

Support Information for

High Yield Direct Synthesis of Dimethyl Ether from CO₂ and H₂ in Dry Reaction Environment

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Experimental

Membrane synthesis and Catalysts preparation

WCM was prepared following the procedure previously reported.¹ Typically, the ceramic hollow fibers were dip-coated in 1 wt.% seeds solution with seed size of 50-250 nm, and then dried and thermally annealed at 200 °C overnight. Membrane growth was conducted at 80 °C for 5 h in the gel with molar composition of 1Al₂O₃: 5SiO₂: 50 Na₂O: 1000 H₂O, prepared by mixing sodium aluminate (NaAlO₂, Al₂O₃: 50-56 wt.%, Na₂O: 37-45 wt.%, Sigma-Aldrich), Ludox colloidal (40 wt.% in water, Sigma-Aldrich), sodium hydroxide (NaOH, 98 wt.%, Sigma-Aldrich) and DI water. After the hydrothermal synthesis, WCM was washed thoroughly and dried for use in MR.

The Cu/ZnO/Al₂O₃ catalyst with an atomic ratio of 6:3:1 was prepared following the procedure previously reported.² A mixed aqueous nitrate solution (total metal concentration of 0.2 M, 500 mL) of Cu(NO₃)₂ · 3H₂O, Zn(NO₃)₂ · 6H₂O, and Al(NO₃)₃ · 9H₂O and an aqueous solution (0.2 M) of Na₂CO₃ were simultaneously added dropwise into 400 mL of preheated DI water (65-70 °C) under vigorous stirring at 400 rpm. During the co-precipitation process, the precipitating solution was maintained at 65-70 °C and at pH of 6.5-7.0. At the end of co-precipitation, the pH of precipitating solution was immediately adjusted to 7.0 by 0.2 M Na₂CO₃. The precipitates were then aged for 30 min at 70 °C under vigorous stirring (400 rpm). Thereafter, the precipitates were filtered under vacuum and rinsed several times with DI water. The resulting catalyst was dried at 110 °C overnight and further calcined in air at 360 °C for 4 h with a heating rate of 2 °C·min⁻¹.

HZSM-5 catalyst was prepared by calcining ammonia-ZSM-5 (SiO₂:Al₂O₃ = 23:1, surface area of 425 m²/g, Alfa Aesar) at 500 °C for 5 h in air with heating rate of 10 °C/min. Bifunctional catalysts with different mass ratios (1:2, 1:1, 4:1, 5:1) were prepared by physically mixing CZA and HZSM-5 powders.

Characterizations

WCM and catalysts were characterized by SEM, TEM, XRD, BET and ICP-AES before the reaction, and the results were consistent with those previously reported^{1,2}. These characterization results, therefore, were not shown here.

The content of coke in spent catalyst was determined by TGA-Q50 (TA Instruments). In order to remove adsorbed water and CO₂ from the catalyst, the sample was heated to 100 °C with a ramping

rate of 10 °C·min⁻¹ under N₂ flow of 100 sccm and stayed for 60 min. Then, the catalyst was heated to 1,000 °C with the same heating rate and N₂ flow rate to determine the coke amount.

DME synthesis in MR

A homemade packed bed membrane reactor system was used to perform the catalytic testing. ~0.34 g of bifunctional catalysts were loaded in the shell side of the membrane reactor and reduced in situ at 250 °C for 10 h with 20 sccm of H₂ before the test. The catalytic reaction was performed with a pre-mixed gas mixture with H₂/CO₂ molar ratio of 3:1 at flow rate of 20-28 sccm (GHSV: 3,500-4,700 L·kg_{cat}⁻¹·h⁻¹) at reaction temperature of 220-260 °C and pressure of 35 bar. The compositions of the permeate (purged with 250 ml·min⁻¹ Helium) and retentate (outlet stream of MR, diluted with 10 sccm Helium, splitting method) were analyzed by an on-line gas chromatography (GC7890, Agilent) equipped with TCD and FID detectors. A long-term run over 100 h of time on stream was performed to evaluate the long-term stability. The flow rate of the outlet stream was measured using a bubble flow meter. For bifunctional catalysts with mass ratio of 1/1, 4/1 and 5/1, only MeOH, CO and DME were detected as the products. For bifunctional catalysts with mass ratio of 1/2, a small amount of an unidentified product was formed when reaction temperature was higher than 220 °C.

