

Supporting Information

Liquid-Phase Permethylation of Diethylenetriamine Using Methanol over Copper Catalysts

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TABLE CAPTIONS

Table S1. Composition (wt%) of the Cu catalysts used in this study.

SCHEME CAPTIONS

Scheme S1. Main products observed in the catalytic tests.

Scheme S2. Proposed transalkylation mechanisms for PMDTA transformation into DMP over [Cu] resulting in (a) TMA (1eq PMDTA) and (b) TMEDA (2 eq PMDTA) formation, inspired from Wilson and Laine.^{S1}

Scheme S3. Possible mechanism for TMEDA formation from DETA *via* dehydrogenation and methanolysis.

FIGURE CAPTIONS

Fig S1. Main by-products obtained in the reaction solution after DETA methylation over 5%Ru/C catalysts. Reaction conditions: 200 °C, 18 h, H₂ (30 bar), MeOH/DETA (molar) = 371, 260 mg of catalyst per mmol of DETA.

Fig S2. GC chromatograms showing oligomer formation from DETA methylation over Cu₃ pre-reduced from 50 °C to 185 °C using a temperature ramp of 5 °C·min⁻¹. Reaction conditions: 200 °C, 20 h, H₂ (50 bar), MeOH/DETA (molar) = 742, 140 mg of Cu₃ per mmol of DETA.

Fig S3. Possible mechanism for TMEDA formation from DETA *via* dehydrogenation and methanolysis.

Fig S4. GC chromatograms for DETA methylation tests over Cu_3 pre-reduced from 50 °C to 200 °C using temperature ramps of (a) 2 °C·min⁻¹ and (b) 5 °C·min⁻¹. Reaction conditions: 200 °C, 20 h, H₂ (50 bar), MeOH/DETA (molar) = 742, 90 mg of Cu_3 per mmol of DETA.

Fig S5. HR-TEM micrograph of Cu_7 pre-reduced reduced from 50 °C to 200 °C using a temperature ramp of 1 °C·min⁻¹.

Fig S6. XRD patterns of fresh and used Cu_3 pre-reduced from 50 °C to 200 °C using different temperature ramps, and further passivated upon exposure to air. For comparison, the XRD pattern of the unreduced Cu_3 is also provided.

Fig S7. (a) Cu 2p and (b) O 1s XPS spectra of Cu_3 pre-reduced from 50 °C to 200 °C using temperature ramps of (a1, b1, c1) 1 °C·min⁻¹ and (a2, b2, c2) 5 °C·min⁻¹, and further passivated upon exposure to air.

Fig S8. (a) Cu 2p and (b) O 1s XPS spectra of Cu_7 pre-reduced from 50 °C to 200 °C using a temperature ramp of 1 °C·min⁻¹, and further passivated upon exposure to air.

Fig S9. GC chromatograms for DETA methylation tests over Cu_3 pre-reduced from 50 °C to 200 °C using a temperature ramp of 1 °C·min⁻¹. Reaction conditions: (a) 50 mg and (b) 90 mg of Cu_3 per mmol of DETA. Other reaction conditions: 200 °C, 20 h, H₂ (50 bar), MeOH/DETA (molar) = 371 or 742.

Fig S10. Representative HR-TEM micrograph and size distribution of Cu_3 particles after the 4th run. Reaction conditions: 200 °C, 20 h, H₂ (50 bar), MeOH/DETA (molar) = 742, 90 mg of Cu_3 per mmol of DETA. The catalyst was pre-reduced from 50 °C to 200 °C using a temperature ramp of 1 °C·min⁻¹ before the 1st run reaction.

Fig S11. (a) Cu 2p and (b) O 1s XPS spectra of the used Cu_3 initially pre-reduced from 50 °C to 200 °C using a temperature ramp of 1 °C·min⁻¹ before the 1st run reaction. Reaction conditions as in Fig S9.

Experimental Section

Chemicals

Diethyltriamine (>99% purity), tetramethylenediamine (>99% purity), pentamethyldiethylene-triamine (>99% purity) were provided by Solvay Novocare, while 1,4-dimethylpiperazine (>99% purity) and anhydrous methanol (>99.99% purity) were procured from Aladdin and Sigma-Aldrich, respectively. The chemicals were used as received without any further purification. Composite Cu catalysts (including binders) were procured from Johnson Matthey (Pricat CU series, 60/35P – Cu_1, 64 wt% Cu; 60/8 P – Cu_3, 64 wt% Cu, 50/8 P – Cu_2, 51 wt% Cu), Clariant (T4419P – Cu_5, 67 wt% Cu), and Süd-Chemie (T8031P – Cu_6, 78 wt% Cu; T4489P – Cu_4, 46 wt% Cu). The catalysts included different binders based on SiO₂, AlOOH, Cr₂O₃, NiO, MgO and MnO₂. The pure CuO catalyst (Cu_7, 80% wt% Cu) was supplied by Sigma-Aldrich. 5%Ru/C (Johnson Matthey), Raney Ni (Solvay), Raney Co (W.R. Grace) and 20%Pd/C (Evonik), were also used as catalysts. Phosphoric acid (AR grade, 85%) and sulfuric acid (AR grade, 98%) were supplied by Sinopharm.

Table S1. Composition (wt%) of the Cu catalysts used in this study

Catalyst	Cu	Si	Al	Cr	Mg	Ni	Mn
Cu_1	64	0.50	-	1.9	0.89	-	-
Cu_2	51	0.35	2.5	0.35	-	-	-
Cu_3	64	0.93	-	-	-	0.32	-
Cu_4	46	-	16	-	-	-	6.8
Cu_5	67	-	-	14	-	-	-
Cu_6	78	0.05	-	-	-	-	-
Cu_7	80	-	-	-	-	-	-

Catalyst characterization

Before structural, volumetric and spectroscopic analysis, the catalysts were outgassed at 573 K to remove adsorbed water.

The phases present in the catalysts were analyzed by powder X-ray diffraction (PXRD) under controlled H₂ atmosphere. The PXRD patterns were recorded on a Rigaku 2200D/max diffractometer provided with Cu-K α radiation ($\lambda = 1.54178 \text{ \AA}$). The spectra were collected in the 2 θ range of 5-40° at a scan speed of 1°·min⁻¹ with a step size of 0.02°. The patterns were indexed using the Joint Committee on Powder Diffraction (JCPDS) database and interpreted using MDI JADE 5.0 software.

High-resolution transmission electron microscopy (HRTEM) was used to measure the average size and distribution of Cu particles using a JEOL JEM 2100F microscope. Electron-dispersive spectroscopy (EDS) was used to measure the local composition of the catalysts using a JED2300 probe.

