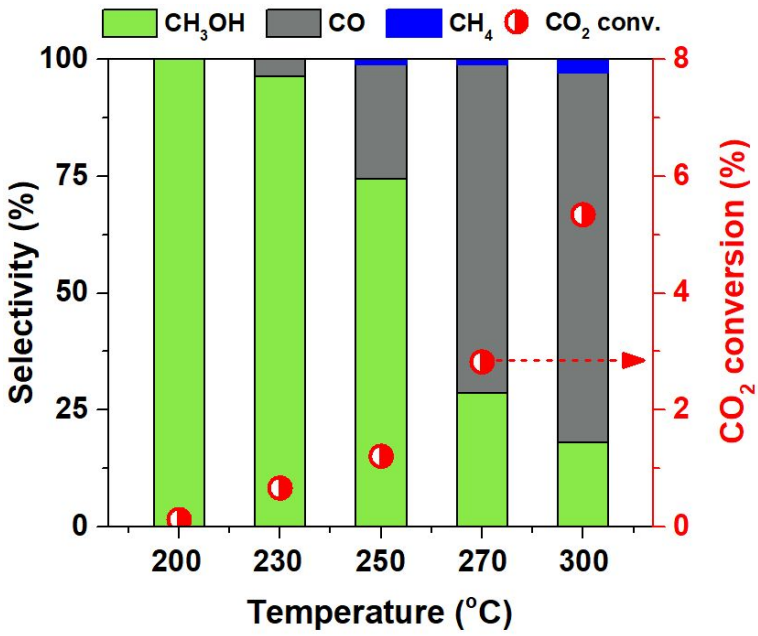

Figure S14. Dependences of the CO_2 conversion and product selectivity on temperature over $Cu/ZnO_x(0.48)$@Na-ZSM-5 catalyst. Reaction conditions: 0.5 g of catalyst, 3.0 MPa, $H_2/CO_2/N_2$ = 71.5/23.5/5.0, and GHSV = 6,000 $mL \cdot g^{-1} \cdot h^{-1}$.

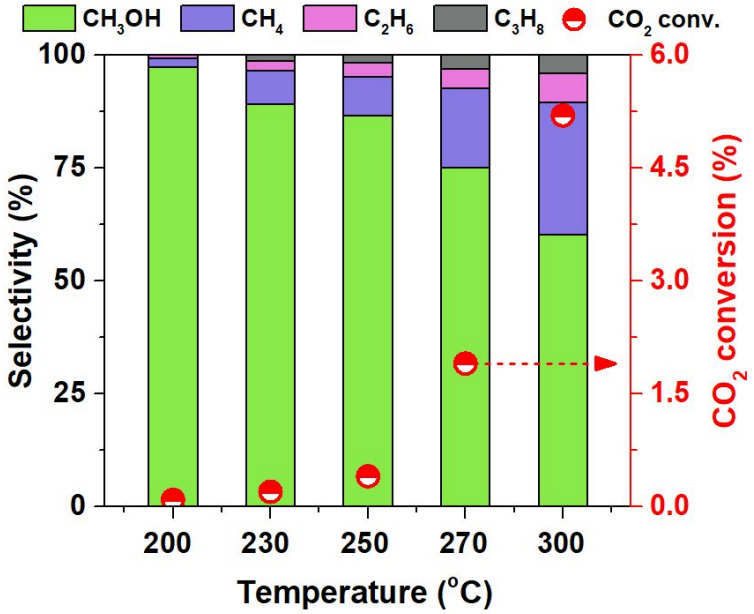

Figure S15. Dependences of the CO conversion and product selectivity on temperature over $Cu/ZnO_x(1.38)$@Na-ZSM-5 catalyst. Reaction conditions: 0.5 g of catalyst, 3.0 MPa, $H_2/CO_2/N_2$ = 71.5/23.5/5.0, and GHSV = 6,000 $mL \cdot g^{-1} \cdot h^{-1}$.

