Supporting Information

Enhancement of CO_2 Hydrogenation to Methanol over Cu-Based Catalyst Mixed with Hydrophobic Additives

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Table S1. The CO_2 hydrogenation performance of the Cu/Zn/Zr-PDVB catalyst for methanol synthesis.

Catalyst	CO_2 Conv. (%)	Selectivity (%)			Productivity ($^{mg_{MeOH}/g_{cat}}$/h)
		MeOH	CH_4	CO	
Cu/Zn/Zr-PDVB-0.5	19.35	38.49	0	61.51	162.4
Cu/Zn/Zr-PDVB-0.75	22.66	48.76	0	51.24	203.7
Cu/Zn/Zr-PDVB-1	23.45	50.23	0	49.77	245.4
Cu/Zn/Zr-PDVB-1.25	22.82	49.23	0	50.77	225.2
Cu/Zn/Zr-PDVB-1.5	20.22	41.82	0	58.18	172.6

Reaction conditions: 260°C, 5 MPa, gas hourly space velocity (GHSV) of 6000 mL/$^{g_{cat}}$/h, with a feed gas composition of $H_2/CO_2/N_2$ molar ratio of 67.5/22.5/10. Cu/Zn/Zr-PDVB-1 represents a PDVB/catalyst mass ratio of 1.

Table S2. CO_2 hydrogenation performance for methanol synthesis over Cu/Zn/Zr and Cu/Zn/Zr-PDVB catalysts at different temperatures.

Catalyst	Temperature (°C)	CO_2 Conv. (%)	Selectivity (%)			Productivity ($^{mg_{MeOH}/g_{cat}}$/h)
			MeOH	CH_4	CO	
Cu/Zn/Zr	240	17.08	51.07	0	48.93	184.8
Cu/Zn/Zr	250	19.37	50.45	0	49.55	198.6
Cu/Zn/Zr	260	20.07	50.22	0	49.78	203.4
Cu/Zn/Zr	270	21.62	43.25	0	56.75	193.8
Cu/Zn/Zr	280	22.74	33.51	0	66.49	165.1
Cu/Zn/Zr-PDVB	240	18.65	51.48	0	48.52	196.5
Cu/Zn/Zr-PDVB	250	22.14	50.84	0	49.16	229.2
Cu/Zn/Zr-PDVB	260	23.45	50.23	0	49.77	245.4
Cu/Zn/Zr-PDVB	270	23.96	45.63	0	54.37	213.9
Cu/Zn/Zr-PDVB	280	24.13	38.43	0	61.57	193.7

Reaction conditions: 5 MPa, GHSV of 6000 mL/$^{g_{cat}}$/h, with a feed gas composition of $H_2/CO_2/N_2$

molar ratio of 67.5/22.5/10. Cu/Zn/Zr-PDVB refers to the mixed catalyst with a PDVB/catalyst mass ratio of 1.

Table S3. CO_2 hydrogenation performance for methanol synthesis over Cu/Zn/Zr catalysts mixed with PDVB of different particle sizes.

Catalyst	PDVB mesh	CO_2 Conv. (%)	Selectivity (%)			Productivity ($^{mg_{MeOH}/g_{cat}}$/h)
			MeOH	CH_4	CO	
Cu/Zn/Zr-PDVB	40-60	21.61	46.20	0	53.80	202.3
Cu/Zn/Zr-PDVB	60-100	22.05	47.01	0	52.99	209.8
Cu/Zn/Zr-PDVB	100-200	23.45	50.23	0	49.77	245.4
Cu/Zn/Zr-PDVB	200-300	21.17	44.14	0	55.86	190.1

Reaction conditions: 260°C, 5 MPa, GHSV of 6000 mL/$^{g_{cat}}$/h, with a feed gas composition of $H_2/CO_2/N_2$ molar ratio of 67.5/22.5/10. Cu/Zn/Zr-PDVB refers to the mixed catalyst with a PDVB/catalyst mass ratio of 1.

Table S4. CO_2 hydrogenation performance for methanol synthesis over Cu/Zn/Zr catalysts with different particle sizes.

Catalyst	Catalyst mesh	CO_2 Conv. (%)	Selectivity (%)			Productivity ($^{mg_{MeOH}/g_{cat}}$/h)
			MeOH	CH_4	CO	
Cu/Zn/Zr	40-60	19.89	50.23	0	49.77	201.8
Cu/Zn/Zr	60-80	20.07	50.22	0	49.78	203.4
Cu/Zn/Zr	80-100	20.37	50.17	0	49.83	206.1
Cu/Zn/Zr	100-200	20.51	50.08	0	49.92	208.5

Reaction conditions: 260°C, 5 MPa, GHSV of 6000 mL/$^{g_{cat}}$/h, with a feed gas composition of $H_2/CO_2/N_2$ molar ratio of 67.5/22.5/10.

