

Supplementary Information

**Cu-ZnO nanoparticles encapsulated with ZSM-5 for selective conversion of
carbon dioxide to oxygenates**

**Xu Wang^{a,b}, Hwi Yeon Woo^a, Dongming Shen^a, Min Jung Park^a, Mansoor Ali^a, Faisal
Zafar^a, Kyun Yeon Kang^c, Jae-Soon Choi^c, Eunjoo Jang^{d,*}, Jong Wook Bae^{a,*}**

^aSchool of Chemical Engineering, Sungkyunkwan University (SKKU), 2066 Seobu-ro,
Jangan-gu, Suwon, Gyeonggi-do 16419, Republic of Korea

^bInstitute of Advanced Study, Chengdu University, Chengdu 610106, China

^cLG Chem., 188 Moonji-ro, Yuseong-gu, Daejeon, 34122, Republic of Korea

^dSKKU Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University (SKKU),
2066 Seobu-ro, Jangan-gu, Suwon, Gyeonggi-do 16419, Republic of Korea

*Corresponding author (E. Jang): Tel.: +82-31-299-4318; Fax: +82-31-299-4119; E-mail
address: ejjang1201@skku.edu

*Corresponding author (J.W. Bae): Tel.: +82-31-290-7347; Fax: +82-31-290-7272; E-mail
address: finejw@skku.edu

Materials

The copper (II) nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), tetrapropyl ammonium hydroxide (TPAOH) (40 wt.%), polyethylene glycol hexadecyl ether, Polyoxyethylene (10) ceetyl ether (Brij-C10) were purchased from Sigma-Aldrich. The tetraethyl orthosilicate (TEOS), aqueous ammonium hydroxide (~28%), aluminum nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) were purchased from Daejung Chemicals. Besides, the cyclohexane and zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) were obtained from Samchun Chemicals and Duksan Pure Chemicals respectively.

Supplementary methods

Conversion of CO_2 (X_{CO_2}) and product distributions (S_j) with a unit of mol% on the hybrid CZ(x)@Z(y)-t catalysts were calculated by using the following separate equations of (1) and (2), where N stands for an inlet and outlet mole of CO_2 reactant (i) and products (j) such as DME, methanol, and hydrocarbons.

$$X_{\text{CO}_2} = (1 - N_{i,\text{out}}/N_{i,\text{in}}) \times 100\% \text{ ----- (1)}$$

$$S_j = (N_j/(N_{i,\text{in}} - N_{i,\text{out}})) \times 100\% \text{ ----- (2)}$$

Turnover frequency (TOF (h^{-1})) of CO_2 conversion was calculated according to the equation (3), where SV represents space velocity (3000 mL/g/h), M_{cat} represents catalyst amount of CZ(x)@Z(y)-t (0.2 g), W_{CuO} stands for CuO content in the CZ@Z catalysts determined by XRF analysis, and N_{Cu} stands for the active copper composition which was estimated from H_2 -TPR analysis (50 - 410 °C). Space-time yield (STY, $\text{g}/(\text{g}_{\text{Cu}} \cdot \text{h})$) was calculated according to the average of Cu content in the catalyst.

$$\text{TOF} = ((\text{SV} \times M_{\text{cat}} \times 24.0\% \times X_{\text{CO}_2}) / (22.4 \times 10^3)) / ((M_{\text{cat}} \times W_{\text{Cu}} \times N_{\text{Cu}}) / 63.546) \text{ ----- (3)}$$

$$\text{STY} = (\text{SV} / 22.4 \times 24.0\% \times X_{\text{CO}_2} \times S_{\text{DME}} \times 46.07) / (W_{\text{CuO}} \times 63.546 / 79.545) \text{ ----- (4)}$$

Figure Captions

Figure S1. Particle size distribution of the fresh Cu-ZnO nanoparticles encapsulated in SiO₂, (a) CZ(1.25)@Si, (b) CZ(0.9)@Z(60)-12, (c) CZ(0.9)@Z(60)-24 and (d) CZ(0.9)@Z(60)-48 based on the TEM images in **Figure 3**.

Figure S2. HAADF images and EDS elemental mapping results of the fresh CZ(0.9)@Z(60)-24 catalyst (a) Local area of Cu-ZnO nanoparticles and (b) Entire CZ(0.9)@Z(60)-24 particle.