DME synthesis in TR

The system and procedure for catalytic testing in TR were similar to those of MR, except WCM was replaced by a non-permeable membrane support with the same size as WCM. The non-permeable membrane support was prepared by applying a thin layer of glaze on the outer surface of a ceramic hollow fiber, followed by curing at 1000 °C for 3 h with increasing and decreasing rates of 2 °C·min⁻¹. Before being applied in TR, it was tested and confirmed to be non-permeable to any gases.

The CO₂ conversion, product selectivity and yield were calculated as follows:

$$X_{CO_2} = \frac{n_{CO_2-in} - n_{CO_2-out}}{n_{CO_2-in}} \times 100 \quad \% \quad (S1)$$

$$S_{CO} = \frac{n_{CO}}{n_{CO} + n_{MeOH} + 2 * n_{DME}} \times 100\% \quad (S2)$$

$$S_{MeOH} = \frac{n_{MeOH}}{n_{CO} + n_{MeOH} + 2 * n_{DME}} \times 100\% \quad (S3)$$

$$S_{DME} = \frac{2 * n_{DME}}{n_{CO} + n_{MeOH} + 2 * n_{DME}} \times 100\% \quad (S4)$$

$$Y_{CO} = \frac{n_{CO}}{n_{CO2-in}} \times 100\% \quad (S5)$$

$$Y_{MeOH} = \frac{n_{MeOH}}{n_{CO2-in}} \times 100\% \quad (S6)$$

$$Y_{DME} = \frac{2 * n_{DME}}{n_{CO2-in}} \times 100\% \quad (S7)$$

where, n_{CO2} , n_{CO} , n_{MeOH} and n_{DME} is mole of CO₂, CO, MeOH and DME, respectively.

For n_{CO2-in} represents the mole of feed-in CO₂, and $n_{CO2-out}$ represents the mole of outlet CO₂. For the mole of outlet CO₂ and other components, it is calculated as follows:

$$n_i = n_{p,i} + n_{o,i} \quad (S8)$$

where, $n_{p,i}$ and $n_{o,i}$ is the mole of component i in the permeate side and outlet stream, respectively. In other words, for MR, mole of component i both in the permeate side and outlet stream was used. For TR, only mole of component i in the outlet stream was used due to that of in the permeate side was zero.

Results and Discussions

Table S1. Comparisons of catalytic CO₂ conversion and DME yields between the results in this study and those reported in literatures.

Number	Temperature and Pressure, °C/bar	CO ₂ conversion, %	DME yield, %	Catalysts	Reactor	References
1	250 & 50	29	18.0	CZZ/FER	TR	3
2	260 & 50	26	14.5	CZZ/FER	TR	4
3	260 & 30	24.5	12.6	CZZ/FER	TR	5
4	260 & 50	23.6	11.1	CZZ/FER	TR	6
5	260 & 30	21.9	8.3	CZZ/FER	TR	5
6	250 & 20	17.5	5	CZZ/FER	TR	7
7	260 & 50	29	18.9	CZA/HZSM-5	TR	8
8	240 & 28	26.2	18.3	CZZA/HZSM-5	TR	9
9	260 & 30	24.3	19.6	CuFeCe/HZSM-5	TR	2
10	260 & 30	20.9	13.2	CuFeCe/HZSM-5	TR	10
11	250 & 30	15.6	7.4	CuTiZr/HZSM-5	TR	11
12	240 & 30	23.6	11.1	CZZ/HZSM-5	TR	12
13	250 & 50	23	5.2	CuZn(Ga)/Al ₂ O ₃	TR	13
14	260 & 50	15	4.5	CZA/Al ₂ O ₃	TR	8
15	270 & 50	9	2.8	CZ/Al ₂ O ₃	TR	14
16	260 & 20	18.1	4.4	CZZ/SO ₄ ²⁻ -ZrO ₂	TR	15
17		25.5	11.5	CZA/H	1/1	TR
18	250 & 35	70.0	54.5	ZSM-5	4/1	This study
19		73.4	47.7		5/1	