The H₂-TPR profiles were collected on a Micromeritics AutoChem II2920 system equipped with a quartz U-type tubular reactor and a TCD detector. A cold trap was used before the detector to avoid any interference of water in the TPR plot. In each test, 50 mg of the given catalyst was loaded into the reactor and purged with 30 mL(STP)/min He at 300 °C for 1 h to remove adsorbed moisture and vapors, and then cooled down to room temperature. The temperature was then increased up to 750 °C at a heating rate of 10 °C·min⁻¹ under a H₂ flow diluted in Ar (10 v/v%). The system was calibrated using an Ag₂O standard (>99% purity) to measure the H₂ consumption in the TPR profiles. All the profiles were normalized to a constant mass of water.

Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-OES) was used to quantify the bulk metal content of the catalysts using a Perkin Elmer 8000 spectrometer and Winlab32 software. Before the measurements, the samples (50 mg) were dissolved at 280 °C using 3 mL of a H₃PO₄/H₂SO₄ (1 : 1 v/v) solution.

The surface composition of the catalysts was analyzed by X-ray photoelectron spectroscopy (XPS) using a ThermoFischer, ESCALAB 250Xi apparatus equipped with a hemispherical analyzer and a delay line detector. The spectra were recorded using an Al monochromated X-ray source (12.5 kV, 16 mA) with a pass energy of 30 eV (0.1 eV/step for high resolution spectra, and a pass energy of 100 eV (1 eV/step) for survey spectrum in hybrid mode and slot lens mode, respectively. The adventitious C1s binding energy (284.8 eV) was used as an internal reference.

Catalytic tests

Before the catalytic tests, the catalysts were pre-reduced at the desired temperature under a 1:10 H₂/Ar flow [40 cm³(STP)·min⁻¹] according to the H₂-TPR profiles. The methylation reaction was conducted in a stainless steel autoclave reactor (30 mL) from Taiatsu. In a typical test, the auto-clave was charged with 0.0768 g (0.74 mmol) of DETA, 15.84 g (494 mmol) of MeOH, and 80 mg of catalyst under N₂. The reactor was then sealed under N₂, purged with H₂ at least 10 times and submitted to a H₂ pressure of 50 bar. The reactor was kept without stirring for 1 h to assess proper sealing. The mixture was then stirred for 1 h at room temperature and 500 rpm, the temperature was raised to the desired value under stirring, and the reaction was carried out for a given time.

After the tests, the reactor was cooled down to room temperature and evacuated in a fume hood, and an accurate weight of biphenyl was added to the reaction mixture as internal standard. After complete dissolution of biphenyl, the reaction mixture was filtered and the reactants and products were analyzed by gas chromatography on an Agilent 7890A GC equipped with a flame ionization detector (FID) and an Agilent 19091J-215 capillary column (length 50 m; inner diameter 0.32 mm; thickness 1.05 μm). The injector temperature was set at 250 °C, the detector temperature was set at 300 °C and the sample injection volume was 1 μL.

GC-MS analyses were carried out on an Agilent 7890B GC equipped with a flame ionization detector (FID) and an Agilent 19091S-433UI capillary column (length 30 m; inner diameter 0.25 mm; thickness 0.25 μm). The injector temperature was set at 275 °C, the detector temperature was set at 300 °C and the sample injection volume was 1 μL.

Volatile amines (*e.g.*, trimethylamine, TMA) were analysed by gas chromatography on an Agilent 7890 GC equipped with a flame ionization detector (FID) and a CP7448 capillary column (length 60 m; inner diameter 0.32 mm; thickness 0.45 μm). The injector temperature was set at 275 °C, the detector temperature was set at 300 °C and the sample injection volume was 1 μL.

NH₃ analysis was carried out with a DR 2800 analyser. In a typical test, a given amount of ammonium salicylate reagent power and ammonium cyanide reagent was added to 0.1 mL of liquid sample in a tube. The tube was shaken and introduced to the analyser after 20 min.

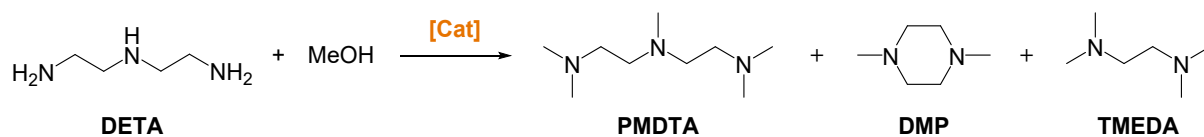
In each test, the DETA conversion, selectivity and yield of each product were defined using the following expressions (eqs 1-3)

$$\text{DETA conversion} = \left(1 - \frac{n_{\text{DETA}}}{n_{\text{DETA}}^0} \right) \times 100\% \quad (\text{S1})$$

$$\text{Selectivity}_i = \left(\frac{n_i}{n_{\text{DETA}}^0 - n_{\text{DETA}}} \right) \times 100\% \quad (\text{S2})$$

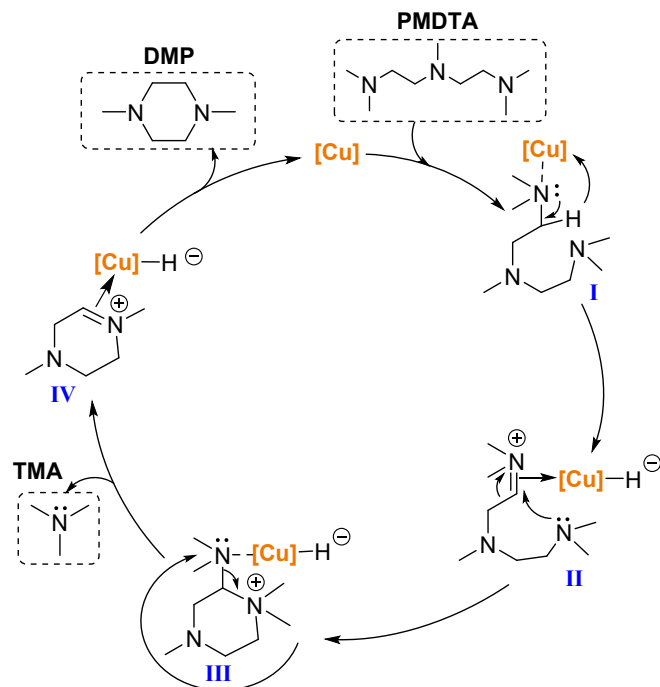
$$\text{Yield}_i = \frac{n_i}{n_{\text{DETA}}^0} \times 100\% \quad (\text{S3})$$

where n_{DETA}^0 and n_{DETA} refer to the initial and final number of moles of DETA, and n_i is the number of moles of the i^{th} product, i.e. PMDTA, DMP and TMEDA (tetramethylenediamine) (Scheme S1). The carbon balance fell into the range 95-99% in all the catalytic tests.