Table S5. CO_2 hydrogenation performance for methanol synthesis over Cu/Zn/Zr catalysts with different mixing manners of PDVB.

Catalyst	Mixed manner	CO_2 Conv. (%)	Selectivity (%)			Productivity ($^{mg_{MeOH}/g_{cat}}$/h)
			MeOH	CH_4	CO	
Cu/Zn/Zr	Unmixed	20.07	50.22	0	49.78	203.1
Cu/Zn/Zr	Quartz sand mixing	20.02	50.21	0	49.79	202.9
Cu/Zn/Zr-PDVB	Dual layers mixing	20.10	50.24	0	49.76	203.6
Cu/Zn/Zr-PDVB	Powder mixing	23.45	50.23	0	49.77	245.4

Reaction conditions: 260°C, 5 MPa, GHSV of 6000 mL/$^{g_{cat}}$/h, with a feed gas composition of $H_2/CO_2/N_2$ molar ratio of 67.5/22.5/10.

Table S6. CO_2 hydrogenation performance for methanol synthesis on pure Cu catalysts mixed with different wetting materials.

Catalyst	CO_2 Conv. (%)	Selectivity (%)			Productivity ($^{mg_{MeOH}/g_{cat}}$/h)
		MeOH	CH_4	CO	
Cu	4.77	54.25	0.32	45.44	21.4
Cu-PDVB	8.36	54.18	0.17	45.65	39.5
Cu-PTFE	5.46	52.79	0.39	46.81	27.8
Cu-PA	3.25	56.42	0.84	42.74	16.7
Cu-TiO2	2.55	59.47	1.32	39.21	14.9
Cu-SiO2	2.00	57.44	1.15	41.41	12.9

Reaction conditions: 240°C, 5 MPa, GHSV of 6000 mL/$^{g_{cat}}$/h, with a feed gas composition of $H_2/CO_2/N_2$ molar ratio of 67.5/22.5/10.

Table S7. Outlet gas composition after reaction of Cu/Zn/Zr-PDVB catalyst.

Gas Composition	Feed Gas (mol%)	Effluent Gas(mol%)
CO_2	67.5	59.96
H_2	22.5	17.40
N_2	10	10.65
CO	-	3.11
MeOH	-	3.14
H_2O	-	5.74

Reaction conditions: 260°C, 5 MPa, GHSV of 6000 mL/g_{cat}/h, with a feed gas composition of $H_2/CO_2/N_2$ molar ratio of 67.5/22.5/10.

Table S8. Distribution of Cu element valence states on different catalyst surfaces.

Catalyst types	Cu^0 Peak(%)	$Cu^{\delta+}$ Peak (%)	Cu^{2+} Peak (%)
Pre-reduced Cu/Zn/Zr	54.35	23.24	21.20
Used Cu/Zn/Zr-PDVB	54.45	21.09	24.46
Used Cu/Zn/Zr	46.30	18.98	34.72

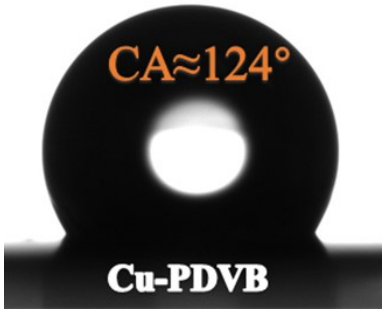

Figure S1. The water contact angle of Cu-PDVB catalyst.

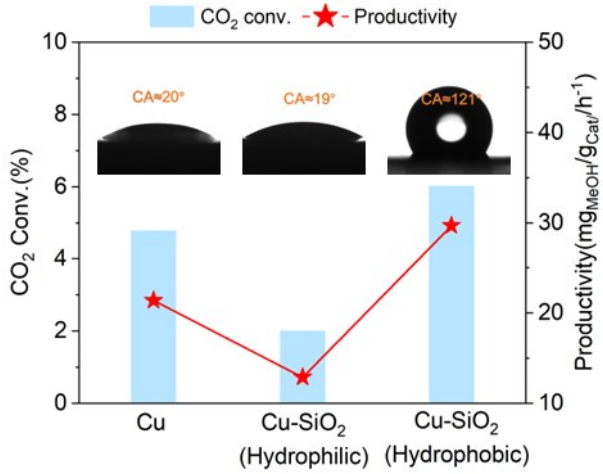

Figure S2. Catalytic performance of Cu-SiO_2 Catalyst with different wettability. Reaction Conditions: 240°C, 5 MPa, GHSV = 6000 mL/g_{cat}/h, and a molar ratio of $H_2/CO_2/N_2$ of 67.5/22.5/10.