Figure S3. TEM image and size distribution of the used CZ(0.9)@Z(60)-24 catalyst after 100 h reaction.

Figure S4. TEM image and EDS elemental mapping results of the used CZ(0.9)@Z(60)-24 catalyst after 100 h reaction.

Figure S5. Py-IR spectra of the fresh CZ(0.9)@Z(60)-t catalysts (t = 12, 24, and 48 h)

Figure S6. EPR spectra of the fresh CZ(0.9)@Z(60)-t catalysts (t = 12, 24, and 48 h).

Figure S7. Catalytic activity with time-on-stream (TOS) on all the CZ(x)@Z(y)-t catalysts such as CO₂ conversion and product distribution measured at the reaction condition of T = 260 °C, P = 5.0 MPa, space velocity (SV) = 3000 mL/(g_{cat}·h) and a feed gas composition of CO₂/H₂/N₂ = 72/24/4.

Table S1. Summarized results of bulk composition and surface properties such as reducibility, acidic and basic sites of the CZ(x)@Z(y)-t catalysts.

Table S2. Comparisons of catalytic activity of the CZ(0.9)@Z(60)-24 with previously reports concerning CO₂ hydrogenation.

Table S3. Catalytic performances of the hybridized reference CZ@Si and ZSM-5 catalysts with different preparation methods

