

Catalytic Coproduction of Methanol and Glycol in One Pot from Epoxide, CO₂, and H₂

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Supporting Information

All manipulations were performed using a N₂-atmosphere glovebox or standard Schlenk techniques. The catalysts **1**, **2** and **3** were obtained from Strem chemicals. Standard solvents were purified by passing through a neutral alumina column (Innovative Technology, Inc., PureSolv™ solvent purification system). All deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. Anhydrous propylene oxide was purchased from Sigma-Aldrich. All other materials were purchased from commercial suppliers and used without further purification unless otherwise mentioned. Monoethyleneimine (MEA), diethylethanolamine (DEEA) and 4-dimethylaminopyridine (DMAP) were purchased from Sigma-Aldrich. Branched polyethylenimine (PEI₆₀₀) was purchased from Polysciences. MEA and DEEA were distilled over CaH₂ and stored in the glovebox. DMAP and PEI₆₀₀ were dried under vacuum overnight and stored in the glovebox. ¹H and ¹³C NMR experiments were recorded on a 500 MHz Varian NMR spectrometer. The NMR chemical shifts were assigned relative to the internal standard, 1,3,5-trimethoxybenzene (TMB). The headspace gas was analyzed using an Agilent Technologies 6850 GC System equipped with a Supelco 10 ft x 1/8 inch carbosieve column equipped with a thermal conductivity detector (TCD). The experimental details for the MAS-NMR was provided in section 3.

1) Standard procedure for cyclic carbonate formation

A 100 mL Parr reactor (Figure S1) was charged with a given amount of epoxide and amine and sealed in a N₂-atmosphere glovebox. The reactor was then pressurized with a 30 bar CO₂ and heated to a set temperature for a given time. After the set time, the reactor was cooled to room temperature and then to 0 °C, the excess pressure was released slowly. TMB (100 mg) was added as an internal standard to the reaction mixture and a small aliquot of the sample was analyzed by ¹H and ¹³C NMR experiments in CDCl₃ (Figure S2).

2) Standard procedure for coproduction of methanol and propylene glycol

- One-pot one-step reaction: A Parr reactor (100 mL) was charged with PO, PEI₆₀₀, metal catalyst and THF, and sealed in a N₂-atmosphere glovebox. The reactor was then pressurized with a 20 bar CO₂, 70 bar H₂ and heated to 140 °C for 24 h (total initial pressure=70 bar). After 24h, the reactor was cooled to room temperature and then to -78 °C, the excess pressure was released slowly. TMB (100 mg) was added as an internal standard to the reaction mixture and a small aliquot of the sample was analyzed by ¹H and ¹³C NMR experiments in CDCl₃.

- One-pot two-step reaction: A Parr reactor (100 mL) was charged with PO, PEI₆₀₀ and THF, and sealed in a N₂-atmosphere glovebox. The reactor was pressurized with a 20 bar CO₂ and heated to 140 °C for 24h. After 24h, the reactor was cooled to room temperature and then to 0 °C, the excess pressure was released slowly. The reactor was opened in the nitrogen atmosphere glovebox and the metal catalyst was added to the reaction mixture. Then the reactor was resealed and pressurized with a 60 bar H₂ and reheated to 140 °C for 16 h. After 16h, the reactor was cooled to room temperature and then to -78 °C, the excess pressure was released slowly. TMB (100 mg) was added as an internal standard to the reaction mixture and a small aliquot of the sample was analyzed by ¹H and ¹³C NMR in CDCl₃ (Figure S4).
- One-pot two-step reaction - Sequential addition of CO₂ and H₂: A Parr reactor (100 mL) was charged with PO, PEI₆₀₀, metal catalyst and THF, and sealed in a N₂-atmosphere glovebox. The reactor was pressurized with a 20 bar CO₂ and heated to 140 °C for 16 h. After 16h, the reactor was cooled to room temperature and then to 0 °C, the excess pressure was released slowly. Then the reactor was pressurized with a 60 bar H₂ and reheated to 140 °C for 16 h. After 16h, the reactor was cooled to room temperature and then to -78 °C, the excess pressure was released slowly. TMB (100 mg) was added as an internal standard to the reaction mixture and a small aliquot of the sample was analyzed by ¹H and ¹³C NMR experiments in CDCl₃ (Figure S5).