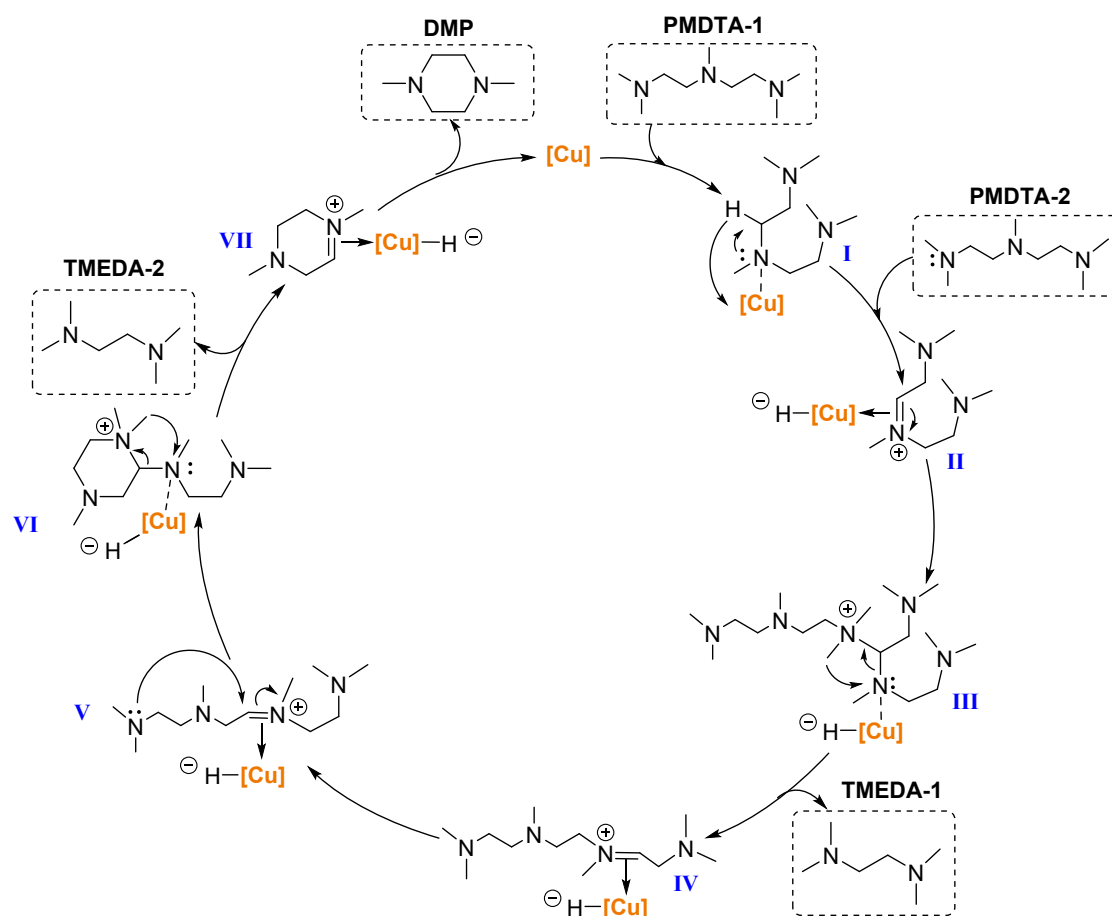


Scheme S1. Main products observed in the catalytic tests.

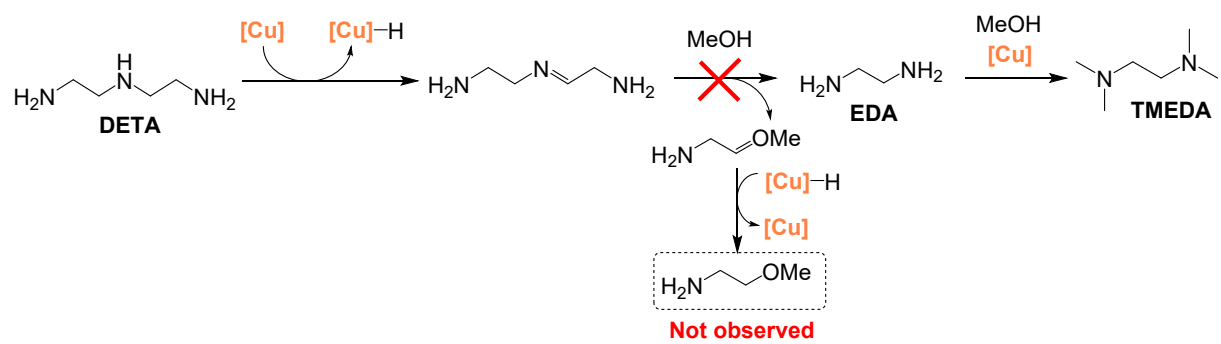
(a) 1 eq PMDTA



(b) 2 eq PMDTA

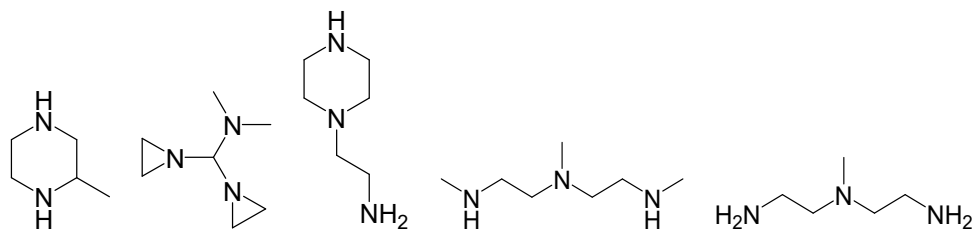


Scheme S2. Proposed transalkylation mechanisms for PMDTA transformation into DMP over $[Cu]$ resulting in (a) TMA (1eq PMDTA) and (b) TMEDA (2 eq PMDTA) formation, inspired from Wilson and Laine.^{S1}



Scheme S3. Possible mechanism for TMEDA formation from DETA *via* dehydrogenation and methanolysis.

Main by-products:



By-products in trace amounts

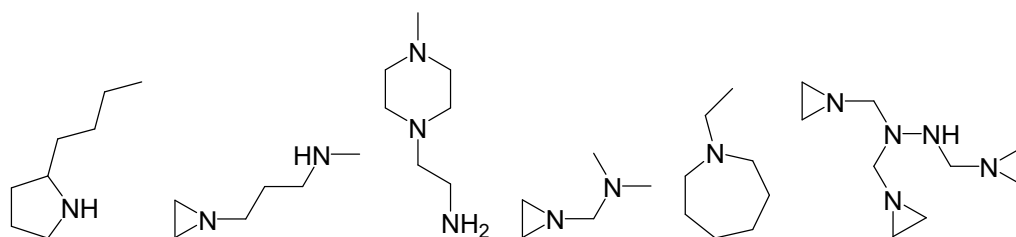


Fig S1. Main by-products obtained in the reaction solution after DETA methylation over 5%Ru/C catalysts. Reaction conditions: 200 °C, 18 h, H₂ (30 bar), MeOH/DETA (molar) = 371, 260 mg of catalyst per mmol of DETA.

