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Hydrogen-efficient non-oxidative transformation of methanol into dimethoxymethane over a tailored bifunctional Cu catalyst

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Supplementary Information

Methods

Materials and catalyst synthesis. $Cu(NO_3)_2{\cdot}3H_2O$ was supplied by ACROS. Fumed SiO_2 (CAB-O-SIL® M-5), colloidal SiO_2 (40 wt%, LUDOX AS-40), tetrapropylammonium hydroxide solution (TPAOH, 20 wt%), tetraethyl orthosilicate (TEOS), and SiC (200–450 mesh) were supplied by Sigma. Hβ(150) and Hβ(650) were supplied by Clariant. Hβ(360), HY(80), and ZSM-5(ammonium, 200–400) were supplied by Alfa.

All zeolite-supported Cu catalysts were prepared via incipient wetness impregnation and denoted as x Cu/zeolite(y), wherein x and y stand for the measured Cu weight loading and SiO_2/Al_2O_3 ratio. All zeolites were calcined in a muffle furnace for 3 h at 550 °C prior to use. A typical preparation procedure of 0.7 wt% Cu/Hβ(836) was described as follows. 0.0378 g of $Cu(NO_3)_2{\cdot}3H_2O$ was added into 1.2 mL of deionized water to prepare a transparent Cu solution. Then, 1 g of Hβ(836) zeolite was quickly added to this Cu solution followed by a vigorous stirring until homogeneous blue solids obtained, which stood at ambient temperature in air for 36 h and then was dried at 120 °C for 12 h. The dried sample was finally calcined in a muffle furnace at 450 °C for 3 h at a heating rate of 5 °C per minute to give 0.7 wt% Cu/Hβ(836) catalyst.

SiO_2-supported Cu catalyst (Cu/SiO_2) was prepared by the ammonia evaporation method described elsewhere[1,2]. Briefly, a certain amount of $Cu(NO_3)_2{\cdot}3H_2O$ was dissolved in 25 mL of deionized water and stirred until the complete dissolution of $Cu(NO_3)_2{\cdot}3H_2O$. The diluted NH_3 aqueous solution, prepared by diluting NH_3 solution (25 wt%) to 50 mL with deionized water, was slowly added to the Cu solution under stirring for 1 h. Afterwards, a certain amount of colloidal silica (40 wt%, LUDOX AS-40) was added to the Cu ammonia complex solution and stirred at 750 rpm overnight at room temperature. The resulting suspension was heated in an oil bath at 90 °C to evaporate NH_3 until the pH value of the suspension reaching 7. The resulting precipitate was filtrated and washed with 2 L of deionized water and subsequently dried at 80 °C overnight followed by a final calcination at 550 °C for 4 h.

Silicalite-1 was synthesized according to the method reported previously by Yu et al[3]. Typically, 11.7 g of TPAOH aqueous solution (20 wt%) was mixed with 8.8 mL of deionized water and stirred for 10 min. 6 g TEOS was then added into this mixture followed by a stirring at 30 °C for 6 h. The resulting reaction mixture was transferred into a stainless steel autoclave (50 mL) with Teflon liner and crystallized at 170 °C for 4 days in a heating block. The solid products was recovered by centrifugation and washed with 1 L of water and 1 L of ethanol, and subsequently dried at 100 °C overnight. Silicalite-1 was finally obtained after calcination at 550 °C for 8 h with a ramping rate of 1 °C/min.

Catalytic tests. The catalytic dehydrogenation of methanol to DMM was performed in a 6 mm stainless steel fixed-bed microreactor (Supplementary Fig. S15). The reactor was typically filled with 0.1 g of catalyst in powder form diluted by 0.9 g of SiC (200–450 mesh) placed between two layers of quartz wool. Prior to test, the catalyst was in situ reduced at 450 °C for 3 h in a pure H_2 flow (20 mL/min). Methanol was pumped to the reactor by a HPLC pump and well mixed with N_2 as carrier gas in an evaporation chamber to generate a homogeneous gaseous methanol flow. The experiment was carried out under typical conditions: 220 °C, atmospheric pressure, GHSV = 14549 mL/h/$g_{cat.}$, n(CH_3OH)/n(N_2) = 0.24 (V/V), N_2 flow rate = 19.4 mL/min. All gas lines were maintained at 140 °C to prevent condensation of liquid products. FA, DME, methanol, MF, DMM, and CH_4 were analyzed using an online gas chromatography system (Scion 456, Bruker) equipped with a flame ionization detector (FID) and a HP-PLOT/U capillary column. By collecting the outlet gas stream in a gas sampling bag, CO and CO_2 were analyzed using an offline GC system (Scion 456, Bruker) configured with three channels including front TCD for H_2, middle TCD for CO and CO_2, and near TCD for hydrocarbons usually not detected in this reaction. Product selectivity and methanol conversion were calculated based on a carbon basis using the absolute calibration factor of each compound. To be specific, DMM selectivity was calculated based on the molar concentration of carbon in DMM divided by the sum of the molar concentration of carbon in all compounds (N_i) in outlet stream including FA, DME, CH_3OH, MF, DMM, CO, CO_2, and CH_4, $S_{DMM} = N_{DMM}/\sum N_i \times 100\%$. Methanol conversion was calculated according to the formula, $\mathrm{X} = \left[1 - \left(N_{CH_3OH}/\sum N_i\right)\right] \times 100\%$. The catalytic performances after 1600 min on stream were typically used for discussions.

The isotope experiment using CD_3OH as a substrate was conducted in the same reactor system following the same procedure as described above. To differentiate the formation of H_2 and HD, the gas outlet of the fixed-bed reactor was first connected to a cold trap to condense methanol and other liquid products (MF, DMM, DME, FA), and then the remaining inorganic gas was collected with a gas bag. The gas sample collected at different time ranges during the time-on-stream experiment was manually injected into a Micromeritics Cirrus 2 mass spectrometer. Mass-to-charge ratios of 2 and 3 were applied as the characteristic signals for qualitative analysis of H_2 and HD, respectively.