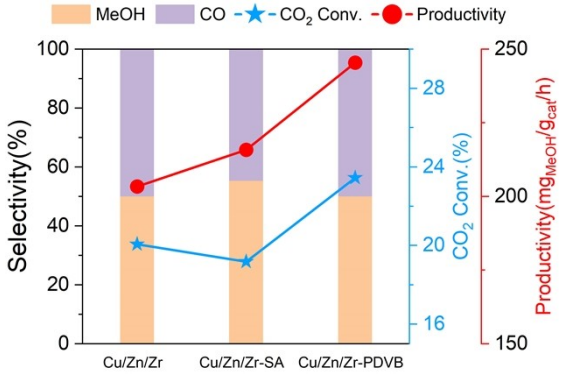

Figure S3. Catalytic performance of stearic acid modified Cu/Zn/Zr Catalyst. Reaction Conditions: 260°C, 5 MPa, GHSV = 6000 mL/g_{cat}/h, and a molar ratio of $H_2/CO_2/N_2$ of 67.5/22.5/10.

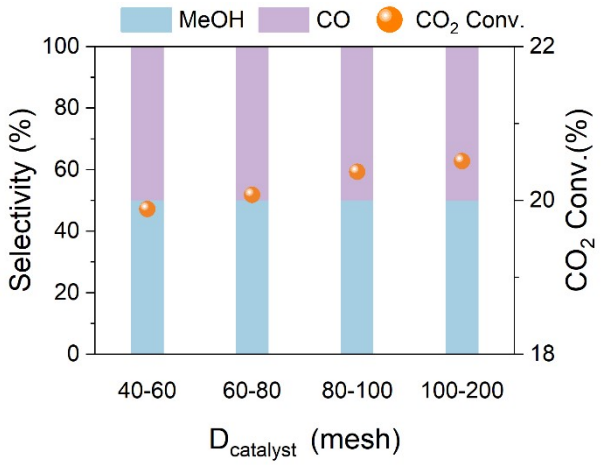

Figure S4. Catalytic performance of Cu/Zn/Zr Catalysts with different particle sizes. Reaction Conditions: 260°C, 5 MPa, GHSV = 6000 mL/g_{cat}/h, and a molar ratio of $H_2/CO_2/N_2$ of 67.5/22.5/10.

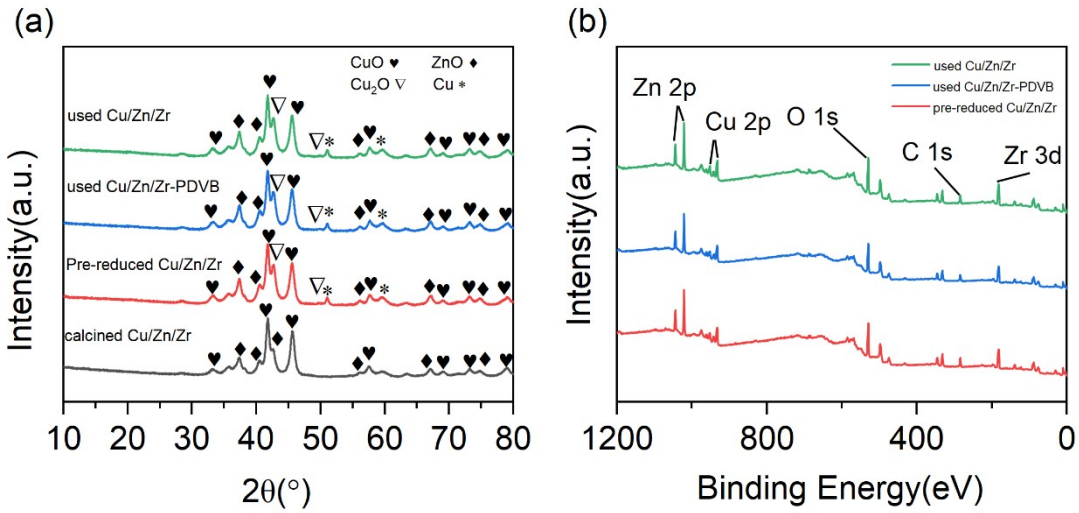

Figure S5. XRD (a) and XPS (b) spectrogram of Cu/Zn/Zr Catalyst.