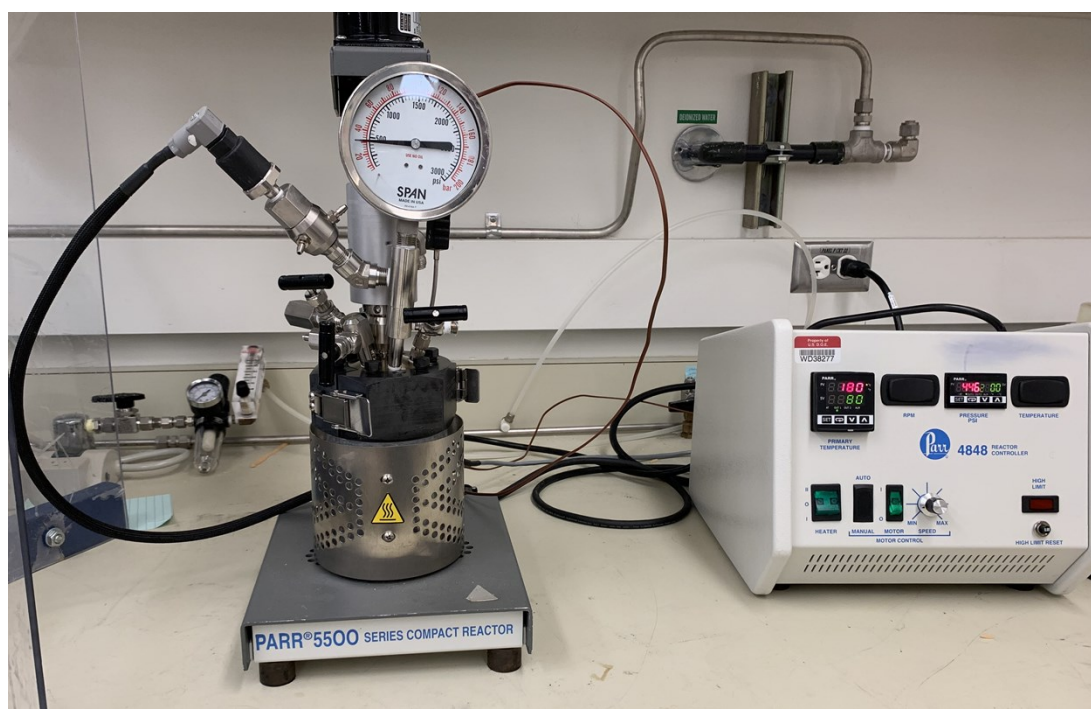


Figure S1. Image of the Parr reactor (left) equipped with internal thermocouple, pressure transducer, pressure gage, gas inlet/outlet valves, internal stirrer and rupture disc. The controller (right) was used to set the temperature and stirring speed. The pressure displayed in the controller was monitored with a camera.