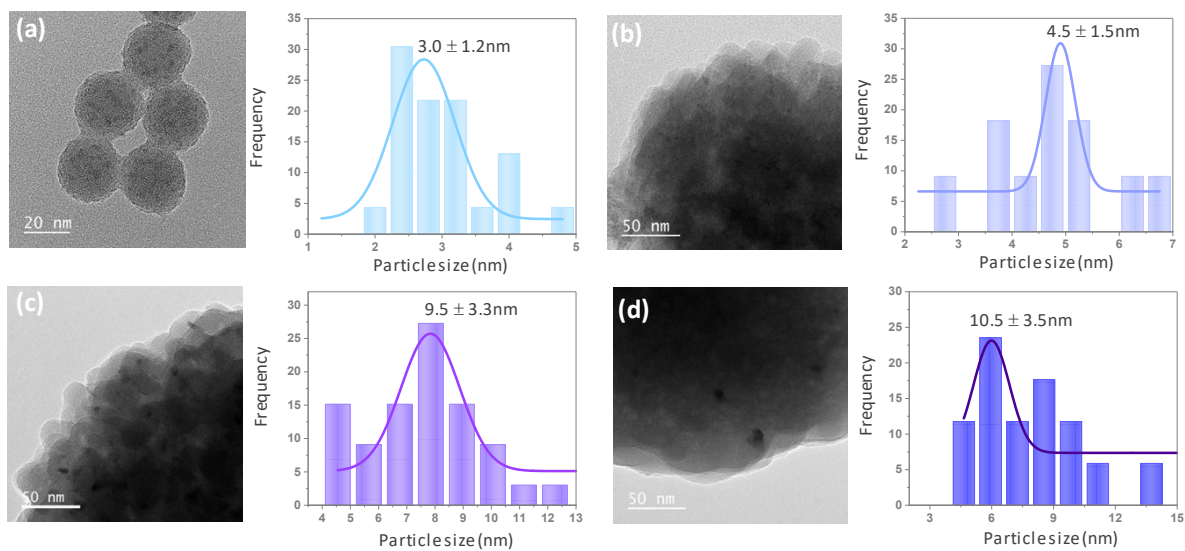


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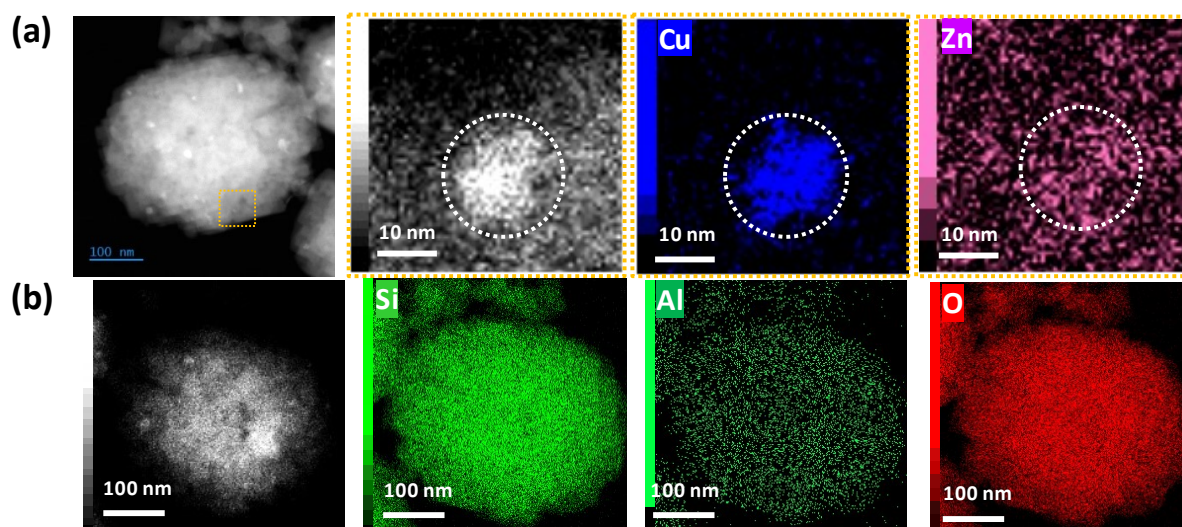


Figure S2. HADF images and EDS elemental mapping results of the fresh CZ(0.9)@Z(60)-24 catalyst (a) Local area of Cu-ZnO nanoparticles and (b) Entire CZ(0.9)@Z(60)-24 particle.

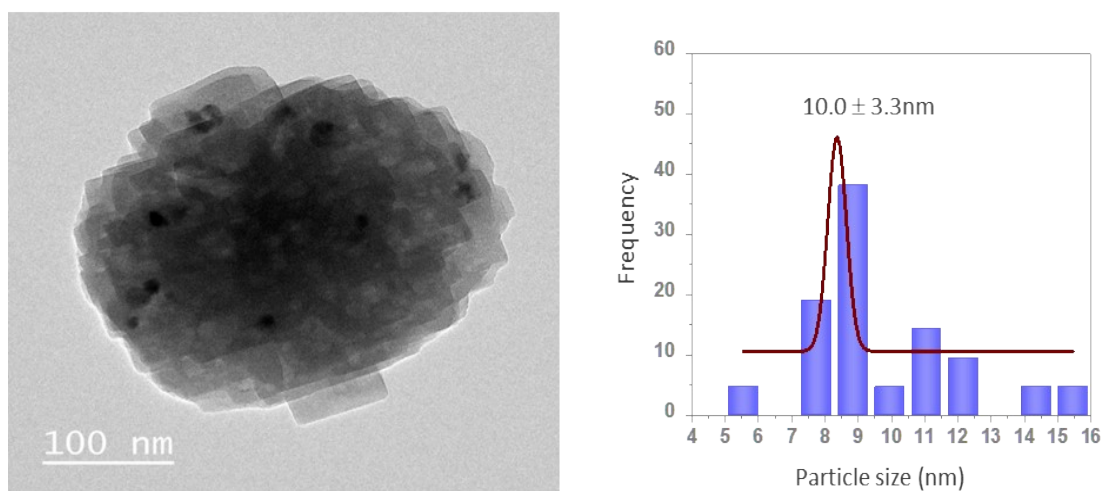


Figure S3. TEM image and size distribution of the used CZ(0.9)@Z(60)-24 catalyst after 100 h reaction.