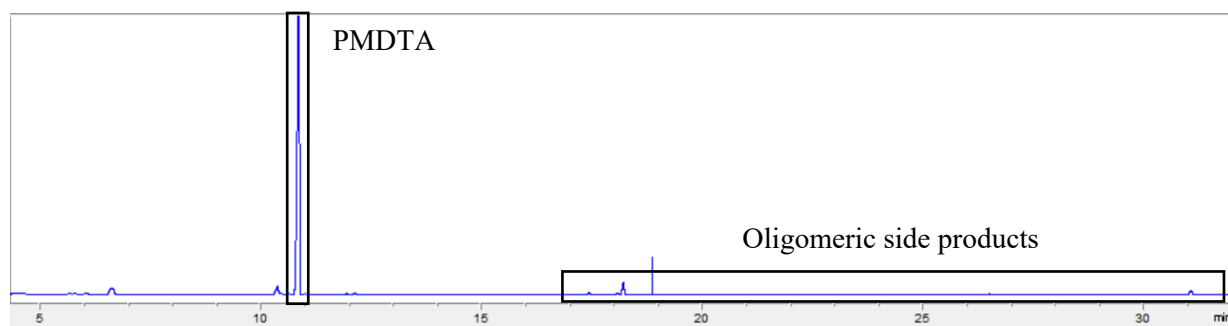


Fig S2. GC chromatograms showing oligomer formation from DETA methylation over Cu₃ pre-reduced from 50 °C to 185 °C using a temperature ramp of 5 °C·min⁻¹. Reaction conditions: 200 °C, 20 h, H₂ (50 bar), MeOH/DETA (molar) = 742, 140 mg of Cu₃ per mmol of DETA.

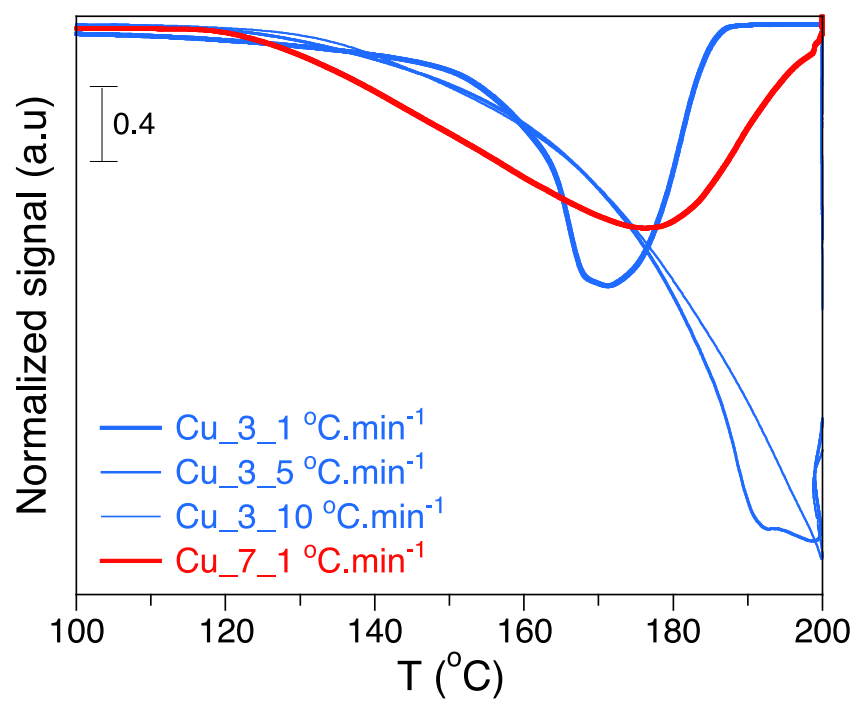


Fig S3. H₂-TPR profiles of Cu₃ and Cu₇ catalysts pre-reduced with different temperature ramps.

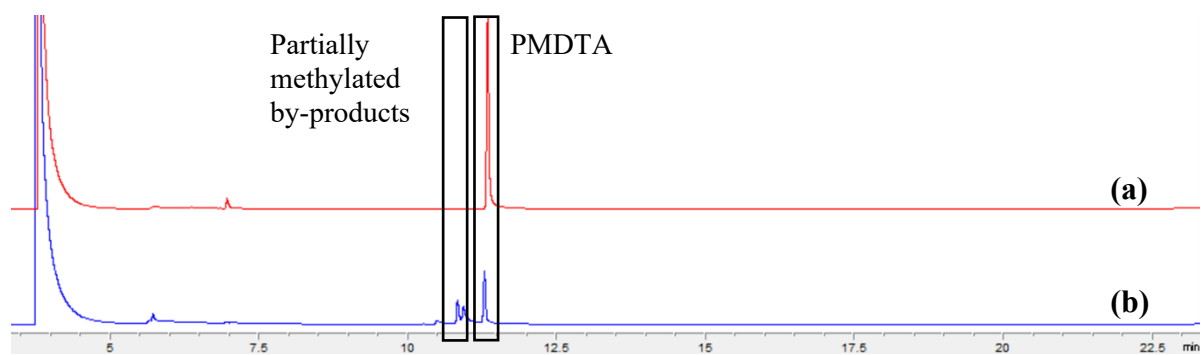


Fig S4. GC chromatograms for DETA methylation tests over Cu₃ pre-reduced from 50 °C to 200 °C using temperature ramps of (a) 2 °C·min⁻¹ and (b) 5 °C·min⁻¹. Reaction conditions: 200 °C, 20 h, H₂ (50 bar), MeOH/DETA (molar) = 742, 90 mg of Cu₃ per mmol of DETA.

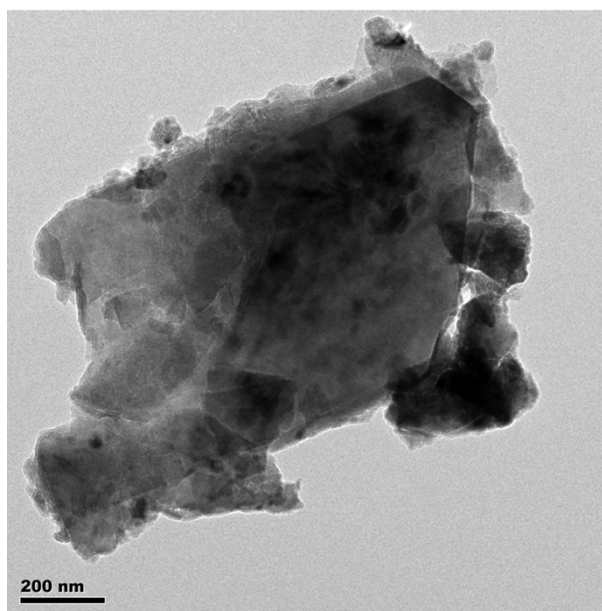


Fig S5. HR-TEM micrograph of Cu₇ pre-reduced reduced from 50 °C to 200 °C using a temperature ramp of 1 °C·min⁻¹.

