Supporting information

Cu/ZnO$_x$@UiO-66 synthesized from a double solvents method as an efficient catalyst for CO_2 hydrogenation to methanol

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1. Loading Zn on MOF(UiO-66)

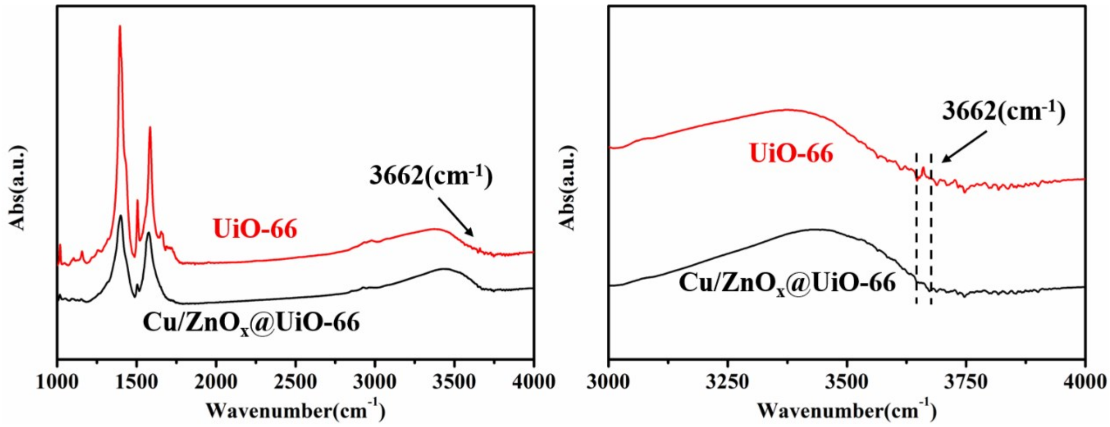

Figure S1. FT-IR spectra of UiO-66.

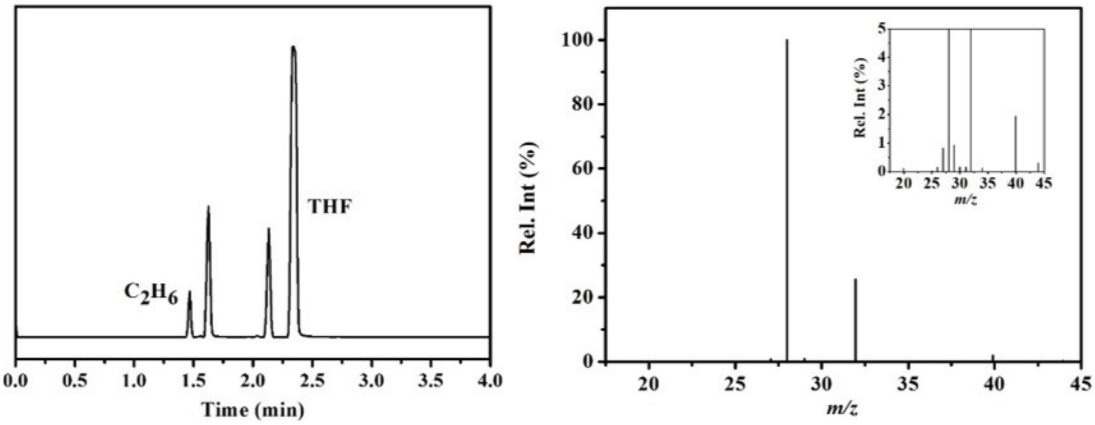

Figure S2. GC-MS results of THF solution which was left from the step of loading Zn with $Zn(Et)_2$.

$$(Zr_3)\mu_3\text{-OH} + ZnEt_2 \rightarrow (Zr_3)\mu_3\text{-O-Zn-Et} + C_2H_6 \quad (1\text{-}1)$$

$$ZnEt_2 + Cu(II) \rightarrow Zn(II) + Cu(0) + C_4H_{10} \quad (1\text{-}2)$$

The disappearance of (O-H) FT-IR peak at 3662 cm^{-1} in the SBUs and appearance of C_2H_6 in the THF solution can verify the correctness of the above equations.