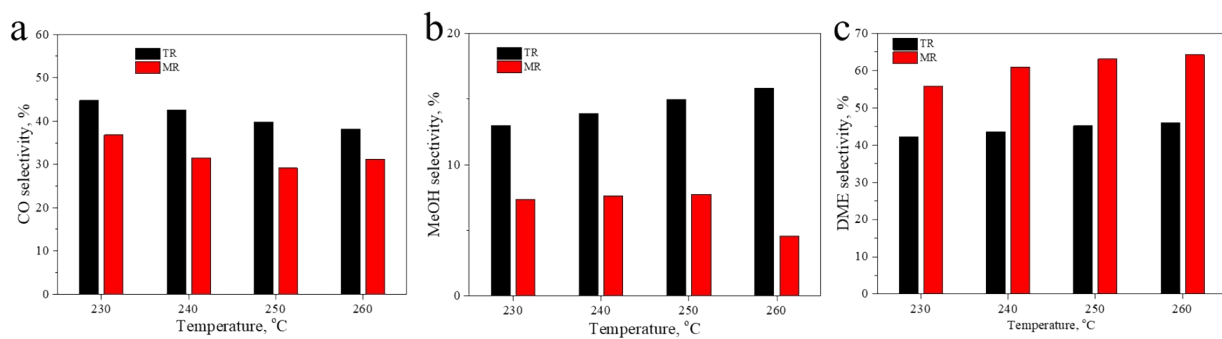


Figure S1. Product selectivity of direct DME synthesis from CO₂ and H₂ at different temperatures and 35 bar in TR (black) and MR (red). Membrane length: 45 mm, CZA/HZSM-5=1/1, GHSV= 4,200 L·kg_{cat}⁻¹·h⁻¹, results were averaged within the first 4 hours of testing.

