Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information for

Catalytic hydrogenation of CO_2 from air via porous silica-supported Au nanoparticles in aqueous solution

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1. Materials and Methods

Hexadecyltrimethylammonium bromide (CTAB, ≥99%), tetramethyl orthosilicate (TMOS, 98%), 1,3,5-trimethylbenzene (TMB, 98%), pentaethylenehexamine (PEHA, technical grade), and water-^{18}O (97 atom % ^{18}O) were purchased from Sigma-Aldrich. Methanol (ACS certified), anhydrous ethanol (ACS certified), and sodium hydroxide (Pellet, ACS certified) were purchased from Fisher Scientific. Water used in preparation procedures was obtained from a Milli-Q system (18 MΩ) except otherwise indicated. All other chemicals were obtained from commercial suppliers and used without further purification.

UV-Visible-NIR spectra were collected on an Agilent Technologies Cary 5000 UV-Vis-NIR.

TEM images were obtained on a FEI Tecnai G2 F20 200 kV Cryo-STEM with a Gatan Ultrascan 4000 4k x 4k CCD Camera System Model 895; EDS analysis was done by an EDAX Octane T Ultra W /Apollo XLT2 SDD and TEAM EDS Analysis System built on the STEM set up. TEM samples were prepared by drop-casting the solution on carbon-coated copper TEM grids (CF-400-Cu, 25/pk, carbon film on 400 Square Mesh copper grids, Electron Microscopy Science).

XPS spectra were recorded on a ThermoFisher Scientific K-alpha instrument equipped with a monochromatic Al Kα X-ray source (1486.6 eV). Survey scans and high-resolution scans were collected on an X-ray spot size of 200 μm with energy steps of 1 and 0.1 eV, respectively. Spectral energies were calibrated by setting the C–C binding energy of C1s at 284.8 eV. Peak fitting was performed using the Thermo Avantage software (version 4.60). XPS samples were prepared by drop-casting a concentrated solution on a copper foil and dried in a vacuum oven overnight.

BET measurements were made on a Micrometritics TriStar 3000 Surface Area and Pore Size Analyzer. The analysis was performed by adsorption-desorption of nitrogen at 77.350 K.

Pressured reactions were carried out on a Biotage® Endeavor™ Catalyst Screening System controlled by Endeavor® Advanced Software (EAS).

^{1}H NMR and non-quantitative ^{13}C NMR spectra were recorded with Bruker AVIIIHD 500 MHz NMR Spectrometer in D_2O; quantitative ^{13}C NMR spectra were recorded with Bruker AVIIIHD 800 MHz NMR Spectrometer in D_2O.

GC-MS experiments were performed on an Agilent Technologies Gas Chromatograph System equipped with a 5973 *Inert* Mass Selective Detector. The column Rtx-5 (30m, 0.25 mm ID, 0.25 μm df) from Restek Corporation was used.

GC-TCD experiments were performed on an Agilent Gas Chromatograph (GC) 6890 equipped with a Split/Splitless injector, an integrate valve switch and a thermal conductivity detector (TCD) was used for the reactor gas analysis. The GC was controlled by Chemstation Software. All injections were manual injections from a sealed gas bag. The syringe system used was VICI Precision Lock Syringe from a volume of 10 μl to 2000 μl. Specifically:

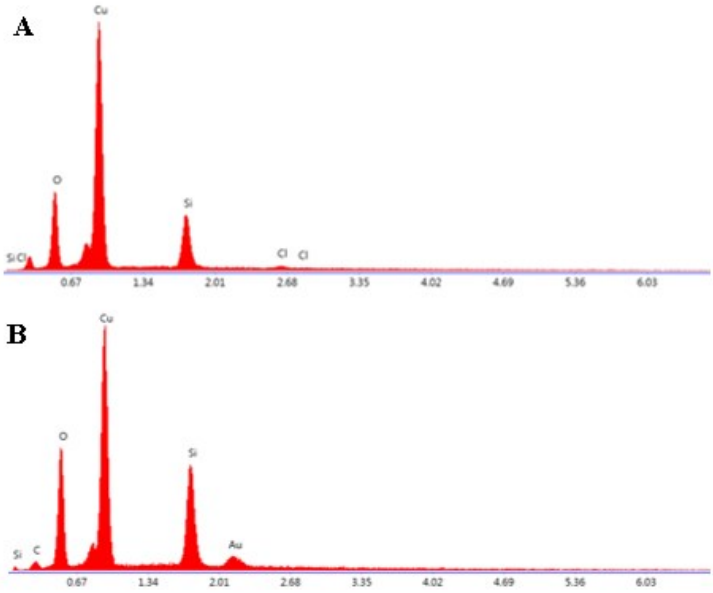
Injector: The injector was used in split mode with a 10:1 split ratio. It was maintained at a constant 200 °C with a total flow of 163 ml/min. The carrier gas was argon (99.995%). The head pressure was maintained at 6.67 psi.

Oven: The oven was initially maintained at 30 °C for 9 minutes. It was then ramped at 50 °C /min to 120 °C and then maintained there for 8 minutes. The total run time was 19 minutes.

Column: Column 1 is an Agilent HP PLOT-Q column (30 m x 0.530 mm, 25.00 micron); Column 2 is an Agilent HP-PLOT MoleSieve (30 m x 0.530 mm, 20.00 micron).

Detector: The TCD was maintained at 210 °C the reference flow was set at 30 ml/min with Ar as the make-up gas at 0.6 ml/min. The filament was set to negative polarity.

Switch Box: The switch box was maintained at 100 °C with value switches at 5.20 minutes and 11.00 minutes.



2. Additional characterizations of Au/SiO_2

Fig. S1. EDS characterization of porous SiO_2 and Au/SiO_2. EDS analysis of porous silica beads (A) before and (B) after the AuNPs embedding. Similar to XPS, the EDS study showed the presence of gold after the AuNP embedding.

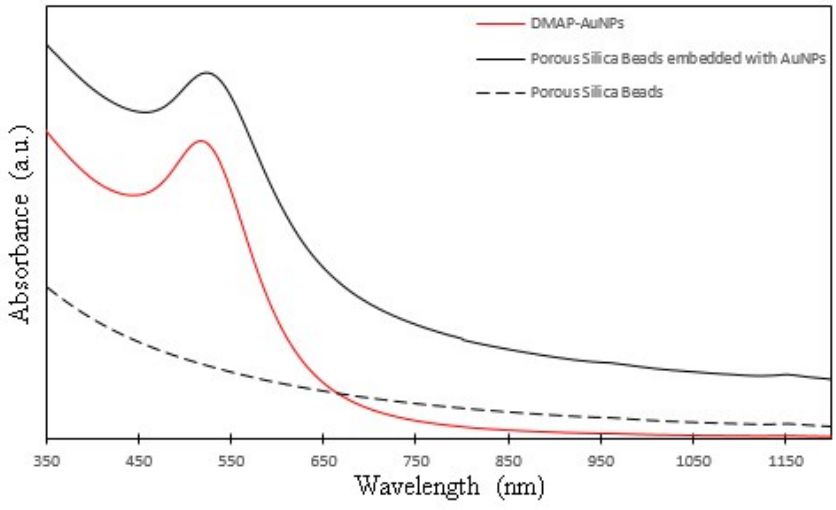


Fig. S2. UV-vis spectra of Au/SiO_2, porous SiO_2 and AuNPs. DMAP-AuNPs (red solid line); Porous silica beads before (black dash line) and after (black solid line) AuNPs

embedding. The resulting catalysts exhibited a similar UV-visible absorption (around 520 nm) as the original AuNPs.