2. H_2-TPR of Cu/ZnO_x@UiO-66

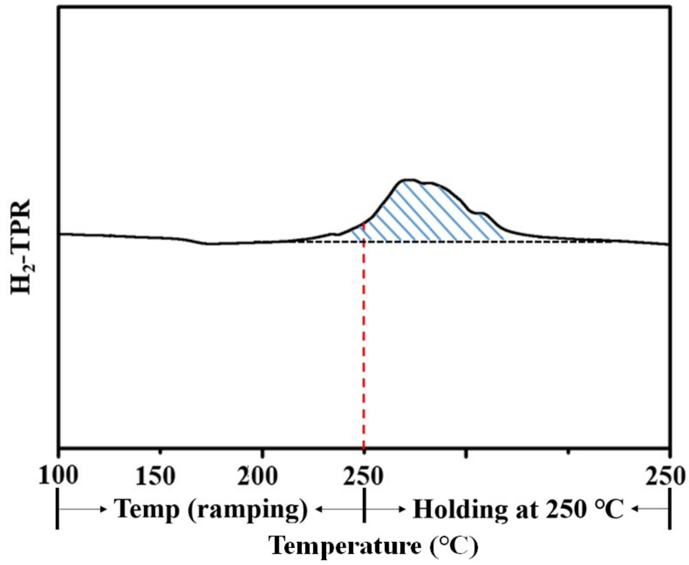

Figure S3. H_2-TPR of Cu/ZnO_x@UiO-66.

3. XRD patterns, TEM, and the performance of catalyst Cu/ZnO on UiO-66

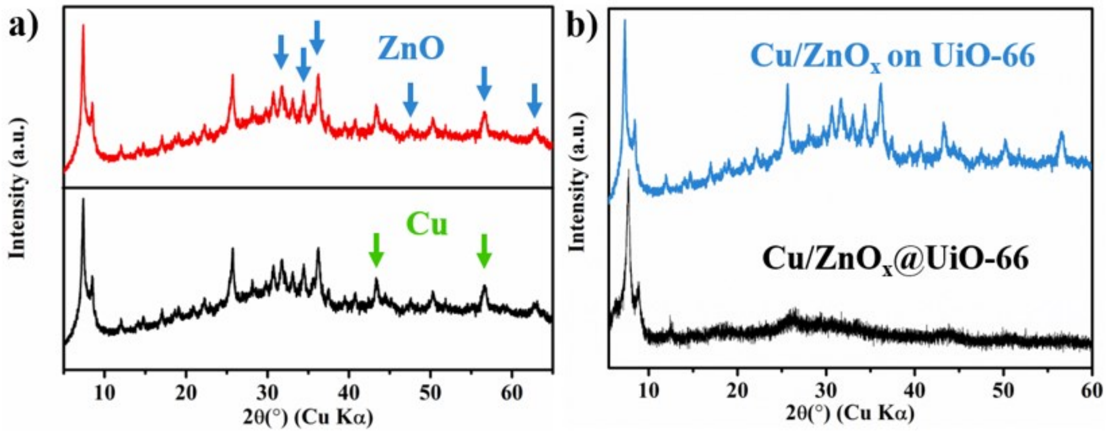

Figure S4. XRD patterns of Cu/ZnO on UiO-66.

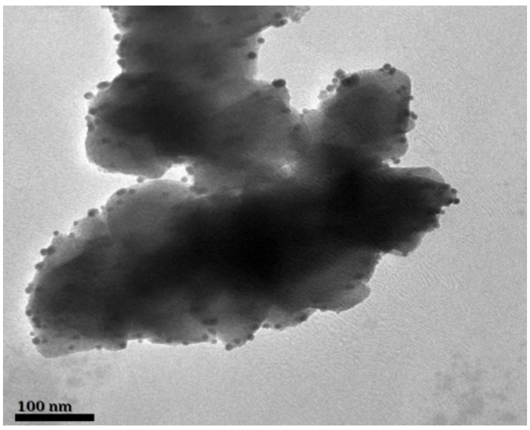

Figure S5. TEM pattern of Cu/ZnO on UiO-66.