Characterizations. Equilibrium calculations were performed in AspenPlus using the REquil reactor model. XRD patterns were recorded using a D5000 Siemens diffractometer with a Cu Kα X-Ray source ($\lambda = 0.154056$ nm) operating at 30 kV and 40 mA. TGA was performed under a N_2 atmosphere on a Netzsch STA 409 apparatus, and the gas effluents were monitored with an online Micromeritics Cirrus 2 mass spectrometer. XPS measurements were performed on a Thermo Scientific K-Alpha spectrometer equipped with an aluminum anode ($h\nu$(Al Kα) = 1486.6 eV) operated at 72 W and a spot size of 400 µm. Samples were handled under inert atmosphere in a N_2 glovebox making use of a vacuum transfer sample holder. Samples were mounted on conductive carbon tape. Sample charging was compensated by the use of an electron flood gun. Binding energies (BE) are referenced to the C1s BE of sp^3 carbon at 284.8 eV. The ATR-IR spectra were obtained on a Vertex 70 spectrometer equipped with an ATR unit and a DTGS detector in the wavenumber range of 4000 to 400 cm^{-1} with a resolution of 2 cm^{-1}. The in situ DRIFTS experiments were performed on a Vertex 70 spectrometer equipped with a Harrick Praying MantisTM High Temperature Chamber and a MCT detector in the wavenumber range of 4000 to 850 cm^{-1} with a resolution of 2 cm^{-1}. Before collecting spectra, the catalyst was in situ reduced in a 20% H_2/N_2 flow at 440 °C for 3 h. Upon the temperature decreasing to 225 °C, a continuous methanol flow was fed into the chamber by N_2 bubbling (12 mL/min). The spectra were simultaneously recorded at different reaction time. Cu weight loading and SiO_2/Al_2O_3 ratio were measured using a SPECTROBLUE inductively coupled plasma optical emission spectrometry (ICP-OES) analyzer. N_2 adsorption and desorption experiments were carried out at liquid N_2 temperature on a Quadrasorb SI (3P Instruments). Prior to measurement, samples were degassed at 350 °C for 5 h. The specific surface area and micropore volume were determined using the BET and t-plot model, respectively. STEM images were obtained on a FEI Tecnai F20 microscope operated at a voltage of 200 keV equipped with an HAADF detector. NH_3-TPD was performed using a ChemBET Pulsar TPR/TPD automated chemisorption analyzer. NH_3 adsorption was performed by dosing pure NH_3 to the sample at 100 °C for 20 min. NH_3 desorption curve was recorded by heating the sample to 1000 °C at a ramping rate of 10 °C min^{-1}. SS MAS ^{29}Si NMR spectra were obtained using Bruker Avance III spectrometer (4 mm MAS rotor, 7 kHz spinning frequencies, 500 MHz). N_2O chemisorption was performed in a U-type quartz reactor connected to an online Micromeritics Cirrus 2 mass spectrometer, which is used for quantitative analysis of the consumed N_2O. Before dosing N_2O, The sample was heated up to 400 °C with a heating ramp of 10 °C min^{-1} and kept for 5 min in a 5% H_2/Ar/He flow (50 mL/min) and then cooled down to room temperature. The oxidation of Cu by dosing N_2O took place at 40 °C using a mixed gas flow N_2O/He/Ar = 0.03/79.97/20 (100 mL/min) containing 300 ppm N_2O.

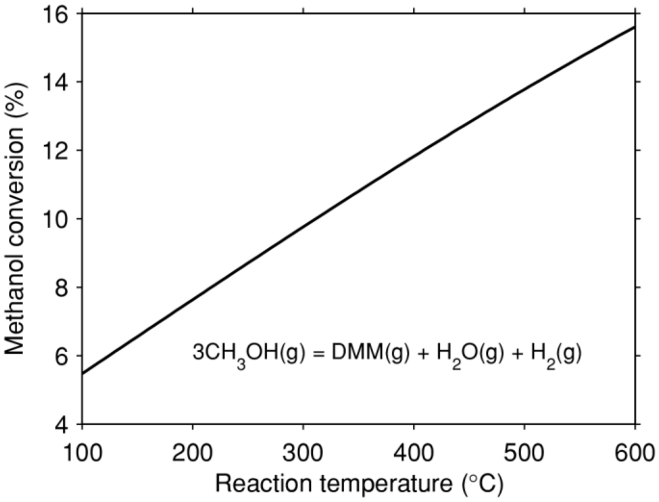


Fig. S1. Equilibrium conversion versus reaction temperature for the single gas phase reaction $3CH_3OH \leftrightharpoons DMM + H_2O + H_2$ (representing a catalyst with perfect selectivity). Equilibrium was calculated in AspenPlus with the REquil reactor model assuming an ideal gas phase and using the DIPPR-107 heat capacity model and pure species properties from the AspenPlus Property Databank APV88 PURE32.

Table S1. Physicochemical properties of zeolites

Zeolites	SiO_2/Al_2O_3 molar ratio	Acidity (μmol/g)[a]		
		Weak	Strong	Total
Hβ (150)	165	223.4	102.8	326.2
Hβ (360)	397	129.4	67.4	196.8
Hβ (650)	836	36.5	n.d.	36.5
HY (80)	110	160.1	89.4	249.5
HZSM-5(200-400)	358	77.6	40.7	118.3
Silicalite-1	∞	-	-	-
0.7 wt% Cu/Hβ(836)	-	129.7	29.4	159.1

[a]Acidity determined by integrating the NH_3 desorption peak in Supplementary Fig. 3

Table S2. Cu loadings of different catalysts measured by ICP

Catalyst	Theoretical Cu loading (wt%)	Measured Cu loading (wt%)
0.4 wt% Cu/Hβ(836)	0.5	0.4
0.7 wt% Cu/Hβ(836)	1	0.7
3.7 wt% Cu/Hβ(836)	5	3.7
7.4 wt% Cu/Hβ(836)	10	7.4
7.2 wt% Cu/Hβ(165)	10	7.2

7.6 wt% Cu/Hβ(397)	10	7.6
7.8 wt% Cu/Silicate -1	10	7.8
7.7 wt% Cu/HZSM-5(358)	10	7.7
7.4 wt% Cu/HY(110)	10	7.4
2.6 wt% Cu/SiO_2	5	2.6