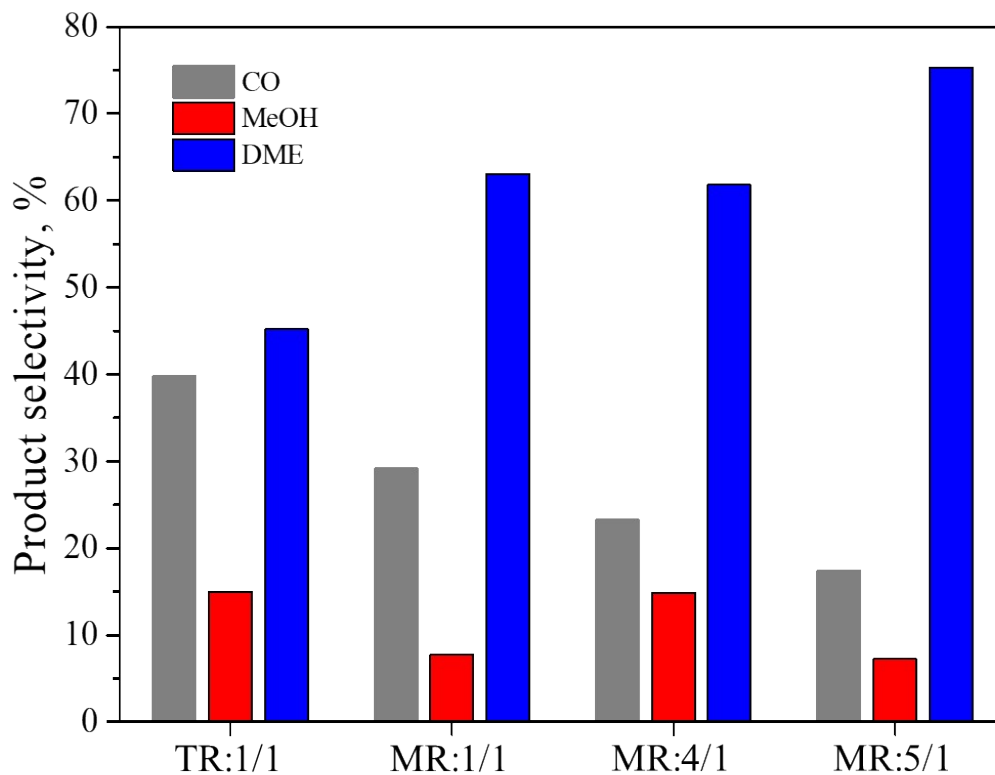


Figure S2. Product selectivity of direct DME synthesis from CO₂ and H₂ over different mass ratios of CZA/HZSM-5 at 250 °C and 35 bar in TR and MR. Membrane length: 45 mm, GHSV= 4,200 L·kg_{cat}⁻¹·h⁻¹, results were averaged within the first 4 h of testing.

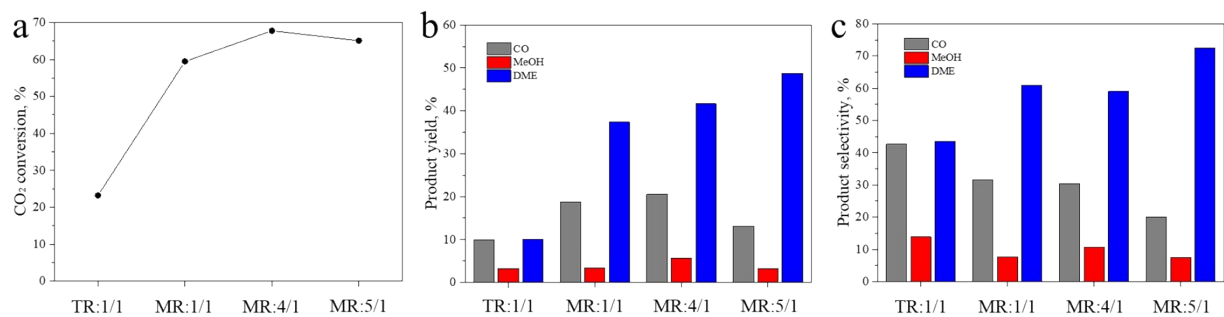


Figure S3. Catalytic CO₂ conversion (a), product yield (b) and product selectivity (c) of direct DME synthesis from CO₂ and H₂ over different mass ratios of CZA/HZSM-5 at 240 °C and 35 bar in TR and MR. Membrane length: 45 mm, GHSV= 4,200 L·kg_{cat}⁻¹·h⁻¹, results were averaged within the first 4 h of testing.