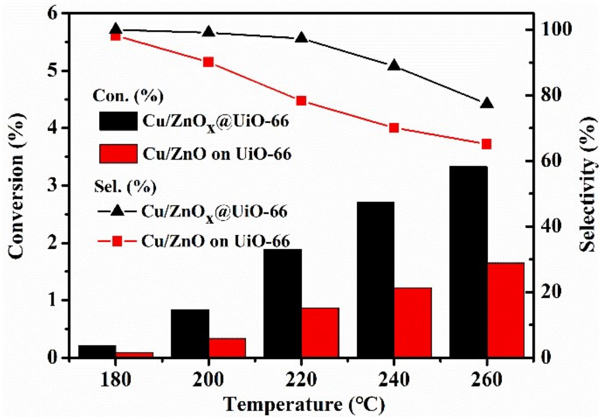

Figure S6. The conversion rate and selectivity of Cu/ZnO on UiO-66.

(P=4.0 MPa, GHSV=12000 h^{-1})

4. XRD patterns and TEM of catalyst Cu@UiO-66

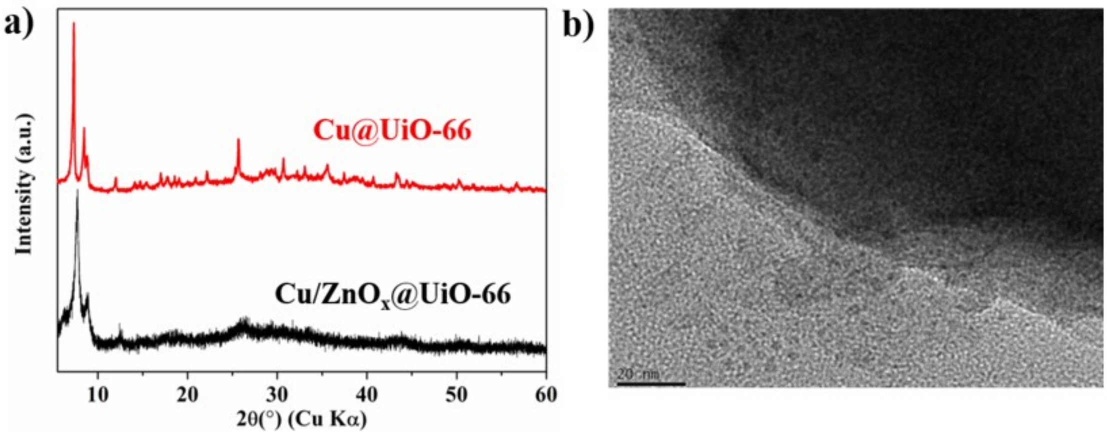

Figure S7. XRD and TEM patterns of Cu@UiO-66.

5. The structure diagram of the reaction tube

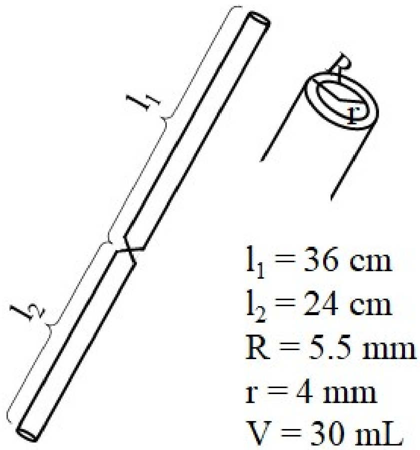

Figure S8. The structure diagram of the reaction tube.