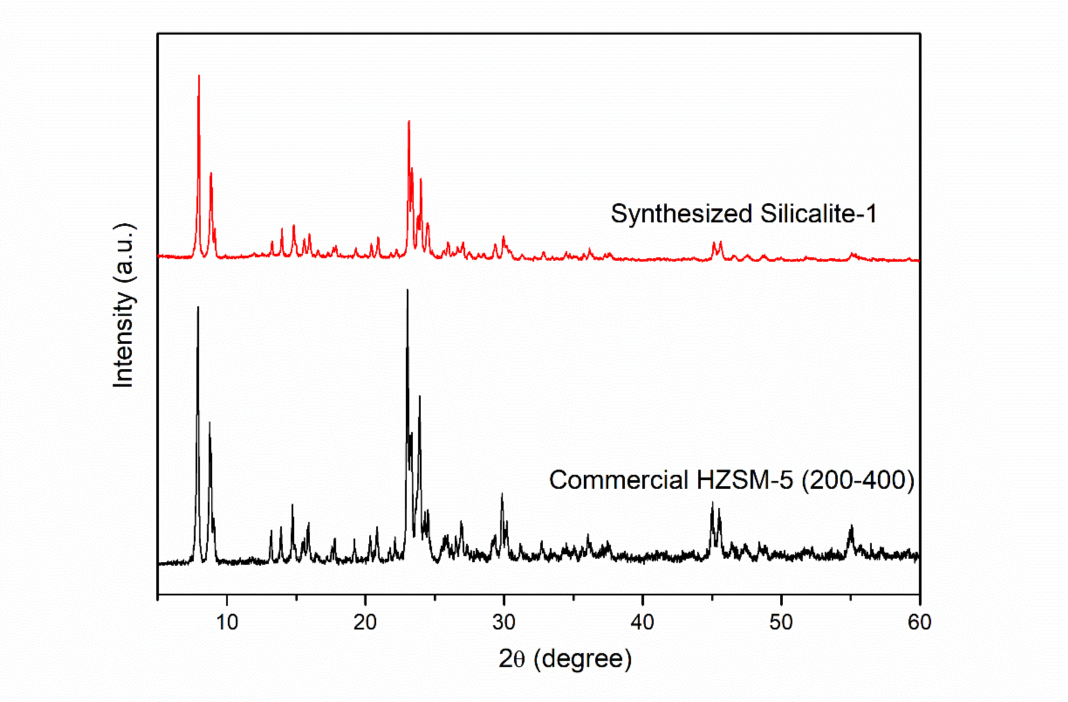


Fig. S2. XRD patterns of the synthesized Silicalite-1 and commercial HZSM-5(358) zeolites.

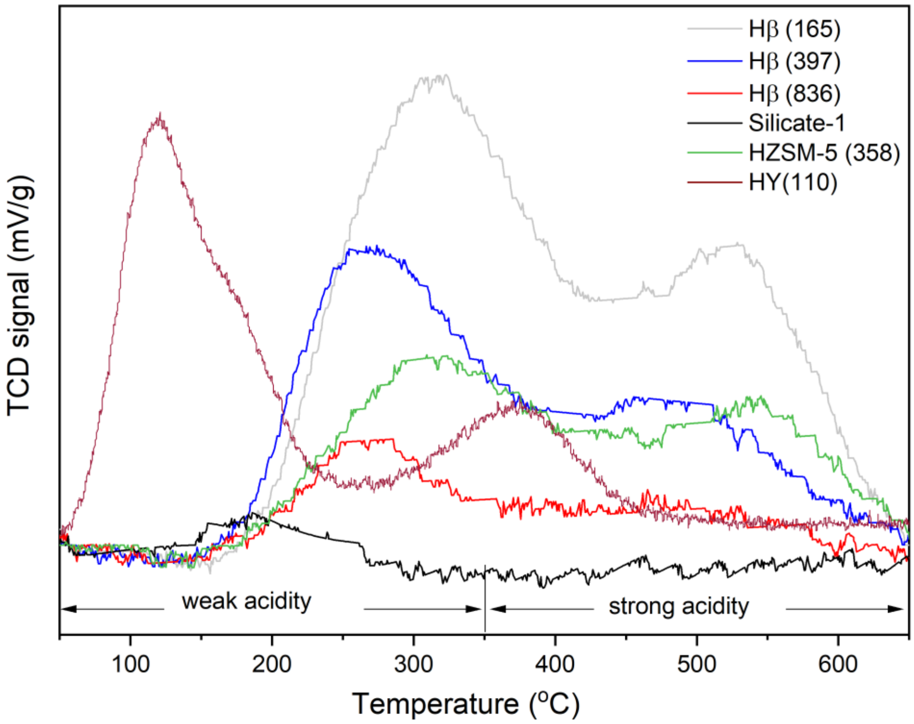


Fig. S3. NH_3-TPD profiles of different zeolites.