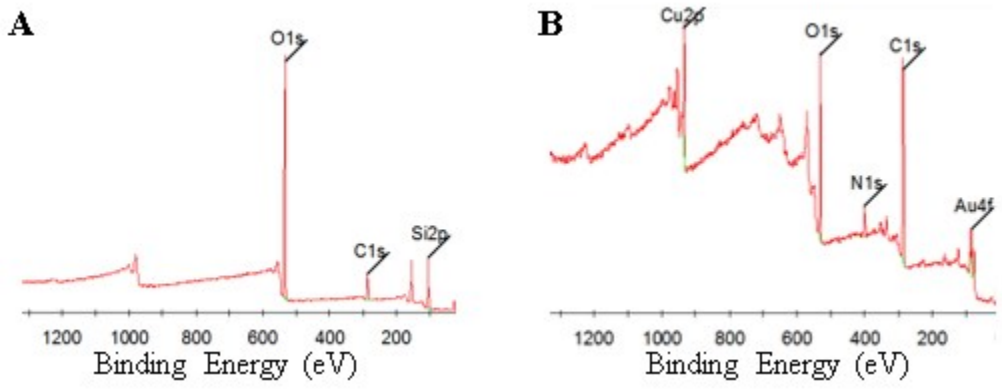


Fig. S3. XPS survey scan of (A) Porous SiO_2 beads and (B) DMAP-AuNPs.

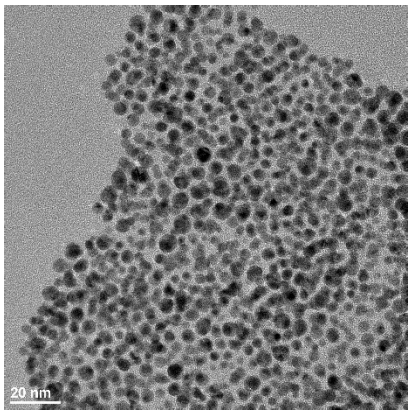


Fig. S4. TEM image of DMAP-AuNPs.

Stability of Au/SiO_2

The aqueous solution of the Au/SiO_2 catalyst (3 mg/ml) was placed in a water bath sonication and was continuously sonicated for 17h.

The comparison was made between the UV-visible absorption spectra of Au/SiO_2 before and after the sonication. It showed that there was negligible difference between the two UV-visible absorption spectra. TEM images of Au/SiO_2 before and after the sonication also showed there was no obvious difference. Both characterizations indicated that the interaction between gold and silica was relatively strong; the Au/SiO_2 was a stable catalyst.

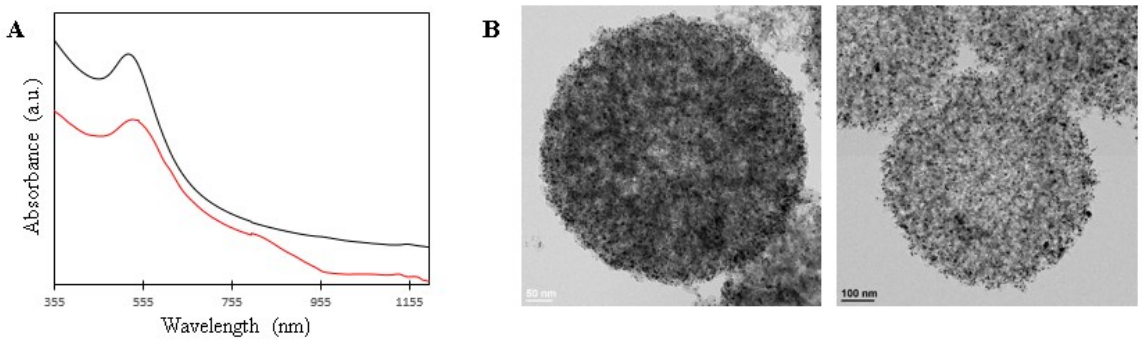


Fig. S5. Stability test of the Au/SiO_2. A. UV-vis spectra of Au/SiO_2 before (black) and after (red) 17 h sonication; B. TEM images of Au/SiO_2 before (left) and after (right) 17 h sonication.; .

Table S1. **Zeta potential of various samples**

Sample Name	Zeta Potential/mV
DMAP-AuNPs	21.02
porous silica beads	-29.81
Au/SiO_2	-19.25

3. The weight percentage of Au in the Au/SiO_2 composite

The weight percentage of Au in the Au/SiO_2 composite was determined by inductively coupled plasma optical emission spectrometry (ICP-OES).