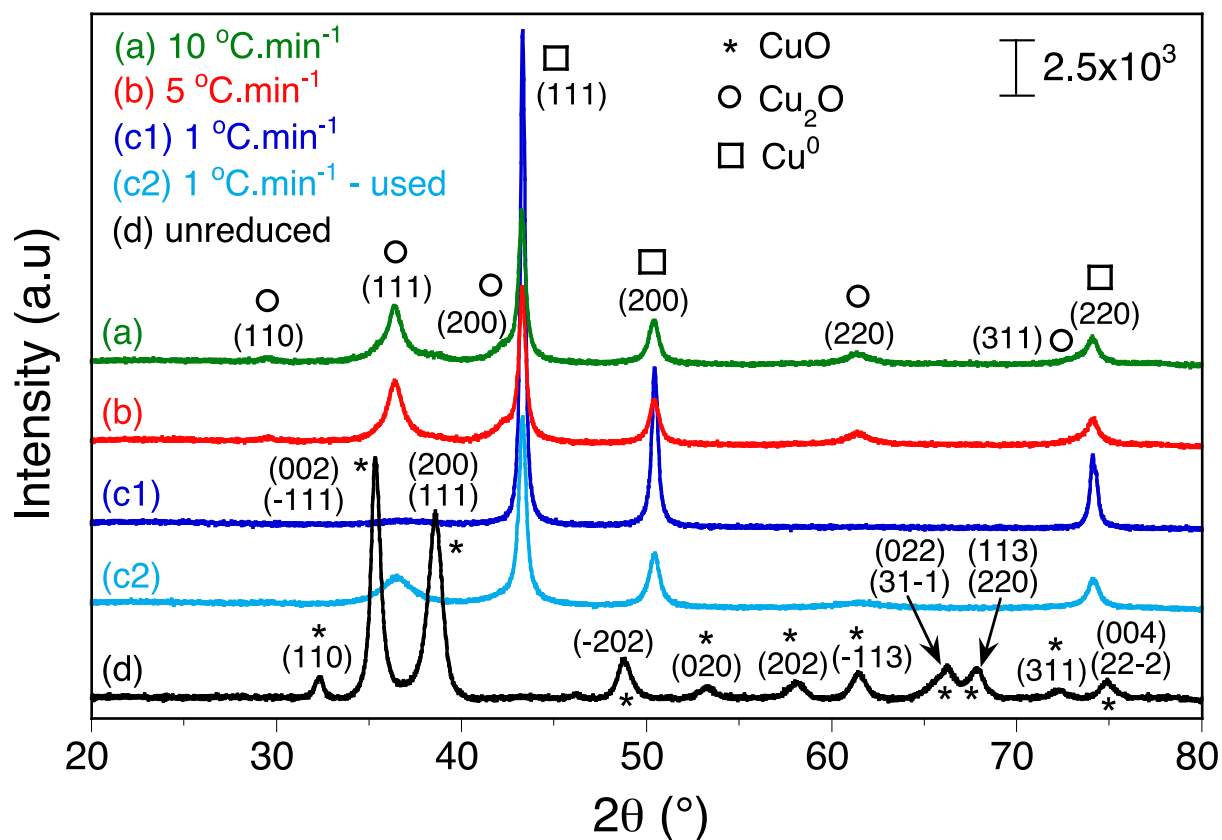


Fig S6. XRD patterns of fresh and used Cu₃ pre-reduced from 50 °C to 200 °C using different temperature ramps, and further passivated upon exposure to air. For comparison, the XRD pattern of the unreduced Cu₃ is also provided.

