

ORIGINAL RESEARCH ARTICLE

Kinetic analysis and process optimization of carbon dioxide hydrogenation to methanol over copper/zinc oxide/self-pillared pentasil-zeolite catalyst

Supplementary Files

Table S1. Carbon dioxide conversion and yields of methanol and carbon monoxide

Temperature (°C)	180	200	220	240	260	280	300
P (bar)				30			
Feed CO ₂ /H ₂				1/2			
X _{CO₂} (%)	0.91	2.00	3.37	8.89	15.76	20.52	23.44
Y _{CH₃OH} (%)	0.51	1.12	1.61	2.50	2.59	2.25	1.57
Y _{CO} (%)	0.37	0.82	1.66	6.17	12.90	18.01	21.68
P (bar)				30			
Feed CO ₂ /H ₂				1/3			
X _{CO₂} (%)	2.28	3.82	8.23	14.61	21.94	24.68	26.91
Y _{CH₃OH} (%)	1.90	3.00	4.45	5.17	5.70	4.67	3.12
Y _{CO} (%)	0.38	0.83	3.78	9.44	16.24	20.01	23.79
Pressure (bar)				30			
Feed CO ₂ /H ₂				1/4			
X _{CO₂} (%)	1.12	2.26	3.69	10.31	19.87	26.65	30.30
Y _{CH₃OH} (%)	0.81	1.49	2.06	3.50	4.08	3.77	2.78
Y _{CO} (%)	0.28	0.71	1.52	6.51	15.38	22.47	27.19
Pressure (bar)				50			
Feed CO ₂ /H ₂				1/3			
X _{CO₂} (%)	1.31	3.04	4.83	12.35	19.64	23.40	26.12
Y _{CH₃OH} (%)	1.08	2.26	2.90	5.26	5.34	4.96	4.19
Y _{CO} (%)	0.21	0.71	1.79	6.72	13.81	17.94	21.48

Note: Carbon dioxide conversion and methanol and carbon oxide yields measured in the fixed-bed micro-reactor at various temperatures and pressures using 0.1 g of catalyst and 30 mL/min feed flow of different compositions.

Table S2. Comparisons of thermodynamic parameters with the widely cited values

Reaction	Equation	ΔH° (kJ·mol ⁻¹)	Equilibrium expressions	Reaction no.
Carbon dioxide to methanol synthesis	$\text{CO}_2 + 3 \text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O}$	-49.4	$\log K_1 = 3,176.3/T - 10.672^a$ $\log K_1 = 3,066/T - 10.592^b$	1
Reversed water-gas shift	$\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$	41.1	$\log K_2 = -2,082.2/T + 1.9316^a$ $\log K_2 = -2,073/T + 2.029^b$	2
Syngas to methanol	$\text{CO} + 2 \text{H}_2 \rightleftharpoons \text{CH}_3\text{OH}$	-90.5	$\log K_3 = 2,610.9/T - 8.5583^a$	3

Notes: ^aCalculated using ΔH° with pressures in bar, and used in the present work. ^bLiterature values that are widely cited (Graaf¹).

Table S3. Comparison of the methanol space-time yield with the literature

Scenario ^[a]	P (bar)	T (K)	Carbon dioxide (vol.%)	Hydrogen (vol.%)	Flow rate (NmL·g _{cat} ⁻¹ /min)	S _{MeOH} (%) ^{a,b}	Normalized WTY _{MeOH} ^b
Reference test	30	523	25	75	500	40	0.85
Temperature variation ^c	30	523	25	75	500	37	0.87
	30	483	25	75	500	54	0.49
Flow rate variation	30	523	25	75	500	42	0.86
	30	523	25	75	1,000	44	1.32
Pressure variation	30	523	25	75	500	43	0.78
	50	523	25	75	500	50	1.14
H ₂ concentration variation	30	523	25	75	500	44	0.78
	30	523	62.5	37.5	500	28	0.32

Notes: Original Table 3 of the benchmark tests of a commercial copper/zinc oxide/aluminum oxide catalyst by Schloegl *et al.*² ^aMethanol (MeOH) and carbon oxide are the only two products. Therefore, S_{CO} = 100 - S_{MeOH}. ^bValues at around 900 h TOS. ^cAfter 600 h TOS. Abbreviations: TOS: Time on stream; WTY: Weight time yield.

Table S4. The single-tube simulation result in the present work for copper/zinc oxide/self-pillared pentasil-zeolite catalyst

Parameter	P (bar)	T (K)	Carbon dioxide (vol.%)	Hydrogen (vol.%)	Gas hourly space velocity (hr ⁻¹)	S _{MeOH} (%) ^{a,b}	Normalized WTY _{MeOH} ^b
Value	50	523	25	75	3,000	87.9	1.75

Notes: ^aMethanol (MeOH) and carbon oxide are the only two products. Therefore, S_{CO} = 100 - S_{MeOH}. ^bSingle-path simulation converged at steady state.

