

Supplementary Material

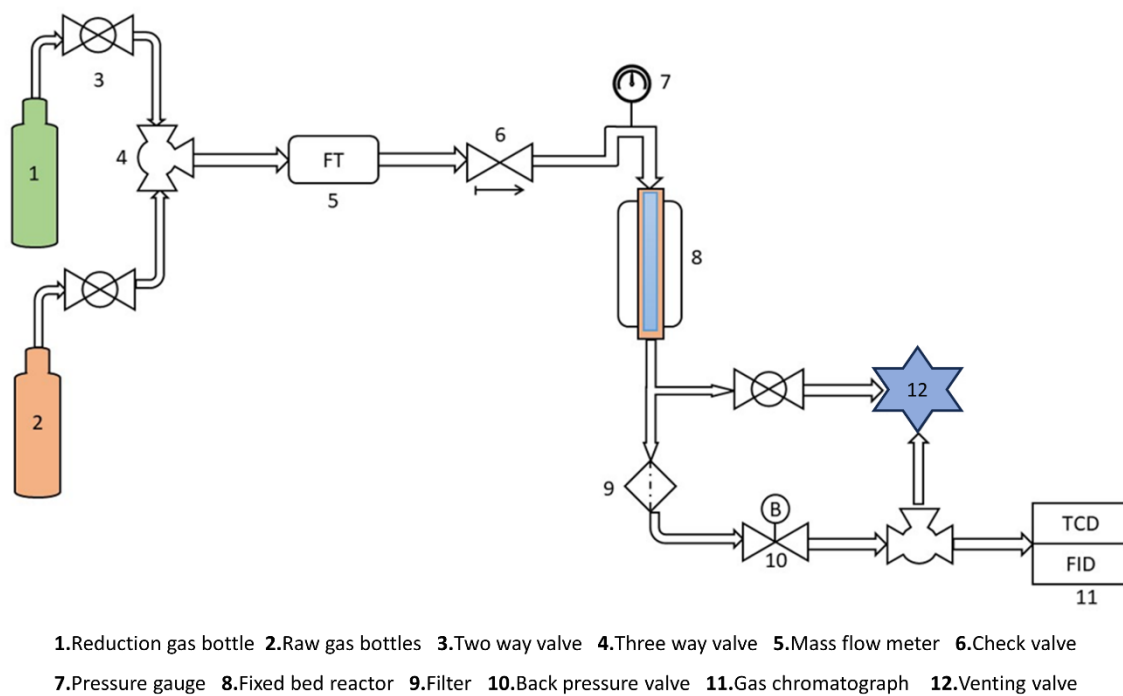


Figure S1. Schematic diagram of the reaction apparatus for CO₂ hydrogenation to methanol.

Table S1. Peak area parameters of the different Cu-ZnO-ZrO₂ catalysts.

Catalyst	A _β /(a.u.)	A _γ /(a.u.)
CZZ-1	17753	9504
CZZ-3	18965	9529
CZZ-6	27823	10977
CZZ-12	12111	18753

Table S2. XPS parameters of the different Cu-ZnO-ZrO₂ catalysts.

Catalyst		BE (eV)			Relative metal content (at%)		
		Cu2p _{3/2}	Zn2p _{3/2}	Zr3d _{5/2}	Cu	Zn	Zr
CZZ-1	calcined	933.1	1021.4	181.8	29.5	41.5	29.0
	reduced	932.0	1021.4	181.7	31.9	38.8	29.3
CZZ-3	calcined	933.2	1021.3	181.8	29.5	20.3	50.2
	reduced	931.7	1021.3	181.9	28.5	21.5	50.0
CZZ-6	calcined	933.1	1021.3	181.8	24.9	21.2	53.9
	reduced	931.7	1021.3	181.9	23.3	20.3	56.4
CZZ-12	calcined	933.2	1021.5	181.8	20.0	46.7	33.3
	reduced	931.9	1021.3	181.7	21.7	45.4	32.9

Table S3. Comparison of the activity of Cu-Zn-Zr catalysts.

Composition	Preparation method	Reaction conditions	Catalytic performance	Ref.
Cu/Zn/Zr = 6:3:1 molar ratio	co-precipitation	T = 250 °C, H ₂ /CO ₂ = 3 (v/v), P = 5 MPa, GHSV = 4600 h ⁻¹	CO ₂ conv. = 21.0%, S _{MeOH} = 59.4%, Y _{MeOH} = 12.5 %	[12]
Cu/Zn/Zr = 5:2:3 molar ratio	combustion	T = 240 °C, H ₂ /CO ₂ = 3 (v/v), P = 3 MPa, GHSV = 3600 h ⁻¹	CO ₂ conv. = 12.0%, S _{MeOH} = 71.1%, Y _{MeOH} = 8.5%	[21]
Cu/Zn/Zr = 6:3:1 molar ratio	complexation by citric acid	T = 240 °C, H ₂ /CO ₂ = 3 (v/v), P = 3 MPa, GHSV = 10000 mL·g _{cat} ⁻¹ ·h ⁻¹	CO ₂ conv. = 12.5%, S _{MeOH} = 51.8%, Y _{MeOH} = 6.5%	[11]
Cu/ZnO/ZrO ₂ =	co-precipitation	T = 250 °C, H ₂ /CO ₂ = 3	CO ₂ conv. = 19.4%, S _{MeOH}	[46]