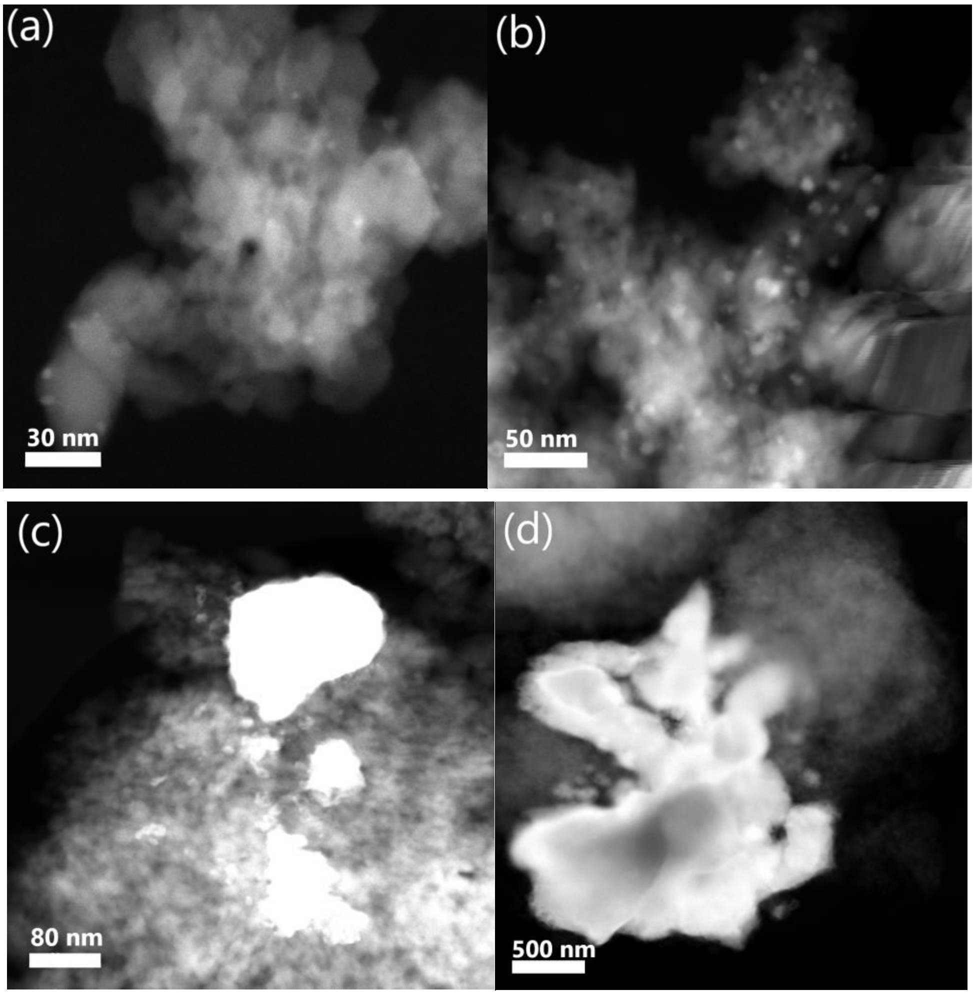


Fig. S4. HAADF-STEM images of Cu/Hβ(836) catalysts with varied Cu loadings after H_2 reduction: (a) 0.4 wt% Cu/Hβ(836), (b) 0.7 wt% Cu/Hβ(836), (c) 3.7 wt% Cu/Hβ(836), (d) 7.4 wt% Cu/Hβ(836).

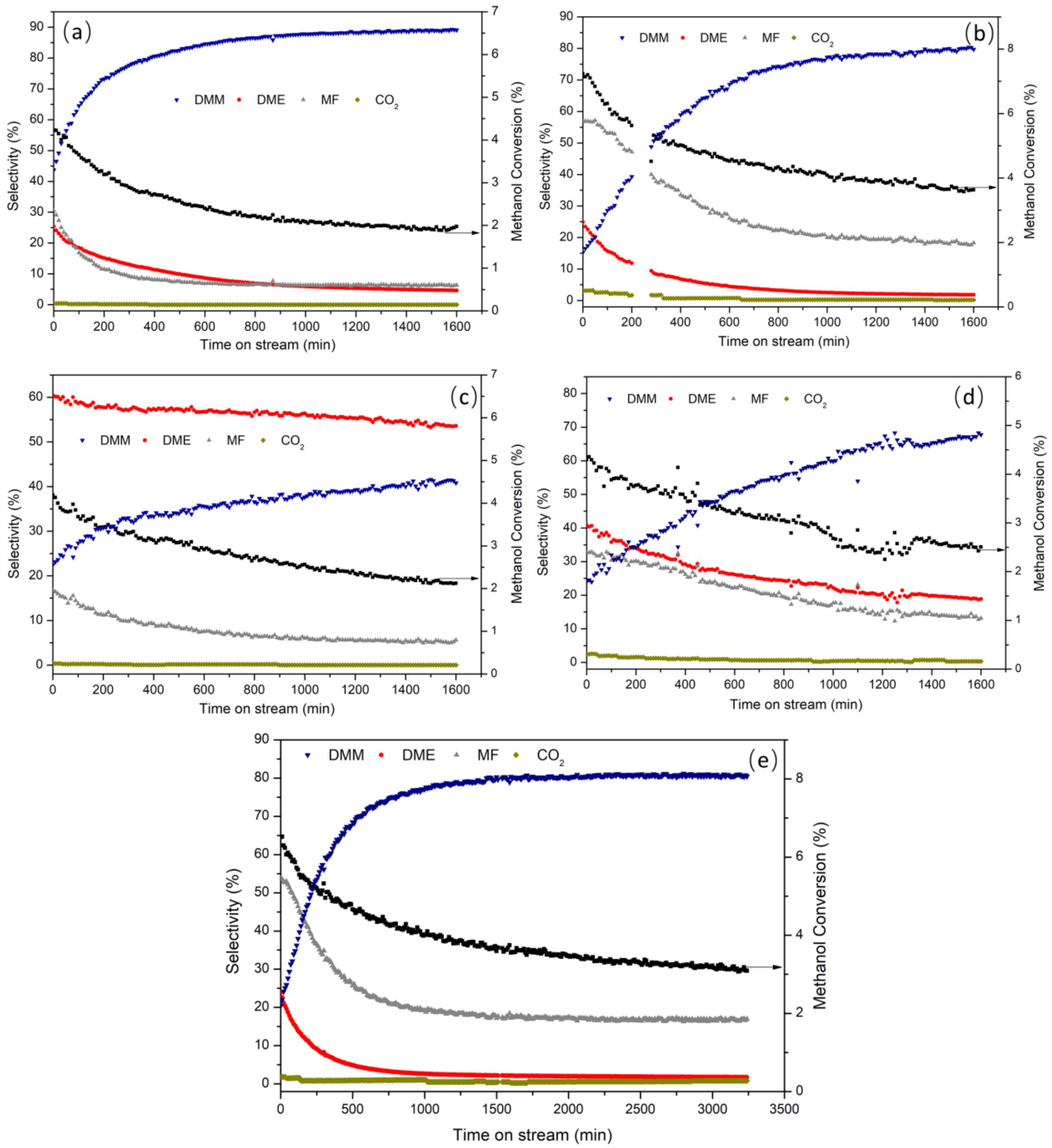


Fig. S5. Stability tests for methanol dehydrogenation to DMM over various Hβ-supported Cu catalysts: (a) 0.4 wt% Cu/Hβ(836), (b) 3.7 wt% Cu/Hβ(836), (c) 7.2 wt% Cu/Hβ(165), (d) 7.6 wt% Cu/Hβ(397), and (e) 0.7 wt% Cu/Hβ(836). The unrecorded data points in (b) are caused by the GC system breakdown. Reaction conditions: 200 °C for (a), (b) and (e), 180 °C for (c) and (d), 1 atm, GHSV = 14549 mL/h/gcat., 0.1 g of catalyst diluted with 0.9 g of SiC, $n(CH_3OH)/n(N_2)$ = 0.24 (V/V), N_2 flow rate = 19.4 mL/min.