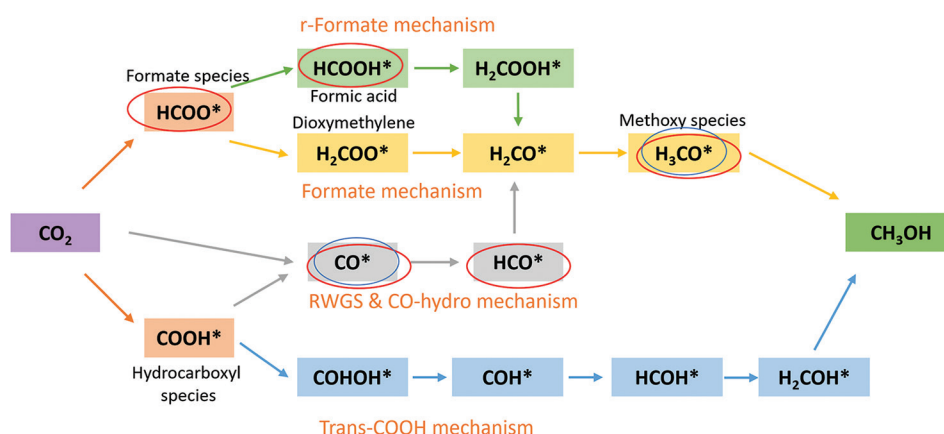


Figure S1. The mechanism diagram of carbon dioxide (CO₂) hydrogenation to methanol,³ with notations of the reaction intermediates recognized for 1–2 nm copper (Cu)/silicalite-1 (red circles)⁴ and 2–8 nm Cu/zinc oxide/self-pillared pentasil-zeolite (blue circles)⁵ catalysts. Abbreviation: RWGS: Reversed water-gas shift.

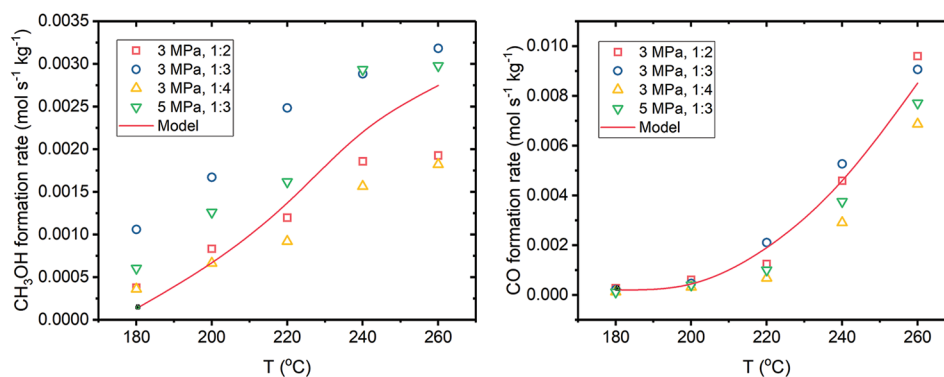


Figure S2. The experimental and Vanden Bussche and Froment model fitted reaction rates for carbon dioxide (CO_2) to methanol (CH_3OH) and reversed water–gas shift reactions

References

- Graaf GH, Stamhuis EJ, Beenackers AAC. Kinetics of low-pressure methanol synthesis. *Chem Eng Sci.* 1988;43(12):3185-3195.
doi: 10.1016/0009-2509(88)85127-3
- Ruland H, Song H, Laudenschleger D, *et al.* CO_2 Hydrogenation with $\text{Cu/ZnO/Al}_2\text{O}_3$: A benchmark study. *ChemCatChem.* 2020;12(12):3216-3222.
doi: 10.1002/cctc.202000195
- Zhong J, Yang X, Wu Z, Liang B, Huang Y, Zhang T. State of the art and perspectives in heterogeneous catalysis of CO_2 hydrogenation to methanol. *Chem Soc Rev.* 2020;49(5):1385-1413.
doi: 10.1039/C9CS00614A
- Ding R, Fu G, Wang S, *et al.* The activity of ultrafine cu clusters encapsulated in nano-zeolite for selective hydrogenation of CO_2 to methanol. *Catalysts.* 2022; 12(11):1296.
doi: 10.3390/catal12111296
- Liu X, Fu G, Lang Q, *et al.* Reaction intermediates recognized by in situ FTIR spectroscopy in CO_2 hydrogenation over the Cu/ZnO/SPP -zeolite catalyst. *RSC Appl Interfaces.* 2025;2(1):114-121.
doi: 10.1039/d4lf00266k