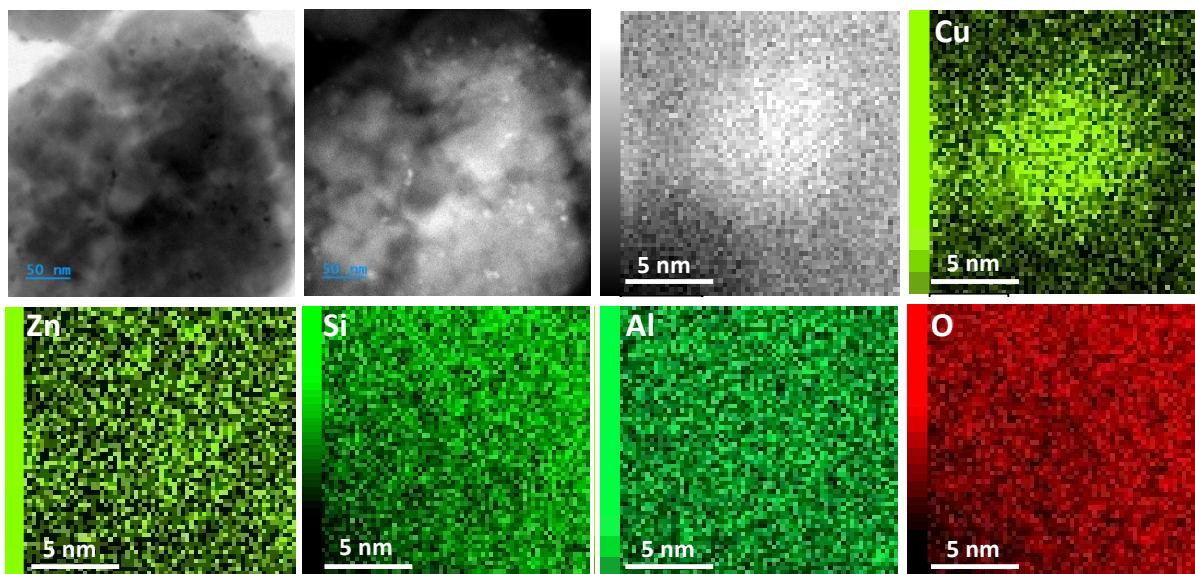


Figure S4. TEM image and EDS elemental mapping results of the used CZ(0.9)@Z(60)-24 catalyst after 100 h reaction.

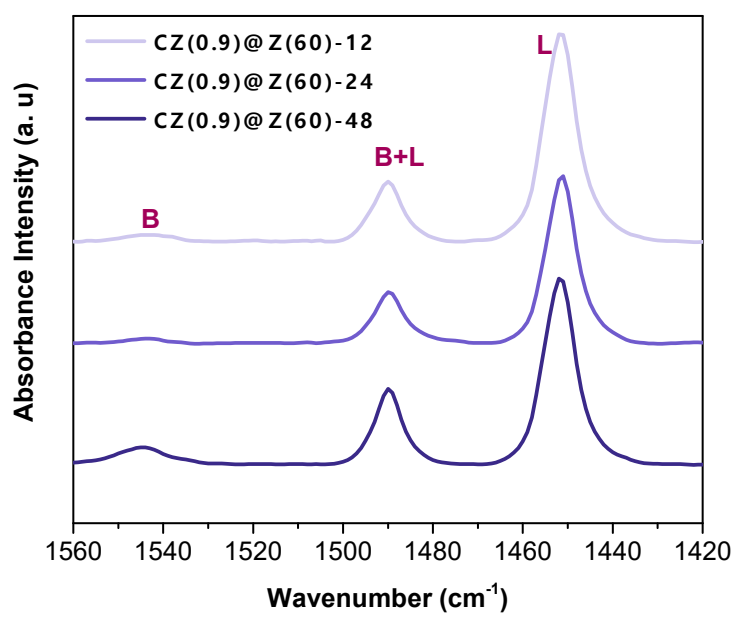


Figure S5. Py-IR spectra of the fresh CZ(0.9)@Z(60)-t catalysts (t = 12, 24, and 48 h).