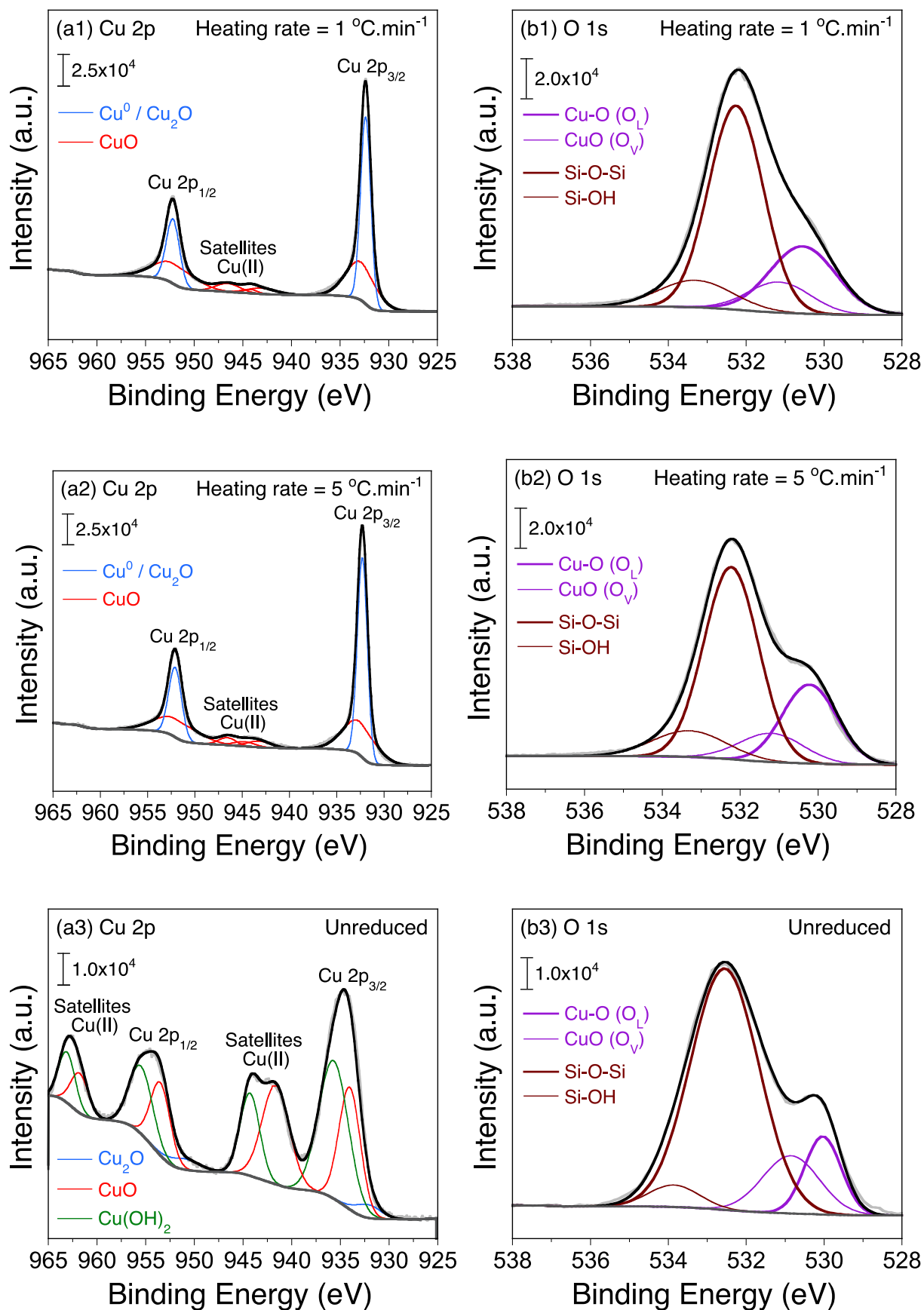


Fig S7. (a) Cu 2p and (b) O 1s XPS spectra of Cu₃ pre-reduced from 50 °C to 200 °C using temperature ramps of (a1, b1) 1 °C·min⁻¹ and (a2, b2) 5 °C·min⁻¹, and further passivated upon exposure to air. For clarity, the Cu 2p and O 1s XPS spectra of unreduced Cu₃ are also provided (a3, b3).

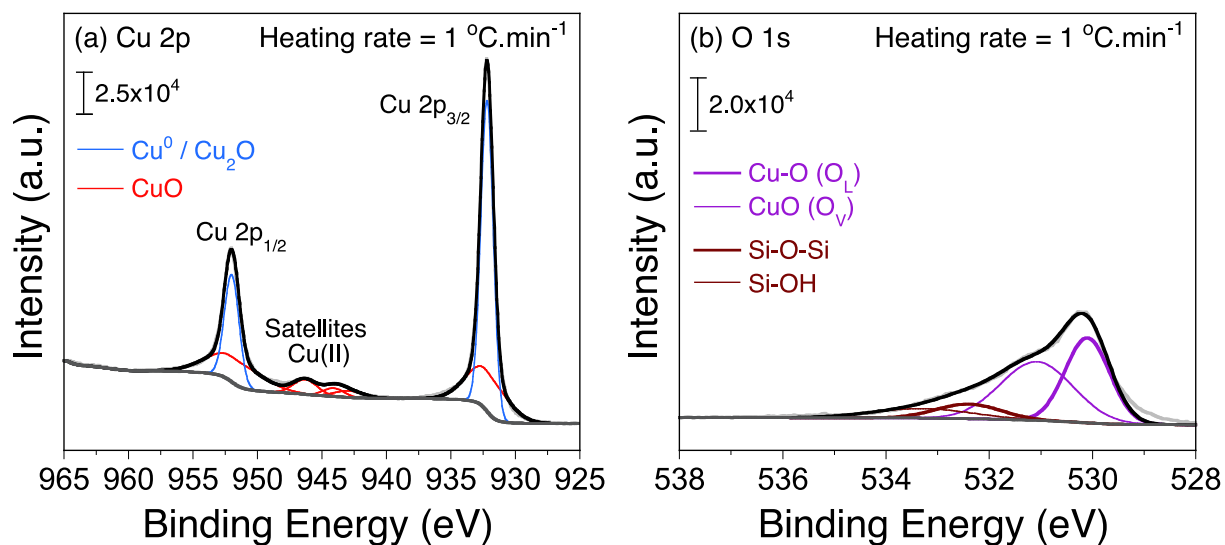


Fig S8. (a) Cu 2p and (b) O 1s XPS spectra of Cu₇ pre-reduced from 50 °C to 200 °C using a temperature ramp of $1\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$, and further passivated upon exposure to air.

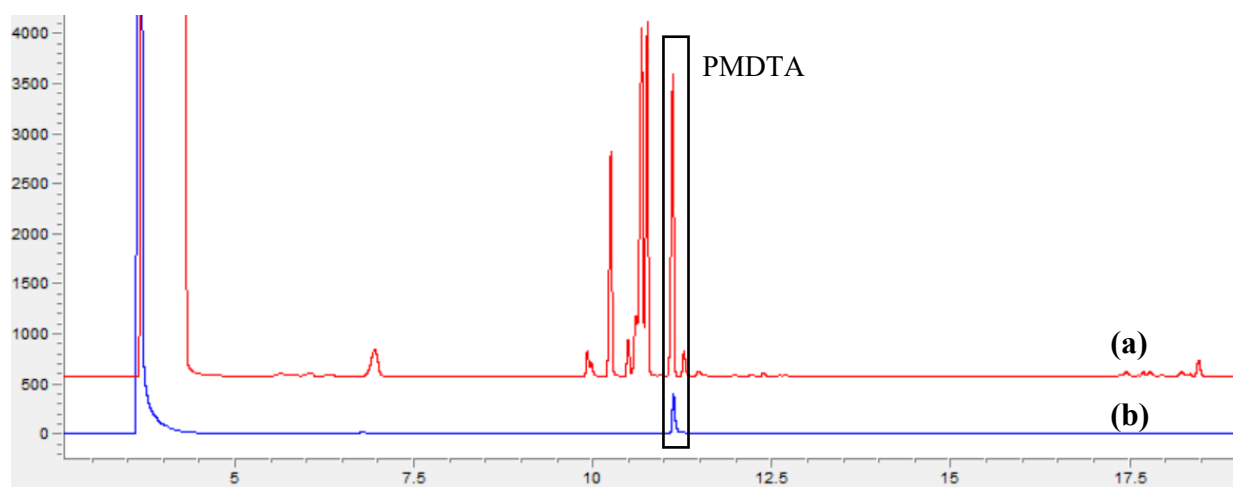


Fig S9. GC chromatograms for DETA methylation tests over Cu_3 pre-reduced from 50 °C to 200 °C using a temperature ramp of 1 °C·min⁻¹. Reaction conditions: (a) 50 mg and (b) 90 mg of Cu_3 per mmol of DETA. Other reaction conditions: 200 °C, 20 h, H₂ (50 bar), MeOH/DETA (molar) = 371 or 742.