6. The XRD of Cu/ZnO$_x$@UiO-66 before and after the reaction

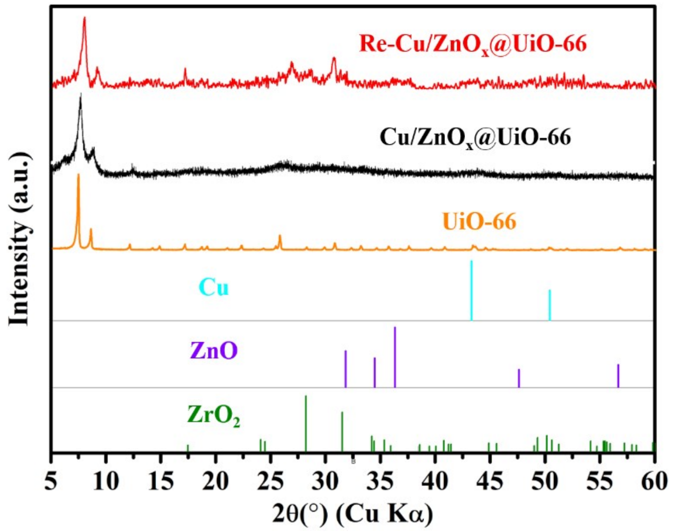

Figure S9. The XRD patterns of Cu/ZnO$_x$@UiO-66 before (black) and after the reaction (red).

7. Table S1. Comparison with copper-based representative catalysts for the hydrogenation of CO_2 to methanol

	Cu (wt.%)	Gas Flow	CO_2 conv. (%)	Select. (%)	STY ($kg_{MeOH}kg_{Cu}^{-1}h^{-1}$)	TOF×10^3 (s^{-1})	STY ($g_{MeOH}kg_{Cat}^{-1}h^{-1}$)
Cu/ZnO$_x$@UiO-66	5.86	18000(h^{-1})	3.00	87.5	1.66	6.62	97.3
(In this work)	5.86	12000(h^{-1})	3.51	86.1	1.27	5.08	74.4
	5.86	6000(h^{-1})	4.39	84.2	0.78	3.12	45.7
	5.86	1500(h^{-1})	7.33	82.4	0.32	1.28	18.8
Cu@UiO-66	6.65	12000(h^{-1})	1.72	60.2	0.38	1.53	25.2
Cu/ZnO on UiO-66	6.21	12000(h^{-1})	0.44	85.3	0.15	0.48	9.3
Cu/ZnO/Al_2O_3	50.13	12000(h^{-1})	9.72	47.2	0.23	-	115.3
	50.13	6000(h^{-1})	10.24	40.1	0.10	-	50.1
Cu-ZnO-Al_2O_3* (3 MPa, 250 °C)[1]	50.8	2600 (mL/g_{cat}/h)	6.30	68.6	0.09	-	44.7
Cu/Zn@UiO-bpy (4 MPa, 250 °C)[2]	6.9	18000(h^{-1})	3.3	100	2.59	2.96	-
Cu⊂UiO-66 (1MPa , 175 °C)[3]	-	28sccm	3	100	-	3.7	-
Cu@ZnO$_x$(core-shell) (3 MPa, 250 °C)[4]	-	18000(h^{-1})	2.3	100	-	-	147.2
$La_{0.8}Zr_{0.2}Cu_{0.7}Zn_{0.3}O_x$ (5 MPa, 250 °C)[5]	-	3600(h^{-1})	12.6	52.5	-	-	100.0
Pd-Cu/SBA-15 (4.1 MPa, 250 °C)[6]	10	3600(h^{-1})	6.5	23	0.23	-	23.0
Pd-Cu/SiO_2 (4.1 MPa, 250 °C)[6]	10	3600(h^{-1})	6.6	34	0.36	-	35.7
LDH30Ga (4.5 MPa, 270 °C)[7]	33.5	18000 (mL/g/h)	~20	~48	1.76	-	590.0
C6Z3Z1-OX (3 MPa, 240 °C)[8]	45.4	10000(h^{-1})	18.0	51.2	0.67	-	305.0

* Commercial benchmark catalyst. In this work, reaction condition: T = 250 °C, P = 4.0 MPa (H_2/CO_2=3).

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