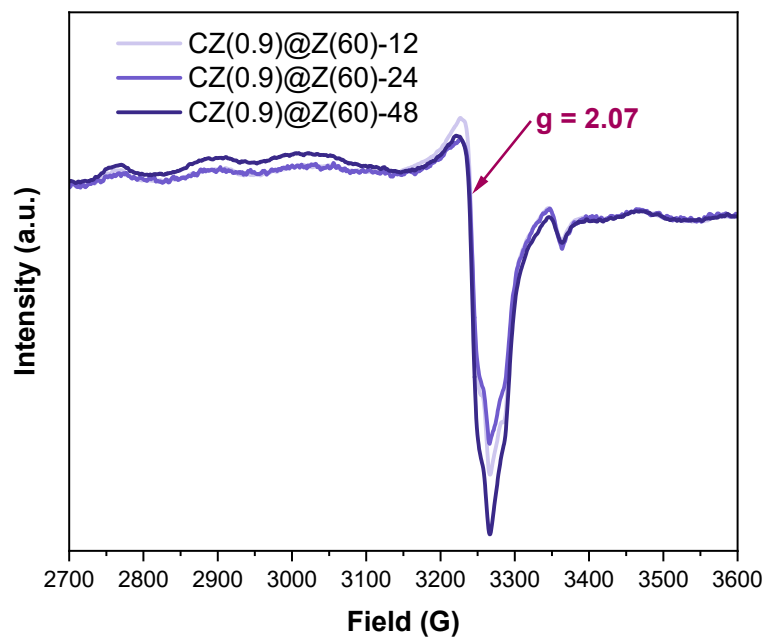


Figure S6. EPR spectra of the fresh CZ(0.9)@Z(60)-t catalysts (t = 12, 24, and 48 h).

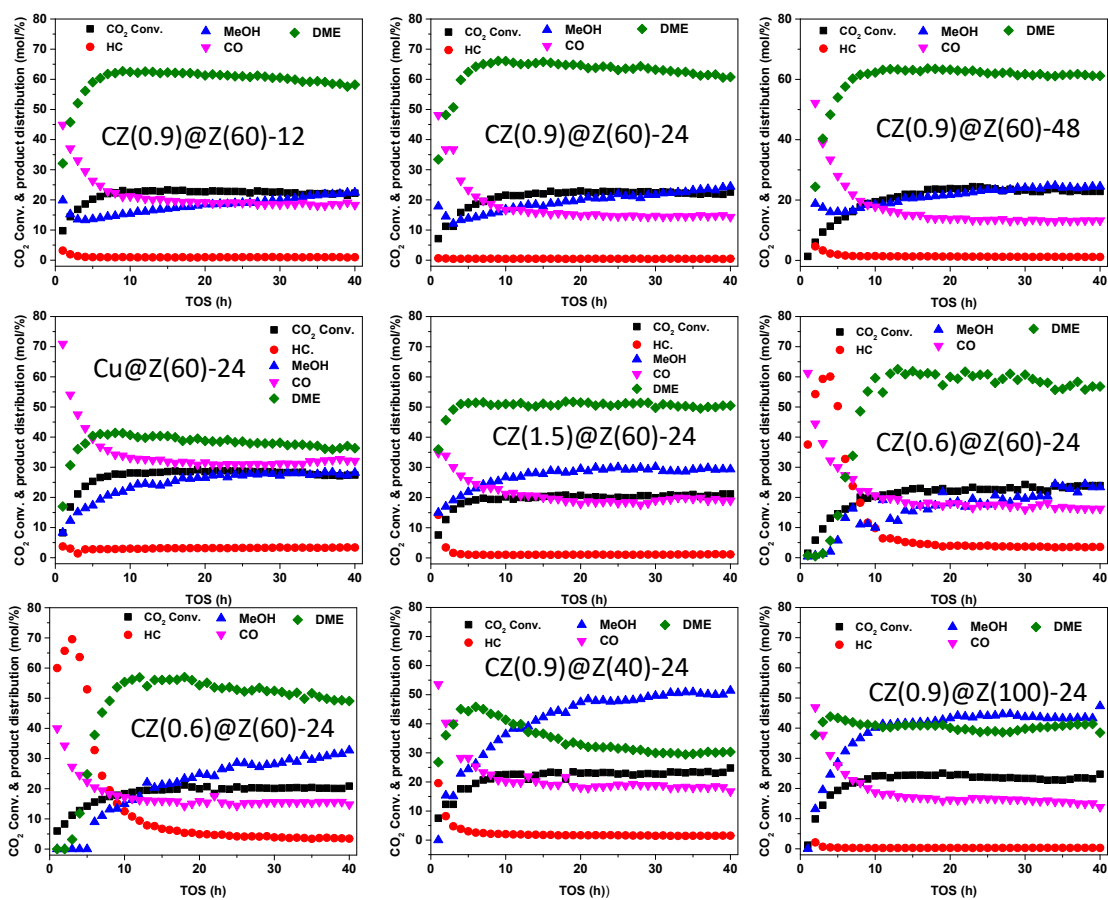


Figure S7. Catalytic activity with time-on-stream (TOS) on all the CZ(x)@Z(y)-t catalysts such as CO₂ conversion and product distribution measured at the reaction condition of T = 260 °C, P = 5.0 MPa, space velocity (SV) = 3000 mL/(g_{cat}·h) and a feed gas composition of CO₂/H₂/N₂ = 72/24/4.