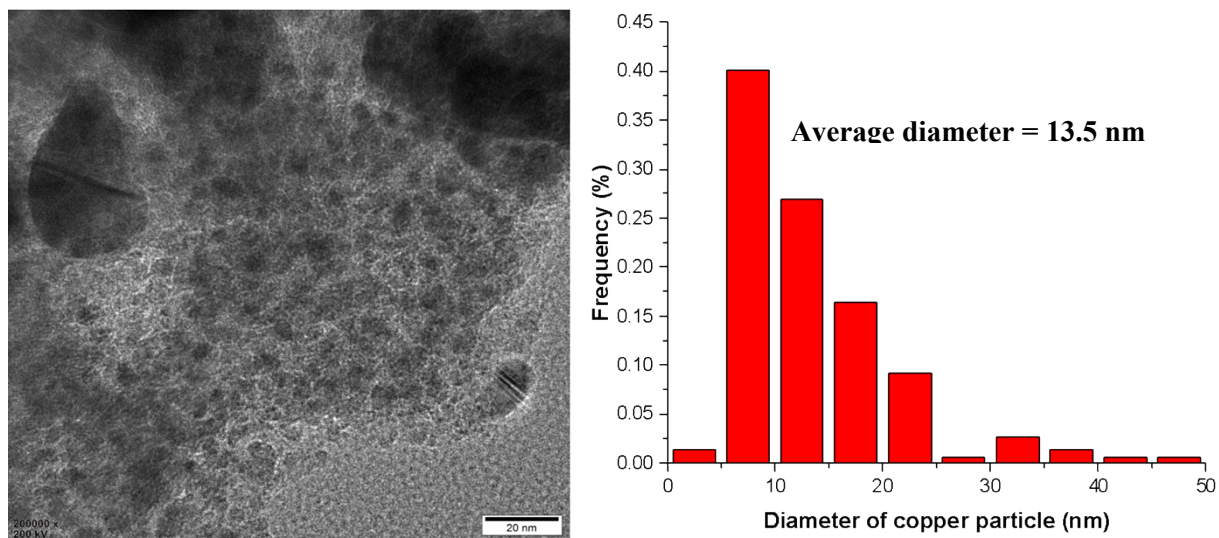


Fig S10. Representative HR-TEM micrograph and size distribution of Cu₃ particles after the 4th run. Reaction conditions: 200 °C, 20 h, H₂ (50 bar), MeOH/DETA (molar) = 742, 90 mg of Cu₃ per mmol of DETA. The catalyst was pre-reduced from 50 °C to 200 °C using a temperature ramp of 1 °C·min⁻¹ before the 1st run reaction.

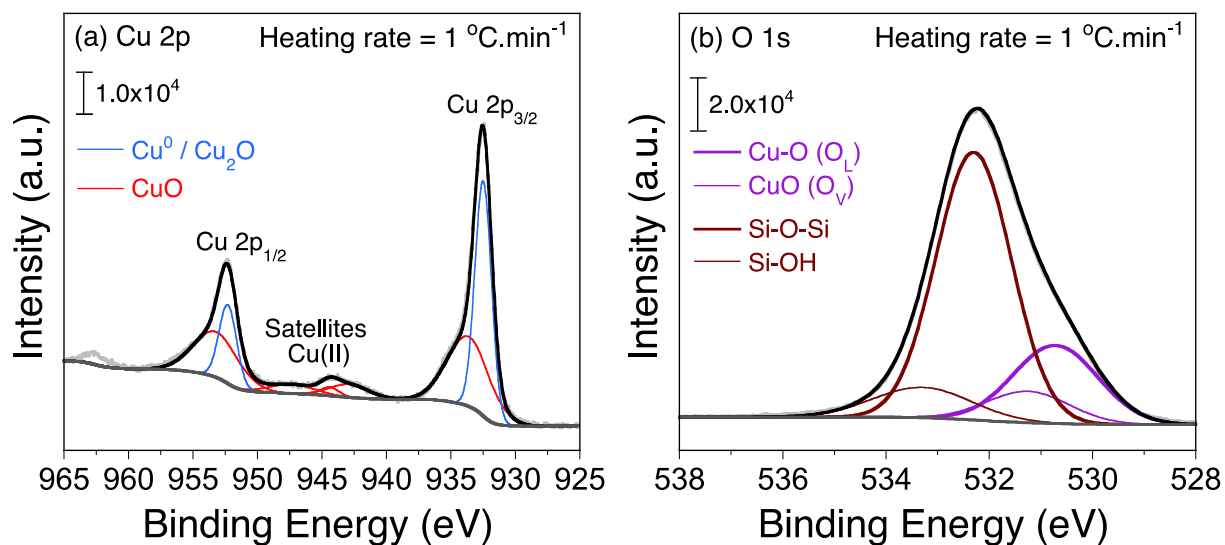
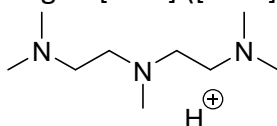


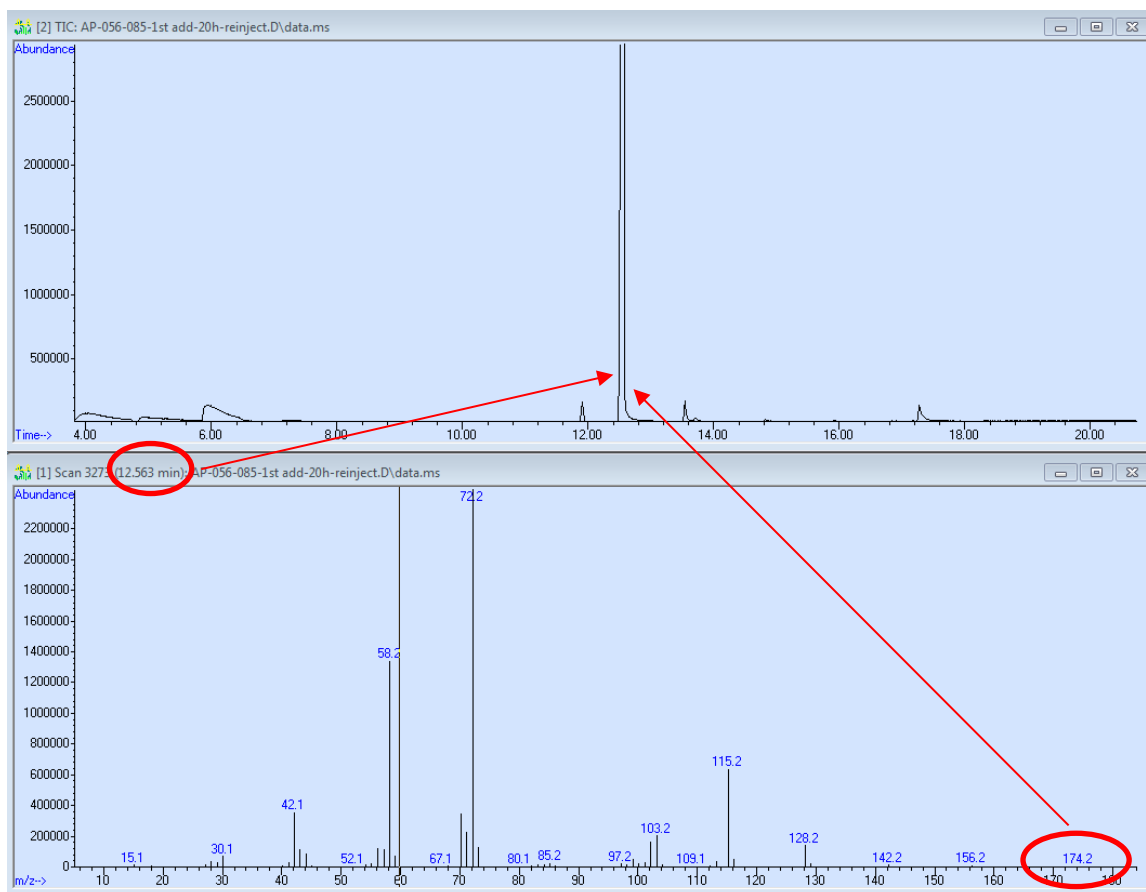
Fig S11. (a) Cu 2p and (b) O 1s XPS spectra of the used Cu₃ initially pre-reduced from 50 °C to 200 °C using a temperature ramp of 1 °C·min⁻¹. Reaction conditions as in Fig S9.