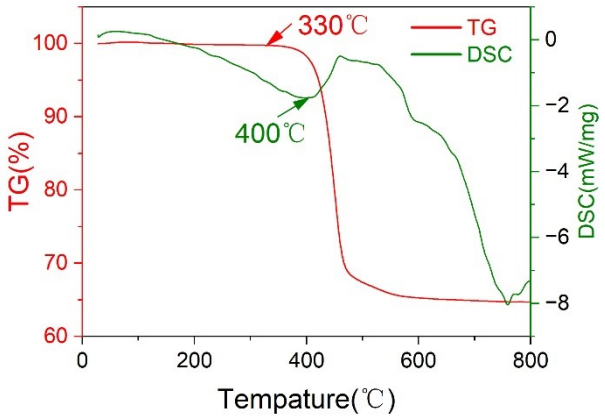

Figure S6. TG-DSC analysis of PDVB.

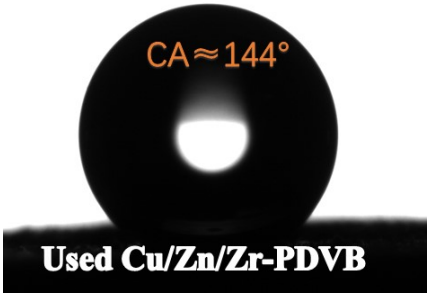

Figure S7. The water contact angle of used Cu/Zn/Zr-PDVB catalyst.

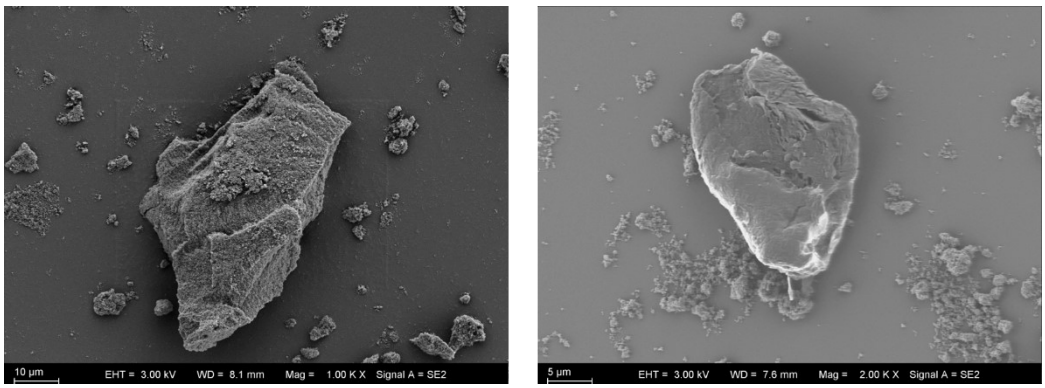

Figure S8. SEM images of PDVB before (left) and after (right) reaction.

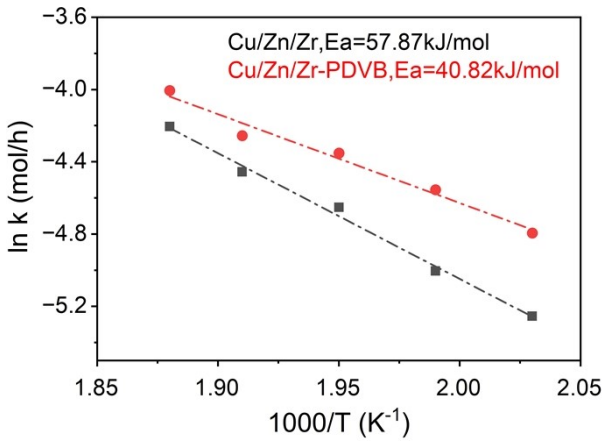

Figure S9. The Arrhenius plots for CO_2 hydrogenation were conducted over Cu/Zn/Zr and Cu/Zn/Zr-PDVB catalysts.

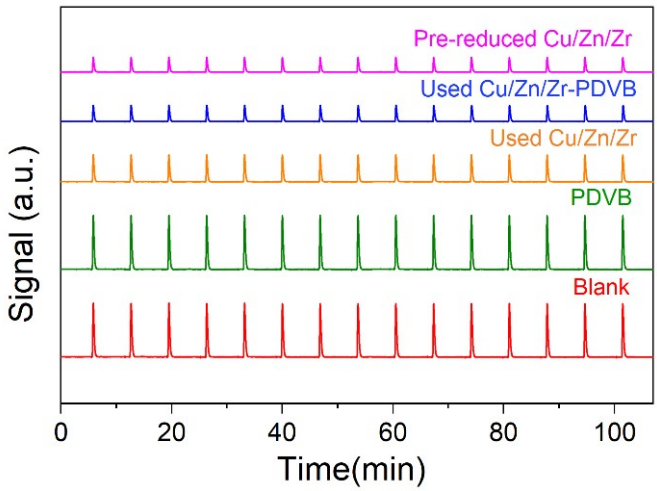

Figure S10. H_2 pulse tests on different catalysts.