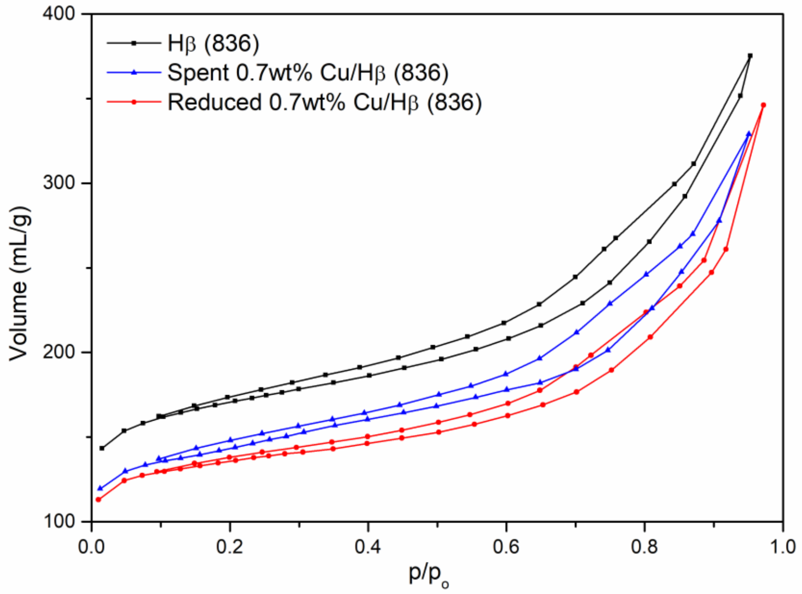
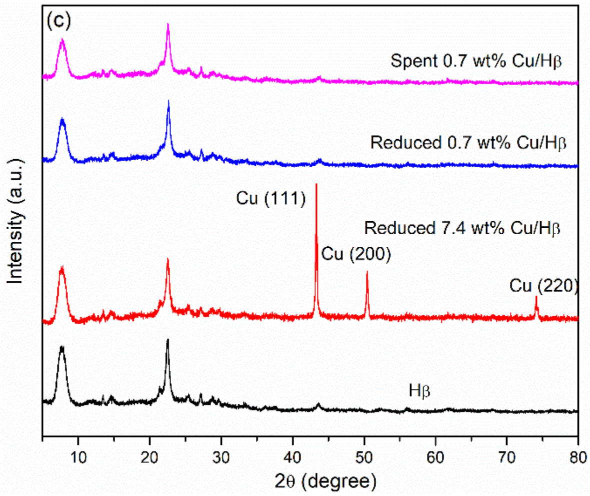


Fig. S6. N_2 adsorption and desorption isotherms of Hβ(836), reduced and spent 0.7 wt% Cu/Hβ(836) catalysts with a offset of 250 mL/g.



Fog S7. XRD patterns of fresh and spent 0.7 wt% Cu/Hβ(836) catalysts.

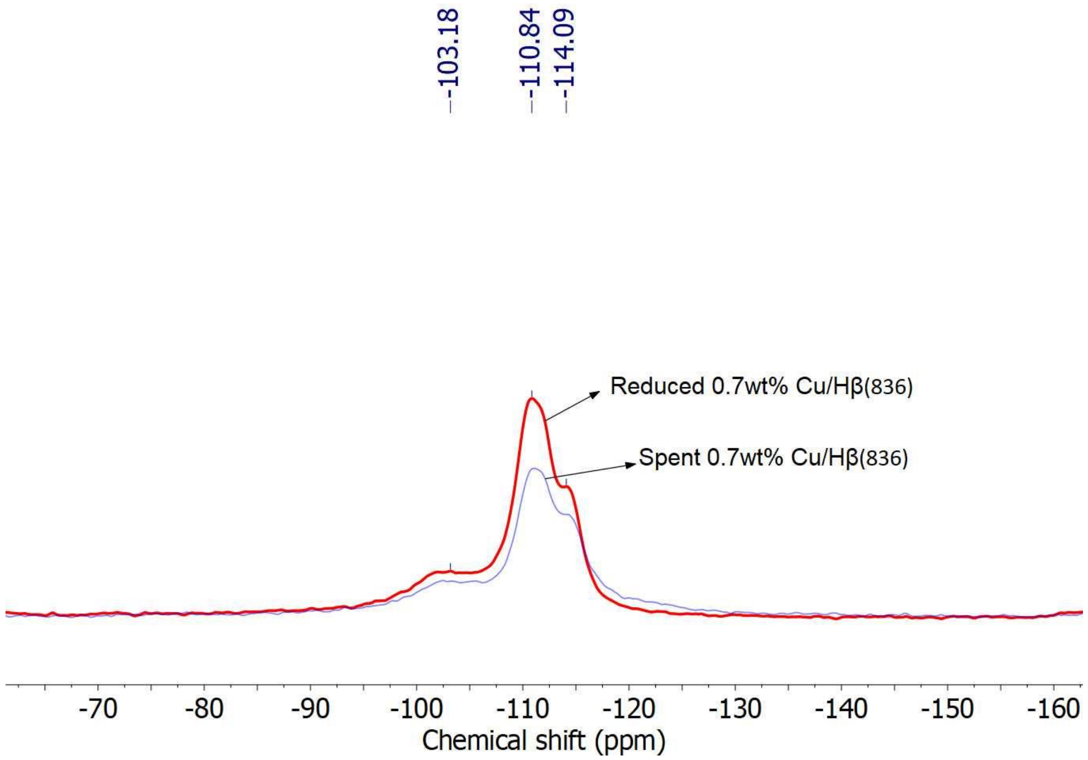


Fig. S8. ^{29}Si SS MAS NMR spectra of reduced and spent 0.7 wt% Cu/Hβ(836) catalysts. Prior to the ^{29}Si NMR measurement, all samples were degased at 420 ^{o}C for 9 h under vacuum (10^{-3} bar).