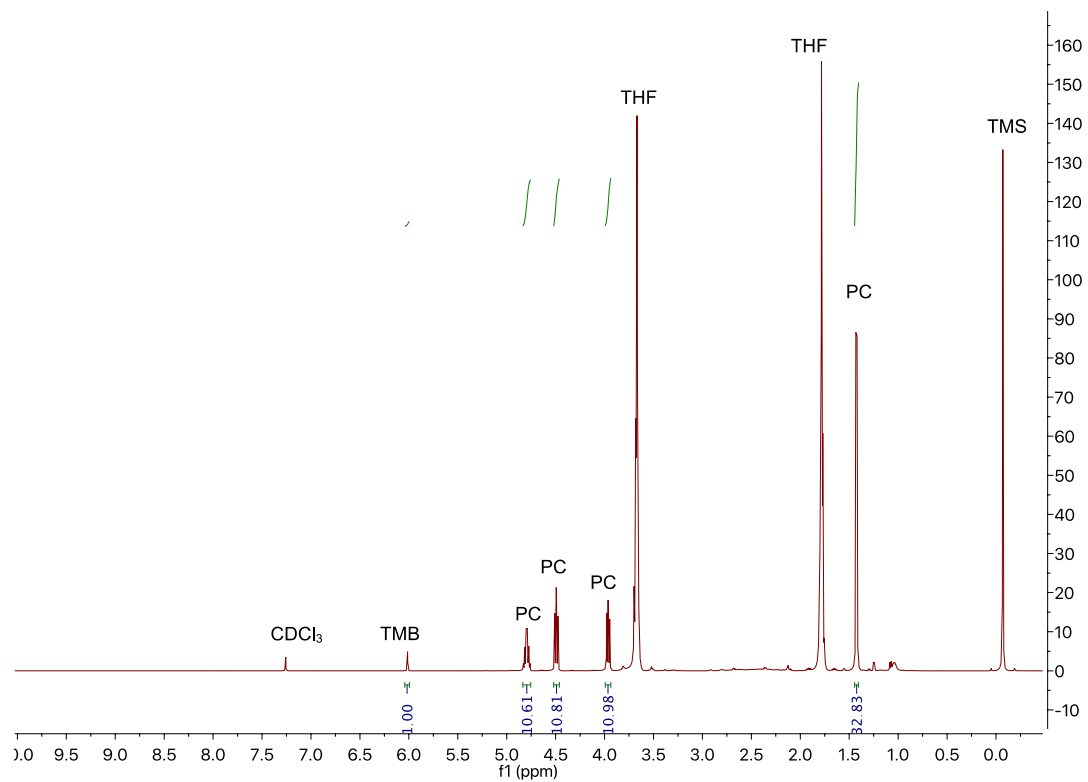


Figure S2. ¹H NMR of the reaction mixture after the reaction of PO with CO₂ in the presence of PEI₆₀₀ (100 mg) at 140 °C (entry 7, Table 1).

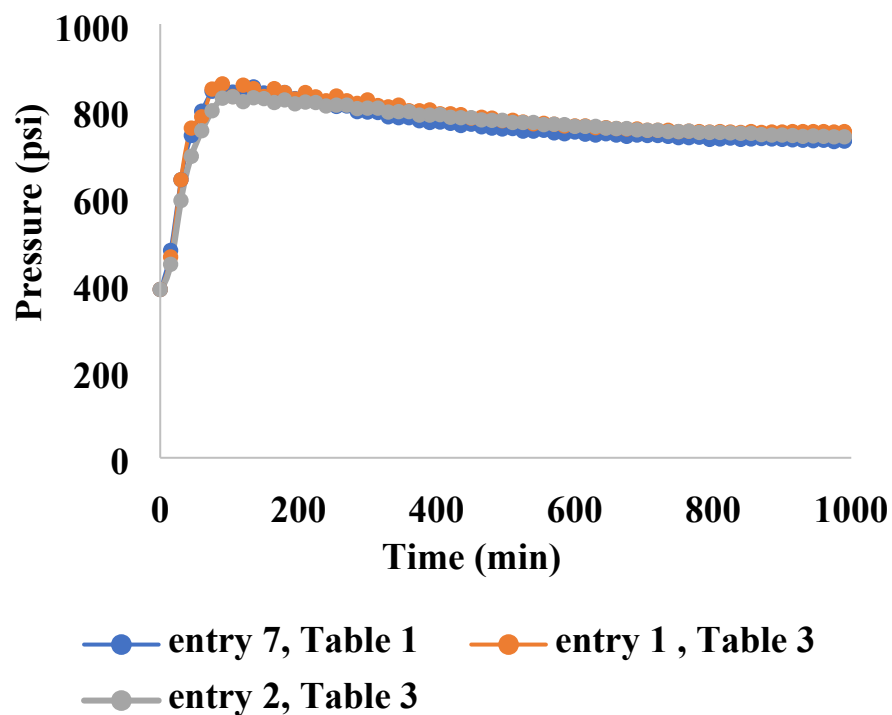


Figure S3. Rate of cyclic carbonate formation for following experiments from the main text: Entry 7, Table 1; entry 1, Table 3; entry 2, Table 3.