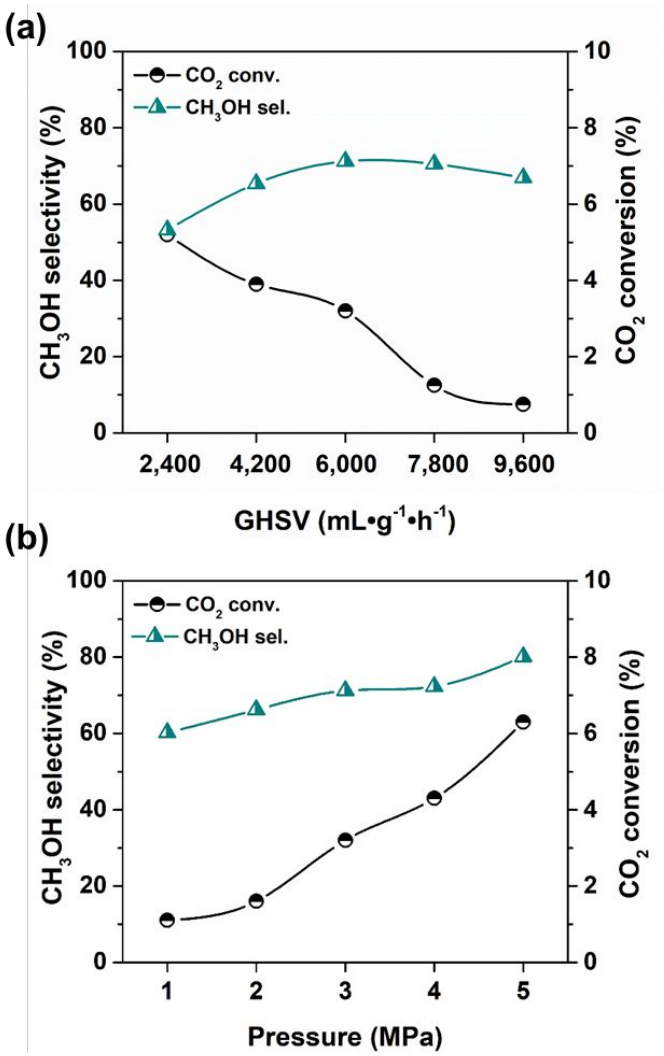

Figure S16. Data characterizing the influences of (a) velocity and (b) pressure to the performances of $Cu/ZnO_x(1.38)$@Na-ZSM-5 catalyst in CO_2 hydrogenation. Standard reaction conditions: 0.5 g of $Cu/ZnO_x(1.38)$@Na-ZSM-5 catalyst, 3.0 MPa, $H_2/CO_2/N_2$ = 71.5/23.5/5.0, 250 °C, and GHSV = 6,000 $mL \cdot g^{-1} \cdot h^{-1}$.