GC-MS spectra

GC-MS was used to assess the formation of PMDTA in our reaction system. The retention time of the PMDTA locates at 12.563 min, and the mass spectra at this retention time includes a fragment with $m/z = 174.2$ corresponding to $[M+1]$ ($[M+H]$) of PMDTA.

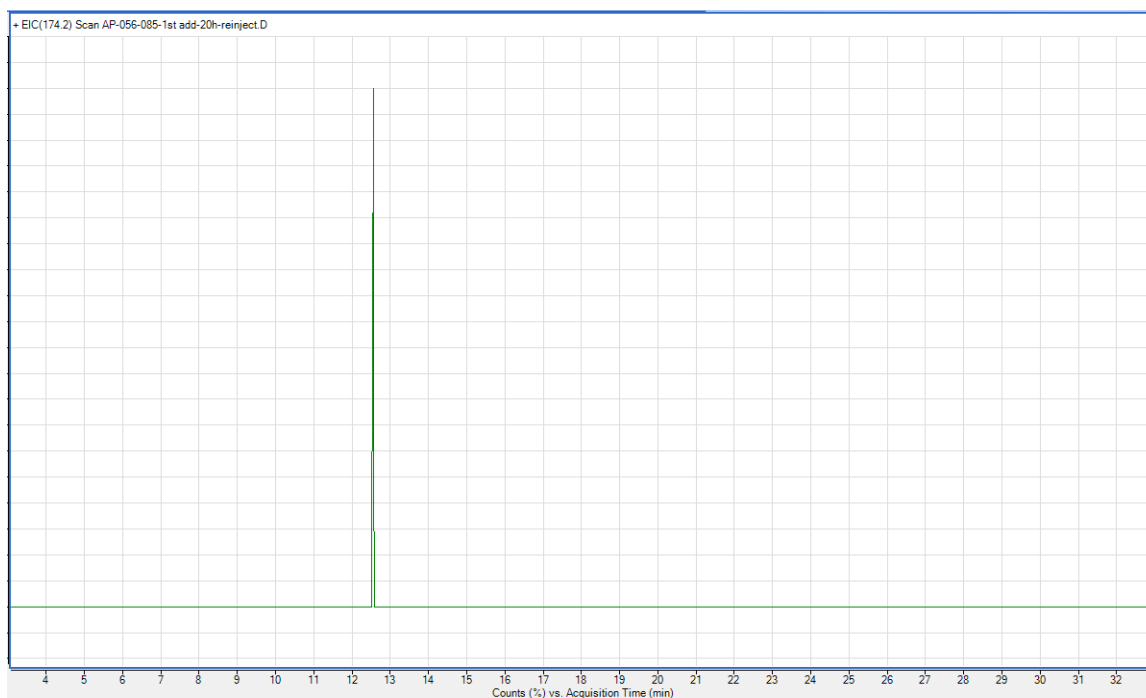


Exact mass of M+1: 174.1965



Example of GC-MS spectra for a reaction with 77% PMDTA yield

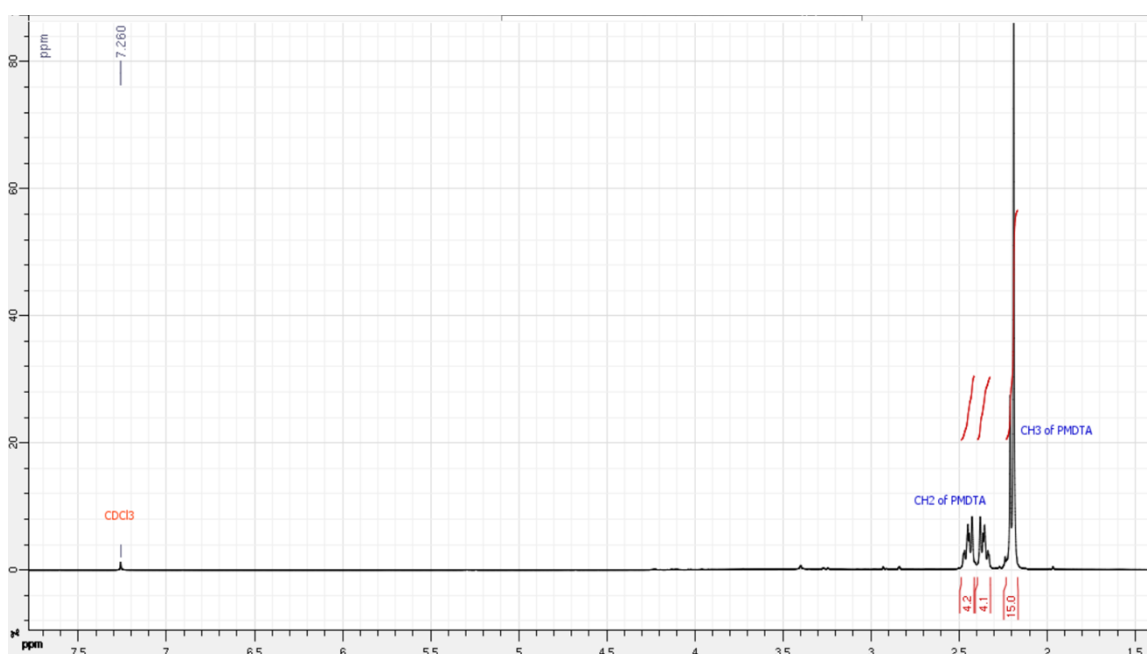
The $[M+H]$ mass of PMDTA is 174.1965, which can be obtained from the retention time appearing at 12.563 min.



MS (PMDTA [M+H] = 174.1965) extraction from GC-MS spectra for a reaction with 77% PMDTA yield

¹H NMR spectra:

We also measured the ¹H NMR spectra of the reaction mixtures dried under vacuum to remove volatile compounds. From the spectra, we can observe that the main product is PMDTA, as inferred from the presence of CH₂ and CH₃ groups. Small peaks belonging to DMP appear overlapped under PMDTA peaks. DETA disappeared completely.



¹H NMR (300MHz, CDCl₃) of the reaction mixture with 75% PMDTA yield after high vacuum purification.

References

[S1] R. B Wilson Jr and R. M. Laine, *J. Am. Chem. Soc.*, 1985, **107**, 361.