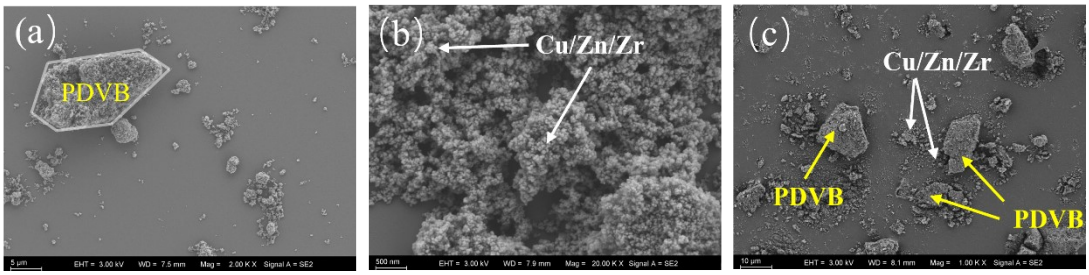

Figure S11. SEM images of PDVB (a), Cu/Zn/Zr (b), and Cu/Zn/Zr-PDVB (c).

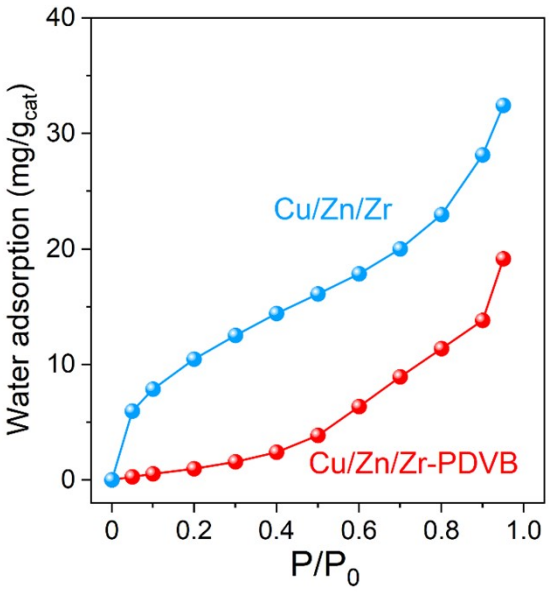

Figure S12. Water vapor adsorption test of Cu/Zn/Zr and Cu/Zn/Zr-PDVB catalysts.

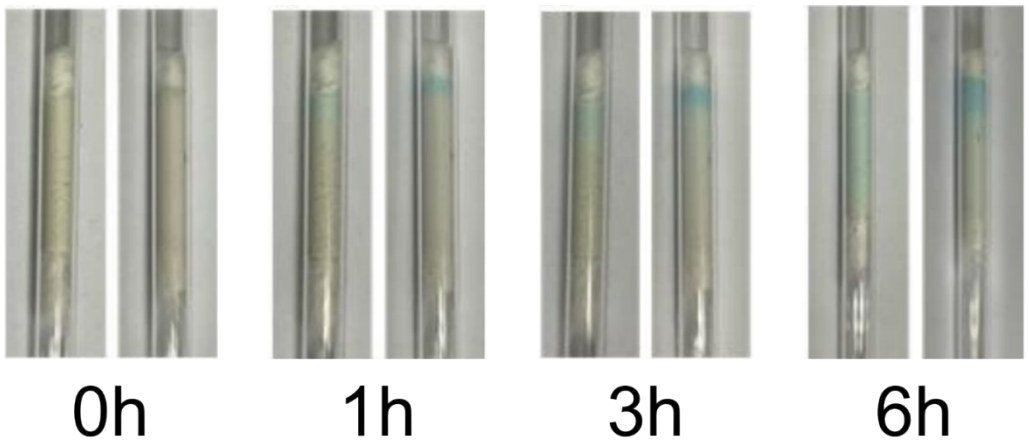

Figure S13. Photos of anhydrous $CuSO_4$ mixed with PDVB (left) and anhydrous $CuSO_4$ mixed with quartz powder (right) with H_2O/N_2 (30 mL/min) flow at room temperature for different periods.