Table S1. Summarized results of bulk composition and surface properties such as reducibility, acidic and basic sites of the CZ(x)@Z(y)-t catalysts.

Catalyst ^a	XRF compound weight (wt.%) ^b	TPR ^c	NH ₃ -TPD ^d	CO ₂ -TPD ^e	XPS ^f
	CuO/ZnO/SiO ₂ /Al ₂ O ₃	H ₂ consumption (mmol/g) [$\alpha/\beta/\gamma/\delta$ /Total]	W/M/S(total) (mmol/g)	W/M/S(total) ((mmol/g)	Surface atomic content (Cu/Zn/Si/Al/O)
CZ(0.9)@Z(60)-12	2.16/2.50/94.19/1.16	0.095/0.131/0.184/0.391/0.801	0.584/0.256/0.218 (1.058)	0.284/0.258/0.112 (0.654)	0.60/0.56/29.1/1.04/68.7
CZ(0.9)@Z(60)-24	1.72/2.16/94.73/1.39	0.052/0.120/0.154/0.354/0.680	0.418/0.233/0.105 (0.819)	0.250/0.158/0.118 (0.526)	0.36/0.74/26.5/1.50/70.9
CZ(0.9)@Z(60)-48	1.11/2.21/95.32/1.36	0.060/0.128/0.097/0.304/0.589	0.340/0.135/0.078 (0.553)	0.222/0.127/0.154 (0.503)	0.30/1.40/25.9/1.50/70.9
Cu@Z(60)-24	5.77/-/92.90/1.33	0.320/1.022/0.916/0.635/2.893	0.238/0.044/0.101 (0.382)	0.473/0.266/0.227 (0.966)	2.70/-/27.2/0.60/69.5
CZ(0.9)@Z(40)-24	1.73/2.31/93.84/2.13	-/0.256/0.385/0.143/0.784	0.317/0.247/0.102 (0.666)	0.229/0.160/0.063 (0.453)	-
CZ(0.9)@Z(100)-24	1.75/2.46/95.00/0.80	0.105/0.233/0.250/0.218/0.806	0.257/0.135/0.075 (0.467)	0.551/0.267/0.042 (0.860)	-
CZ(0.3)@Z(60)-24	1.05/3.95/93.70/1.30	0.174/0.099/0.123/0.108/0.504	0.357/0.348/0.158 (0.863)	0.512/0.211/0.069 (0.792)	-
CZ(0.6)@Z(60)-24	1.51/3.21/93.99/1.30	0.153/0.176/0.211/0.223/0.763	0.294/0.230/0.138 (0.662)	0.472/0.405/0.169 (1.046)	-
CZ(1.5)@Z(60)-24	3.30/2.13/93.26/1.31	0.205/0.357/0.443/0.225/1.230	0.298/0.214/0.105 (0.617)	0.392/0.223/0.183 (0.798)	-

^aCZ(x)@Z(y)-t represents CuZnO nanoparticles encapsulated with ZSM5 shells prepared at different crystallization time (t=12, 24, 48 h), the Cu/Zn molar ratio (x = 0.3, 0.6, 0.9 and 1.5), and the Si/Al molar ratio (y = 40, 60 and 100). ^bChemical composition (wt%) of Cu, Zn, Si and Al species obtained from XRF analysis. ^cAmount of H₂ consumption (mmol/g) was estimated by H₂-TPR analysis with four different reduction peaks at 150 - 250 °C (α), 250 - 350 °C (β), 350 - 400 °C (γ) and >400 °C (δ). ^dAcidic sites measured by NH₃-TPD analysis, categorized with weak (W), medium (M) and strong (S) acid sites with its total amount at maximum desorption of NH₃ at temperature ranges of 100 - 300, 300 - 500 and >500 °C, respectively. ^eAmount of CO₂ desorption (mmol/g) was calculated according to the different desorption temperature of CO₂ such as weak (W) at 100 - 300 °C, medium (M) at 300 - 450 °C and strong (S) basic sites at >450 °C, respectively. ^fThe molar ratios on the reduced catalysts were measured by XPS analysis.