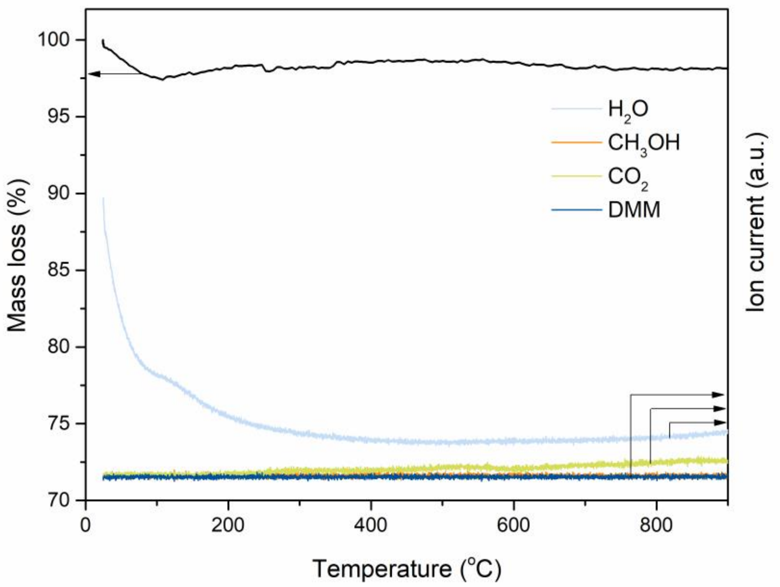


Fig. S9. Thermogravimetric analysis profile of spent 0.7 wt% Cu/Hβ(836) catalyst with the outlet gas monitored using an online mass spectrometer .

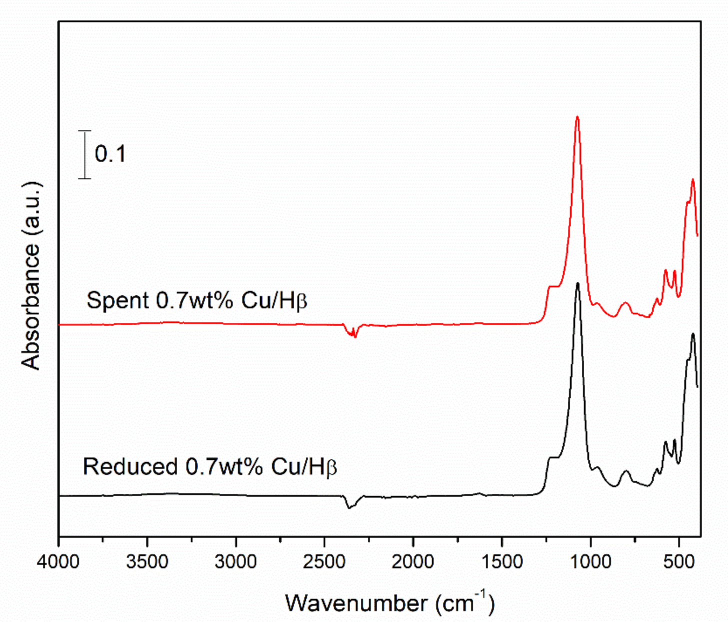


Fig. S10. ATR-IR spectra of reduced and spent 0.7 wt% Cu/Hβ(836) catalysts.

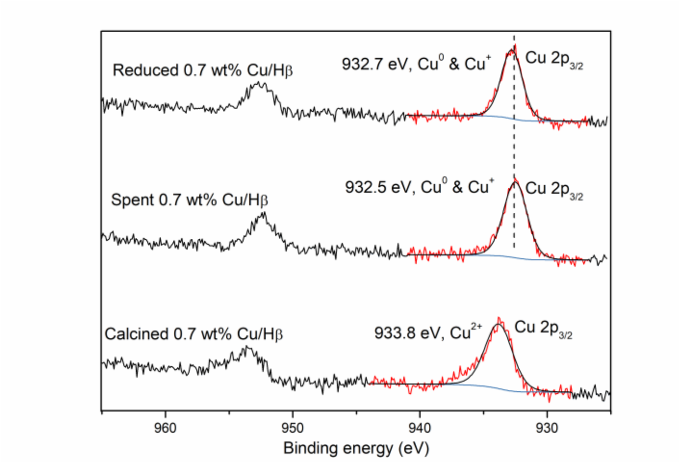


Fig. S11. Cu 2p XPS spectra of calcined, reduced and spent 0.7 wt% Cu/Hβ(836) catalysts. For the measurement of reduced catalyst, 0.7 wt% Cu/Hβ(836) was first reduced in reactor at 450 °C for 3 h. The sealed reactor with the reduced catalyst inside was transferred into a N_2 glove box, where the catalyst was loaded into the sample holder. By a glove box transfer system, the sample was finally transferred to the XPS measurement chamber without exposure to air. Measurement of the spent catalyst was performed in the same way.

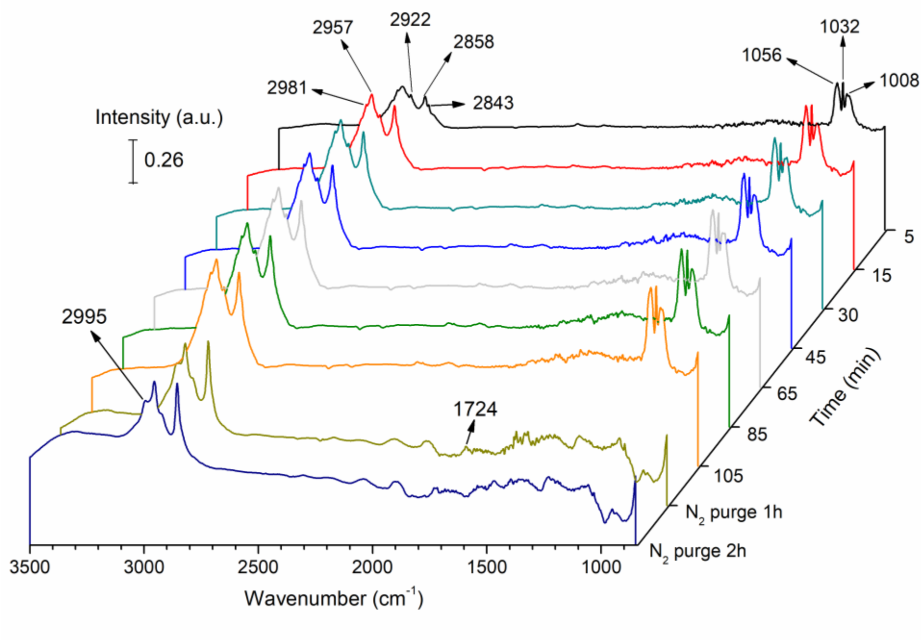


Fig. S12. Time-resolved in situ DRIFT spectra of the dehydrogenation of methanol to DMM over 0.7 wt% Cu/Hβ(836) catalyst at 225 °C. 0.7 wt% Cu/Hβ(836) catalyst was in situ reduced in a 20% H_2/Ar flow at 440 °C for 3 h.