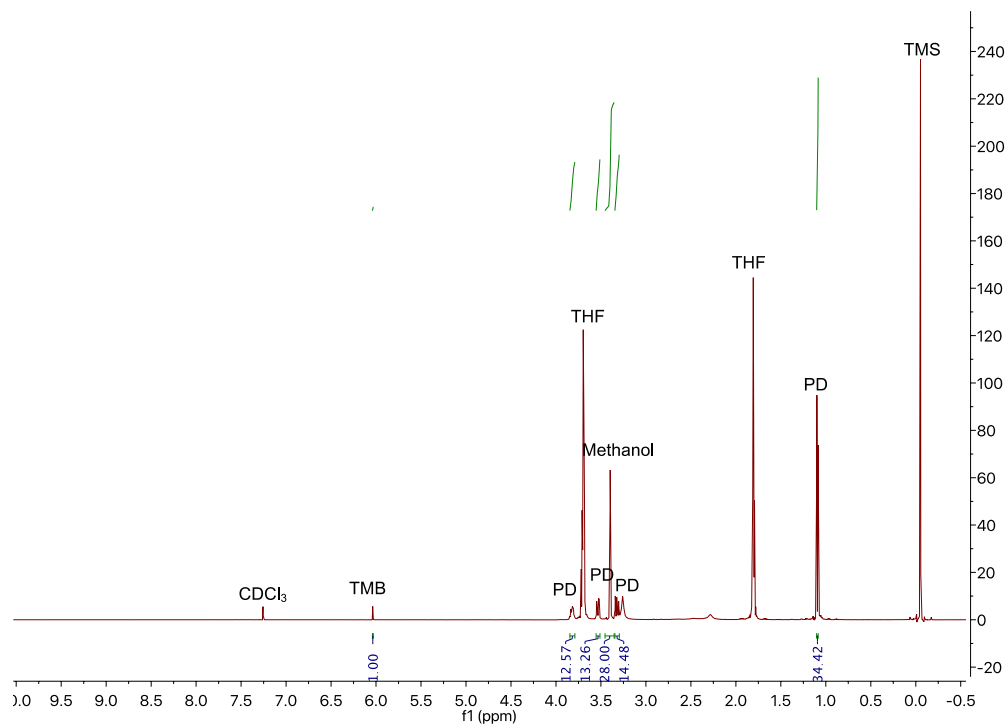


Figure S4. ^1H NMR of the reaction mixture from entry 4, Table 2.