Table S2. Comparisons of catalytic activity of the CZ(0.9)@Z(60)-24 with previously reports concerning CO₂ hydrogenation

Catalyst	Reaction conditions			X _{CO2} (%)	Selectivity (%)					Productivity ^c (g/(g _{Cu} ·h))	Ref.
	T (°C)	Space velocity (SV)	P (MPa)		HC ^b	CO	Methanol (MeOH)	DME	MeOH + DME		
CZ(0.9)@ZSM(60)-24	260	3000 ml/(g·h)	5.0	20.8	0.5	17.9	19.4	62.2	81.6	13.9	This Work
		3000 ml/(g·h)	3.0	17.4	1.4	19.4	41.4	37.8	79.2	7.1	
		6000 ml/(g·h)	5.0	10.0	0.9	24.9	33.5	40.7	74.2	8.8	
CuZnOZrO ₂ /HZSM5	240	10000 L/(kg _{cat} ·h)	3.0	~14	-	56	12	32	44	1.4	[1]
CIZO-SAPO	250	6000 mL/(g _{cat} ·h)	3.0	4.3	-	32.4	7.1	60.6	67.7	0.56	[2]
CZZ-MFI				21.3	-	46.6	12.9	40.5	53.4	1.0	
CZZ-MOR	260	8800 L/(kg _{cat} ·h)	5.0	23.2	-	38.1	11.2	50.8	62.0	1.0	[3]
CZZ-FER				26.0	-	31.5	12.8	55.7	68.5	1.2	
Mh-ZSM5-AlCu	260	9000 L/(kg _{cat} ·h)	3.0	4.25	-	-	31.0	24.4	56.4	0.26	[4]
CZZ&Al-TUD-1	260	10000 h ⁻¹	2.0	~7	-	~76	~14	9.2	~24	0.27	[5]
CuZnZr-FER	280	8800 NL/(kg _{cat} ·h)	5.0	30	-	24	14	62	76	3.73	[6]
CuOZnOAl ₂ O ₃ /MCM41	250	40000mL/(g _{cat} ·h)	4.5	-	-	37.3	33.6	29.1	62.7	3.30	[7]
CuOZnOZrO ₂ /WO _x Al ₂ O ₃	260	65 mL/min	3.0	18.9	-	67.8	18.1	13.2	31.3	1.05	[8]
Cu _{2.4wt%} /Al ₂ O ₃	270	30 mL/min	2.5	0.9	-	~58	~18	~24	~42	0.4	[9]

^aCatalytic performances were obtained at the reference feed gas composition of H₂/CO₂ = 3. ^bHC represents hydrocarbons products. ^cProductivity for DME and methanol (MeOH) was presented with the unit of (g/(g_{Cu}·h)).

Table S3. Catalytic performances of the hybridized reference CZ@Si and ZSM-5 catalysts with different preparation methods

Catalyst ^a	X_{CO_2} (mol%)	Product distribution (mol%)			
		CO	HC	Methanol	DME
CZ@Si	17.7	31.2	9.0	59.8	0
CZ@Si/ZSM-5(1/1)	23.1	41.5	4.7	30.2	23.6
CZ@Si/ZSM-5(1/2)	13.1	47.6	36.2	11.6	4.6
CZ(0.9)@Z(60)-24	20.8	17.9	0.5	19.4	62.2
CZ(0.9)/ZSM-5(60)	12.5	34.5	0.5	34.2	30.8

^aCO₂ conversion (X_{CO_2}) and product distribution (selectivity to CO, hydrocarbons (HC, mainly CH₄), methanol and dimethyl ether (DME)) were measured at the reaction condition of T = 260 °C, P = 5.0 MPa, space velocity (SV) = 3000 mL/(g_{cat}·h) with a feed gas of CO₂/H₂/N₂ = 72/24/4. The CZ@Si/ZSM-5(1/1 or 1/2) represents the Cu-ZnO(0.9) nanoparticles-encapsulated with SiO₂ shells and physically mixed with the ZSM-5(60) zeolite at different CZ@Si/ZSM-5 ratio of 1/1 or 1/2. The CZ(0.9)/ZSM-5(60) represented the hybridized catalyst prepared by a simple wet impregnation method. The data were presented with steady state values when they were stabilized after its initial induction period.

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