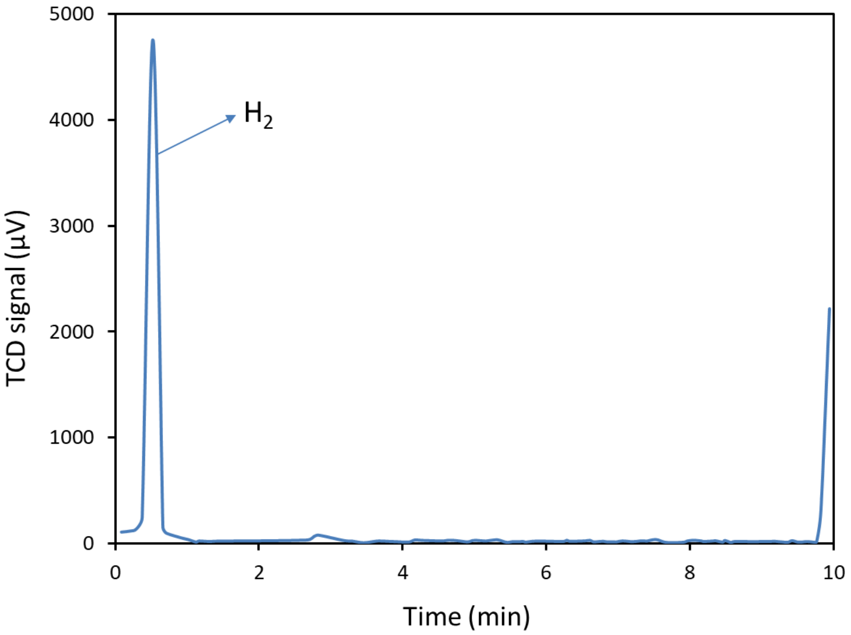


Fig. S13. A typical GC chart for H_2 produced in the dehydrogenation of methanol to DMM over 0.7 wt% Cu/ Hβ(836) catalyst. H_2 was detected by injecting the collected gas sample to an offline GC (Scion 456, Bruker) equipped with TCD.

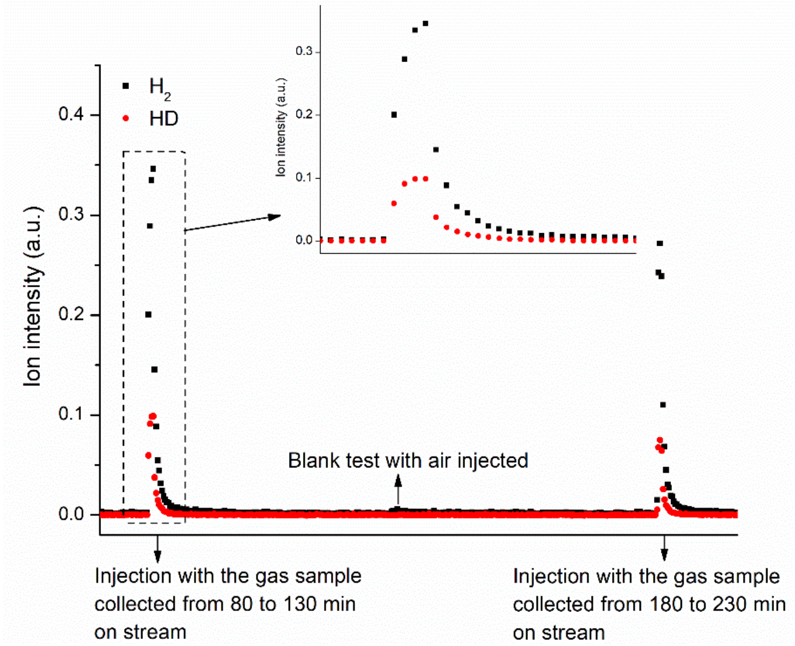


Fig. S14. Mass spectrum of the isotope-labeled hydrogen produced in the dehydrogenation of CD_3OH to DMM over 0.7wt% Cu/ Hβ(836) catalyst at 220 °C and 14549 mL/h/g_{cat}. The spectrum was obtained on a Micromeritics Cirrus 2 mass spectrometer by manually injecting the gas sample collected at different time ranges during the time-on-stream experiment. The gas outlet of the fixed-bed reactor was first connected to a cold trap to condense methanol and liquid products (MF, DMM, DME, FA), and the remaining inorganic gas was collected with a gas bag.