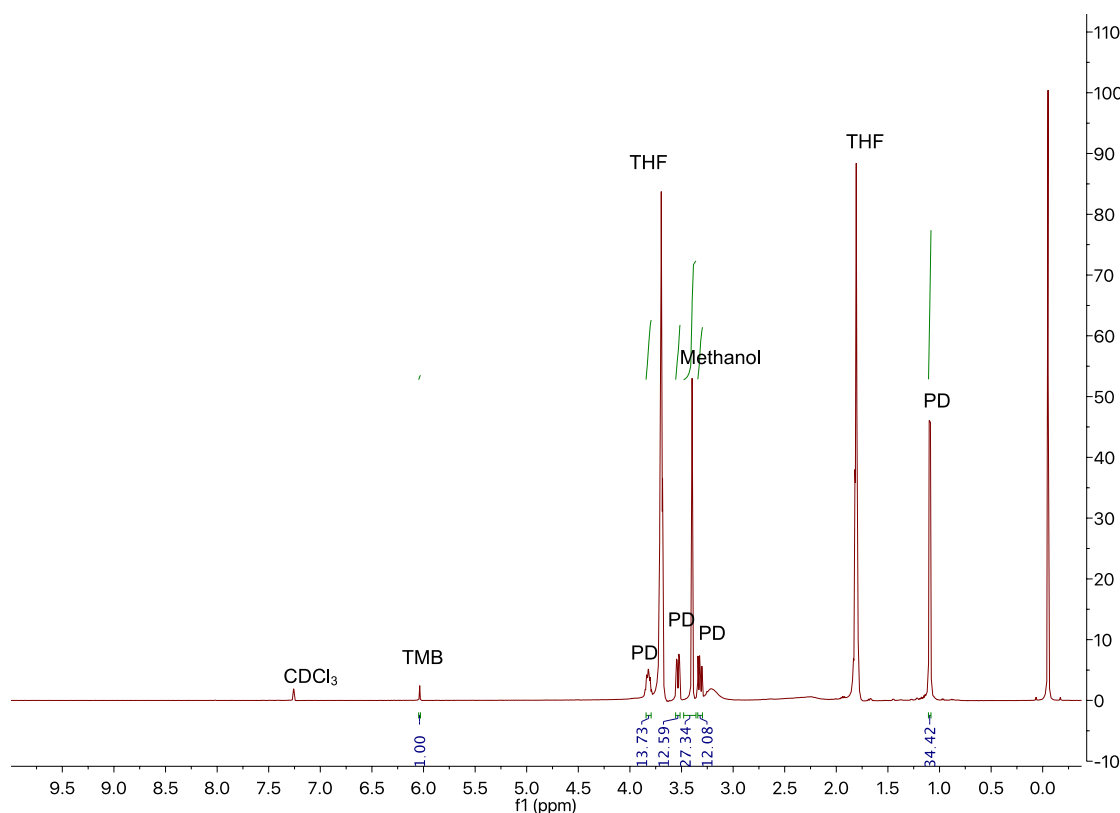


Figure S5. ^1H NMR of the reaction mixture after sequential addition of CO_2 and H_2 to PO-PEI₆₀₀-THF mixture in the presence of catalyst **3** at 140 °C (from entry 1, Table 3).

3) Standard procedure for *in situ* high pressure and high temperature MAS-NMR

The MAS-NMR experiments were performed on an Agilent-Varian VNMRs NMR spectrometer equipped with a 7.05 T magnet, operating at 75.43 MHz for the ^{13}C channel and 299.969 MHz for ^1H channel, and using a 5 mm Chemmagetics design HXY probe. The rotors were Varian/Agilent-style cavern rotors (Revolution NMR LLC), modified for high pressure samples as described previously.¹ A premixed solution containing propylene oxide (240 mg), PEI₆₀₀ (60 mg), catalyst **3** (2.4 mg) and THF- d_8 (1 mL) was transferred to a MAS NMR rotor in a N_2 -atmosphere glovebox. The rotor was charged with a 15 bar $^{13}\text{CO}_2$ and 45 bar H_2 at room temperature (total initial pressure=60 bar) and heated to 140 °C. When the set temperature reached, the rotor was kept at this temperature while an array of ^{13}C NMR spectra collected for 16 h. The T_1 for $^{13}\text{CO}_2$, $^{13}\text{CH}_3\text{OH}$ and PC was 1.2 seconds, 11 seconds and 100 seconds, respectively. A 45 degree pulse was used. A recycle delay of 20 seconds and spinning speed of 5 kHz were applied. The spectra were acquired with 180 scans, and acquisition times of 300 ms.

4) Standard procedure for GC-MS

GC-MS analyses were performed by a gas chromatograph system Shimadzu GC-2010 equipped with a quadrupole ion trap system Shimadzu GCMS-QP2010S; ionization was accomplished by electron ionization. MS acquisition was carried out in scan mode in the range 21–550 m/z. GC separations were performed on a capillary column RXi®-5Sil MS (30 m × 0.25 mm × 0.50 μm, Restek) and helium was used as carrier gas with a constant column flow rate of 0.6 mL/min. The GC temperature program was as follows: hold at 30 °C for 6 minutes, from 30 to 250 °C at 15°C/min, hold at 250°C for 5 min. The injector temperature was set at 60°C in split ratio 5 : 100. Five standards were prepared with known concentration of methanol and propylene glycol in THF. Standards and samples were diluted with 1.453 wt% benzene (internal standard) in THF for calibration and analysis.

5) References

1. Walter, E. D.; Qi, L.; Chamas, A.; Mehta, H. S.; Sears, J. A.; Scott, S. L.; Hoyt, D. W., Operando MAS NMR Reaction Studies at High Temperatures and Pressures. *J Phys. Chem. C* **2018**, *122* (15), 8209-8215.