50/40/10 wt%		(v/v), P = 3 MPa, GHSV = 3000 h ⁻¹	= 29.3%, Y _{MeOH} = 5.7%	
Cu/Zn/Zr = 6:3:1 molar ratio	oxalate-gel coprecipitation	T = 200 °C, H ₂ /CO ₂ = 4 (v/v), P = 3 MPa, WHSV = 48,000 cm ³ h ⁻¹ g _{cat} ⁻¹ .	CO ₂ conv. = 4.5%, S _{MeOH} = 85.0%, Y _{MeOH} = 3.8%	[47]
Cu/Zn/Zr = 4:3:3 molar ratio	reverse co- precipitation	T=240 °C, H ₂ /CO ₂ =3, P = 2 MPa, GHSV=14400 mLg _{cat} ⁻¹ h ⁻¹	CO ₂ conv. = 13.2%, S _{MeOH} = 32.3%, Y _{MeOH} = 4.3%	[7]
CuO/ZnO/ZrO ₂ = 37.5/41/21.5 wt%	micro-fluidic continuous coprecipitation	T = 240 °C, H ₂ /CO ₂ = 3.89 (v/v), P = 50 bar, GHSV = 10000 h ⁻¹	CO ₂ conv. = 9.3%, S _{MeOH} = 47.0%, Y _{MeOH} = 4.4%	[48]
Cu/Zn/Zr = 6:3:1 molar ratio	co-precipitation	T = 240 °C, H ₂ /CO ₂ = 3 (v/v), P = 3 MPa, GHSV = 10000 mL·g _{cat} ⁻¹ ·h ⁻¹	CO ₂ conv. = 16.0%, S _{MeOH} = 48.7%, Y _{MeOH} = 7.8%	[11]
CuO/ZnO/ZrO ₂ = 15.1/41.8/43.1 wt%	reverse co- precipitation	T = 240 °C, H ₂ /CO ₂ = 3 (v/v), P = 3 MPa, GHSV = 4400 mL·g _{cat} ⁻¹ ·h ⁻¹	CO ₂ conv. = 17.5%, S _{MeOH} = 48.4%, Y _{MeOH} = 8.5%	[49]
Cu/Zn/Zr = 6:3:1 molar ratio	reverse co- precipitation	T = 260 °C, H ₂ /CO ₂ = 3 (v/v), P = 4 MPa, WHSV = 5400 mL·g _{cat} ⁻¹ ·h ⁻¹	CO ₂ conv. = 22.0%, S _{MeOH} = 30.0%, Y _{MeOH} = 6.6%	[50]
Cu/Zn/Zr = 45:45:10 molar ratio	gel-oxalate coprecipitation	T = 240 °C, H ₂ /CO ₂ = 3 (v/v), P = 2 MPa, GHSV = 3600 h ⁻¹	CO ₂ conv. = 18.5%, S _{MeOH} = 38.4%, Y _{MeOH} = 7.1%	[51]
Cu/Zn/Zr = 6:3:1 molar ratio	gel-oxalate coprecipitation	T = 240 °C, H ₂ /CO ₂ = 3 (v/v), P = 3 MPa, GHSV = 10000 mL·g _{cat} ⁻¹ ·h ⁻¹	CO ₂ conv. = 18.0%, S _{MeOH} = 51.2%, Y _{MeOH} = 9.2%	[11]
Cu/Zn/Zr = 5:2:3 molar ratio	CTAB assisted co-precipitation	T = 240 °C, CO ₂ :H ₂ = 1:3 (v/v), P = 3.0 MPa, GHSV = 3600 h ⁻¹	CO ₂ conv. = 12.1%, S _{MeOH} = 54.1%, Y _{MeOH} = 6.5%	[52]
Cu/Zn/Zr = 30/15/55 wt%	P123 assisted co-precipitation	T = 250 °C, CO ₂ :H ₂ = 1:3 (v/v), P = 3.0 MPa, GHSV = 6000 mL·g _{cat} ⁻¹ ·h ⁻¹	CO ₂ conv. = 23.0%, S _{MeOH} = 34.0%, Y _{MeOH} = 7.8%	[53]
Cu/Zn/Zr = 5:2:3 molar ratio	microwave assisted	T = 240 °C, CO ₂ :H ₂ = 1:3 (v/v), P = 3.0 MPa, GHSV =	CO ₂ conv. = 17.4%, S _{MeOH} = 37.5%, Y _{MeOH} = 6.5%	[24]

	hydrothermal	2400 mL·g _{cat} ⁻¹ ·h ⁻¹		
Cu/Zn/Zr = 5:2:3 molar ratio	polymeric precursor	T = 240 °C, CO ₂ :H ₂ = 1:3 (v/v), P = 3.0 MPa, GHSV = 2400 mL·g _{cat} ⁻¹ ·h ⁻¹	CO ₂ conv. = 16.8%, S _{MeOH} = 41.4%, Y _{MeOH} = 7.0%	[15]
Cu/Zn/Zr = 4:5:1 molar ratio	solid-state	T = 240 °C, H ₂ /CO ₂ = 3 (v/v), P = 3 MPa, GHSV = 7000 h ⁻¹	CO ₂ conv. = 11.9%, S _{MeOH} = 93.5%, Y _{MeOH} = 11.1%	[54]
Cu/Zn/Zr = 5:2:3 molar ratio	solvothermal	T = 240 °C, CO ₂ :H ₂ = 1:3 (v/v), P = 3.0 MPa, GHSV = 2400 mL·g _{cat} ⁻¹ ·h ⁻¹	CO ₂ conv. = 15.6%, S _{MeOH} = 46.1%, Y _{MeOH} = 7.2%	this work