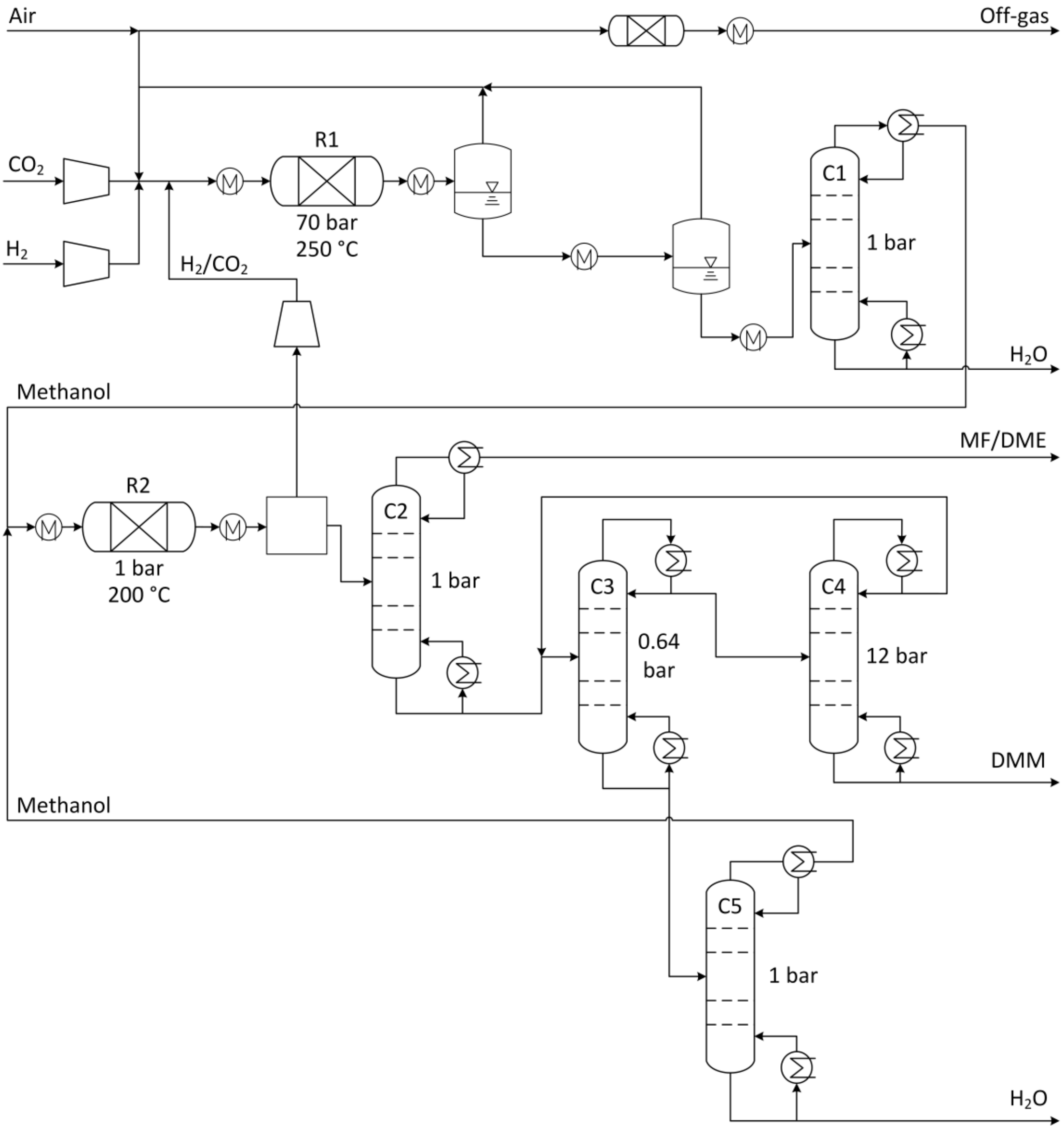


Fig. S15. Process flowsheet for DMM production via CO_2 hydrogenation and methanol dehydrogenation. We simulated the process in Aspen Plus v8.8. We subsequently estimated the energy demand of the distillation column using intermediate-fidelity models[5]. We consider nonideal thermodynamics using the NRTL model[6] throughout the process (parameters from: APV88 VLE-IG for methanol-water, methanol-DMM, water-DMM, methanol-MF; Faitakis et al. (2009)[7] for methanol-DME, water-DME; Breitkreuz et a. (2018)[8] for DME-MF; Deutz et al. (2017)[9] for DMM-MF, water-MF; APV88 ENRTL-RK for CO_2-water; NISTV84 NIST-HOC for CO_2-DME). The separation of H_2 and CO_2 after R2 is modeled with a separator block for the sake of simplicity. We consider the compression work for the educts H_2 and CO_2 as well as the compression of the recycle stream from R2 back to R1 explicitly. Additionally, pinch-based heat integration is conducted for the entire flowsheet.

Table S3. Mass and energy balances for the base and idealized case of DMM production. All values are given per mass of DMM produced.

	Base case	Idealized case
Mass balances (kg/kg)		
H_2	+ 0.264	+ 0.223
CO_2	+ 2.248	+ 1.819
DMM	- 1.000	- 1.000
CO_2 in exhaust	- 0.070	- 0.057
MF / DME	- 0.285 (91 mol.% MF)	- 0.012 (100 mol.% MF)
Energy balances (MJ/kg)		
Heat demand at 100 °C	+ 27.09	+ 5.76
Heat demand at 60 °C	+ 0.00	+ 2.24
Compression of H_2 and CO_2	+ 1.73	+ 1.33

Table S4. Specific exergies for exergy efficiency calculations. The chemical exergies are approximated as the Gibbs free energy change upon combustion based on the higher heating values. The exergy content of heat flows are calculated considering an ambient temperature of 25 °C.

Component	Value (MJ/kg)
H_2 (gaseous, 30 bar)	122
CO_2 (gaseous, 1 bar)	0
DMM (liquid, 1 bar)	25
MF (gaseous, 1 bar)	16
DME (gaseous, 1 bar)	30

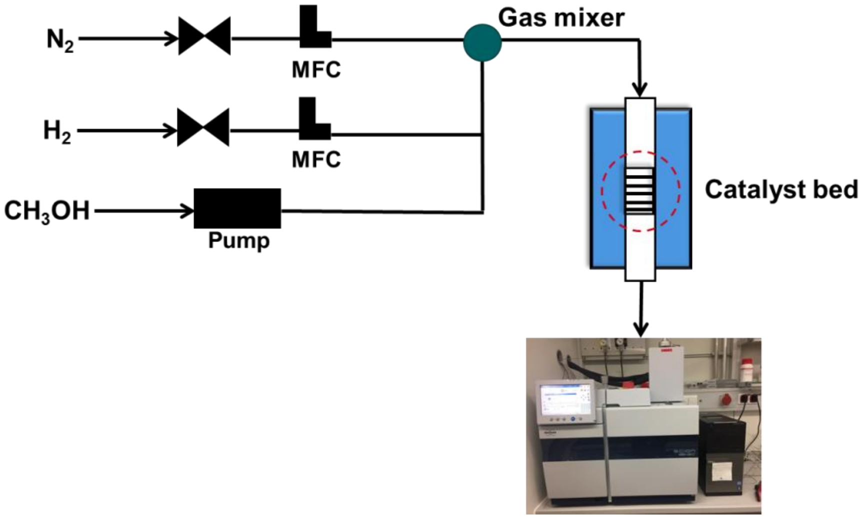


Fig. S16. Simplified flow diagram of the experimental set-up used for the catalytic activity tests.

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