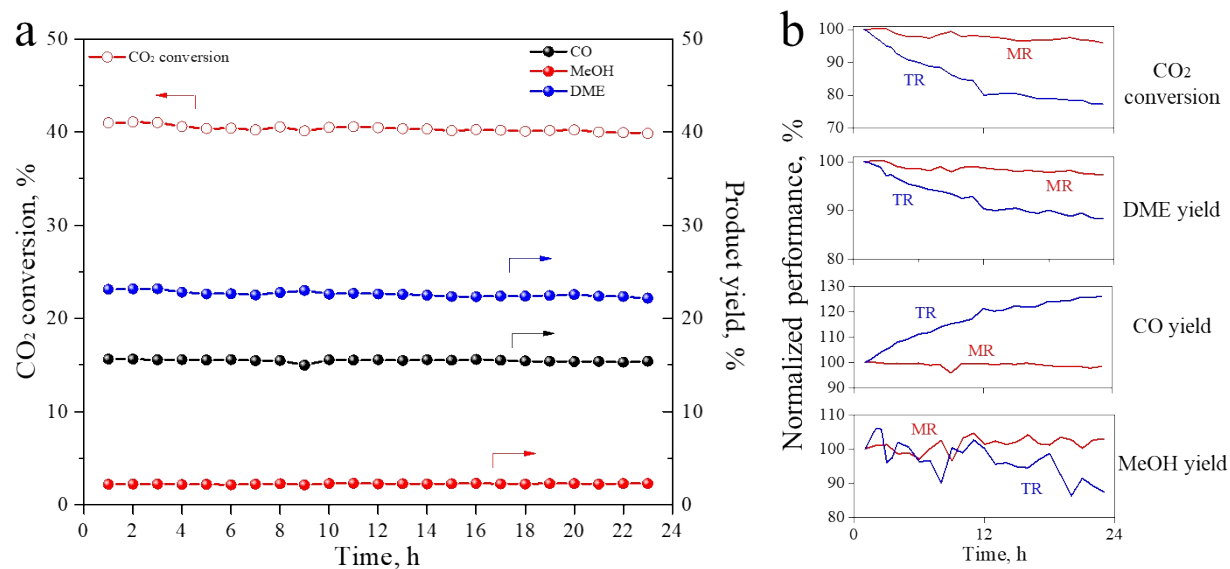


Figure S4. Stability of DME synthesis in MR. a) Long-term stability testing on CZA/HZSM-5=1/2 at 220 °C and 35 bar. b) Comparisons of catalytic performance change in MR and TR².

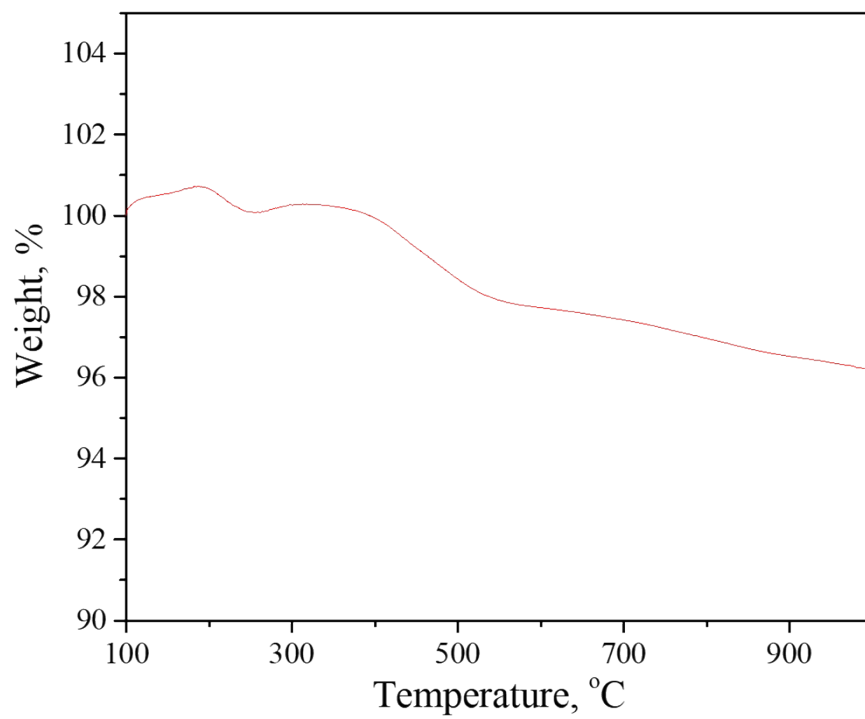


Figure S5. TGA of spent bifunctional catalyst with CZA/HZSM-5=5/1 in MR.

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