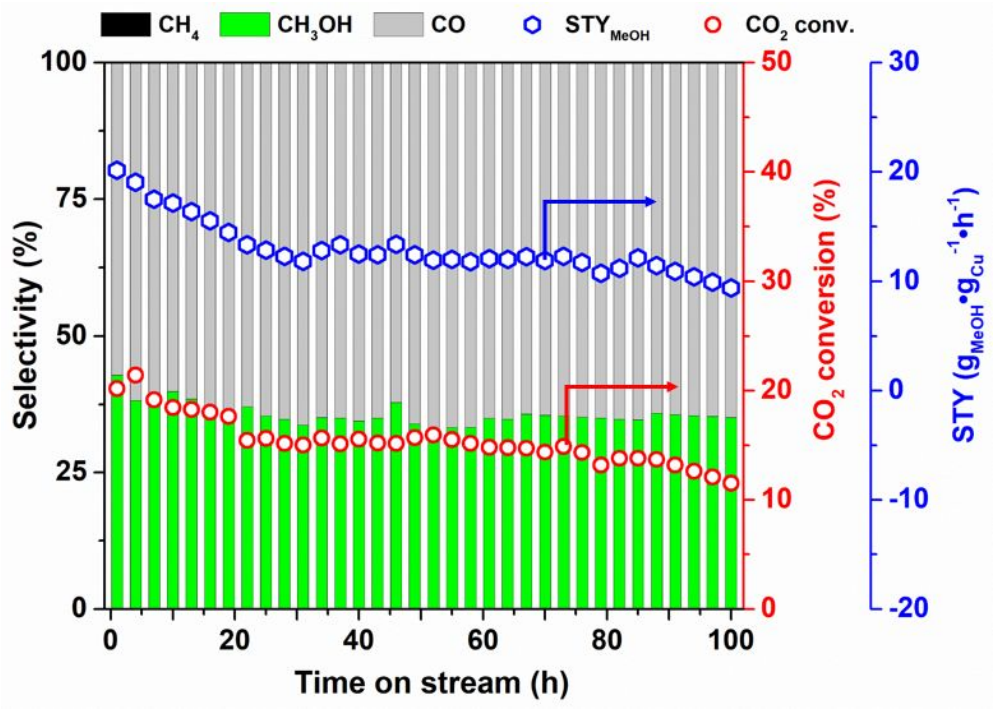

Figure S17. The durability of the industrial $Cu/ZnO/Al_2O_3$ catalyst in CO_2 hydrogenation. Reaction conditions: GHSV = 6,000 $mL \cdot g_{cat.}^{-1} \cdot h^{-1}$, 250 °C, 3.0 MPa, $H_2/CO_2/N_2$ = 71.5/23.5/5.0.

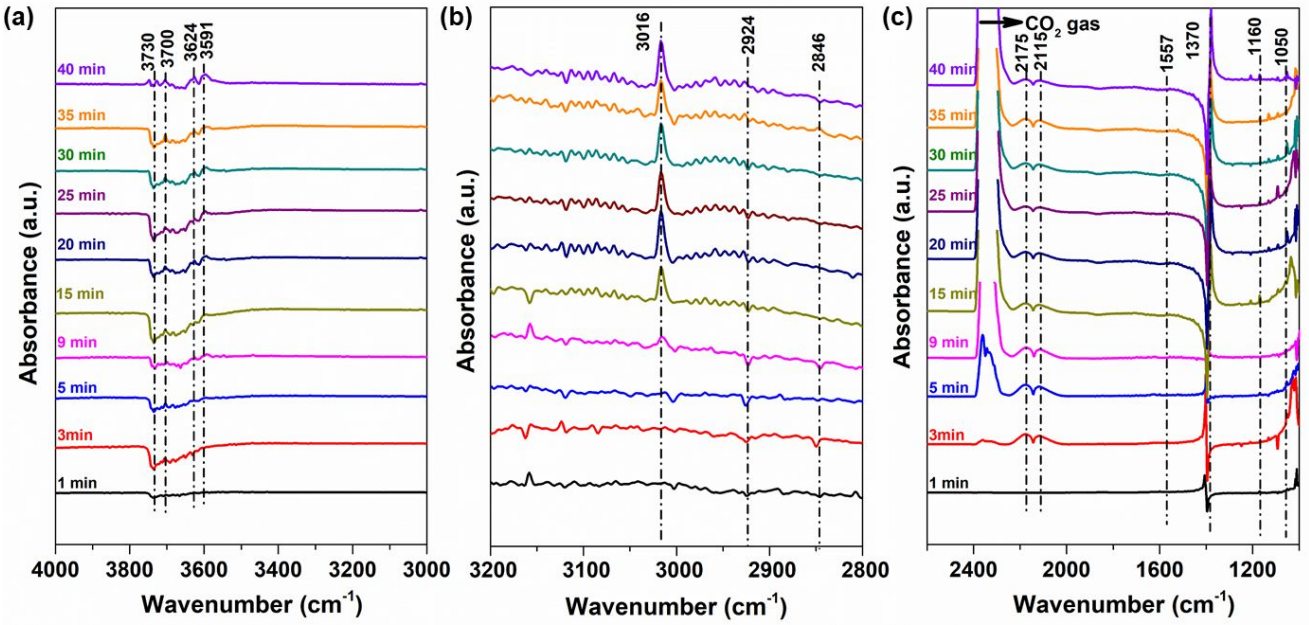

Figure S18. In situ FTIR spectra of the CO_2 hydrogenation reaction on Cu@Na-ZSM-5 catalyst. The catalyst was exposed to 71.5%H_2/23.5% CO_2/5%N_2 (20 mL·min^{-1}) atmosphere at 250 °C for 40 min.