Sample preparation: 100 μL aqua regia (excess amount) was added to 500 μL of Au/SiO_2 catalyst solution with a known concentration of SiO_2 (the concentration of SiO_2 was

calculated from the original weight of SiO_2 beads dissolved in the water). After the gold was completely dissolved, the solution was centrifuged, and the silica beads were removed. 292 μL of the supernatant was added into 11.708 mL of 2% (weight percentage) HNO_3.

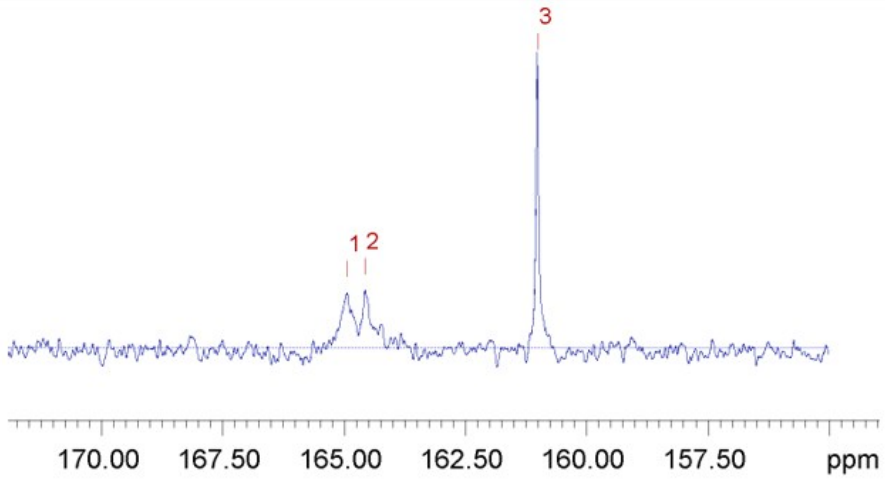
Characterization details: ICP-OES analysis was performed on a Thermo Scientific ICAP 6000 series with Liquid Argon ICP-grade (Megs) as gas and RACID 86 Charge Injection Device (CID) as the detector.

4. Quantitative ^{13}C NMR

To establish a quantitative ^{13}C NMR method, we took carbon relaxation time (T1) and Nuclear Overhauser Enhancement (NoE) into our criteria. Unless special mention, all the NMR samples for quantitative ^{13}C NMR contained 400 μL D_2O, 300 μl PEHA CO_2 capture solution, and a known amount of imidazole (around 1 mmol). All the NMR spectra were taken at 25 °C.

T1 measurements were done on a Bruker AVIIIHD 800 MHz NMR Spectrometer. An NMR sample that contained 3.2 wt.% PEHA CO_2 capture solution was measured (Fig. S6). The longest T1 is 16.5s, belonging to bicarbonates. Given that the delay time (D1) should not be less than 5*T1 in order to obtain a quantitative ^{13}C NMR, D1 was chosen to be 85s. To eliminate NoE, two pulse sequences can be used: zg and zgig. The internal standard imidazole was used as a compound to test if NoE is eliminated. Both pulse sequences fit our needs.

The final quantitative ^{13}C NMR method was chosen to have the following parameters: Number of Scan=128; D1=85s; zgig (an inverse gated-decoupling pulse sequence).



Peak name	F2 [ppm]	Io	error	T1 [s]	error	a	error	fitInfo
1	164.502	1.02e+07	1.907e+06	11.7	7.630	1.14	0.1999	Done
2	164.110	9.79e+06	1.810e+06	5.86	3.458	1.41	0.2798	Done
3	160.335	5.82e+07	1.505e+06	16.5	1.268	1.39	0.03198	Done

Fig. S6. ^{13}C NMR and T1 measurements of carbamates and bicarbonates in 3.2 wt.% PEHA CO_2 capture solution. Peak 1 and 2 are the signals of carbamates, and Peak 3 is the signal of bicarbonates.

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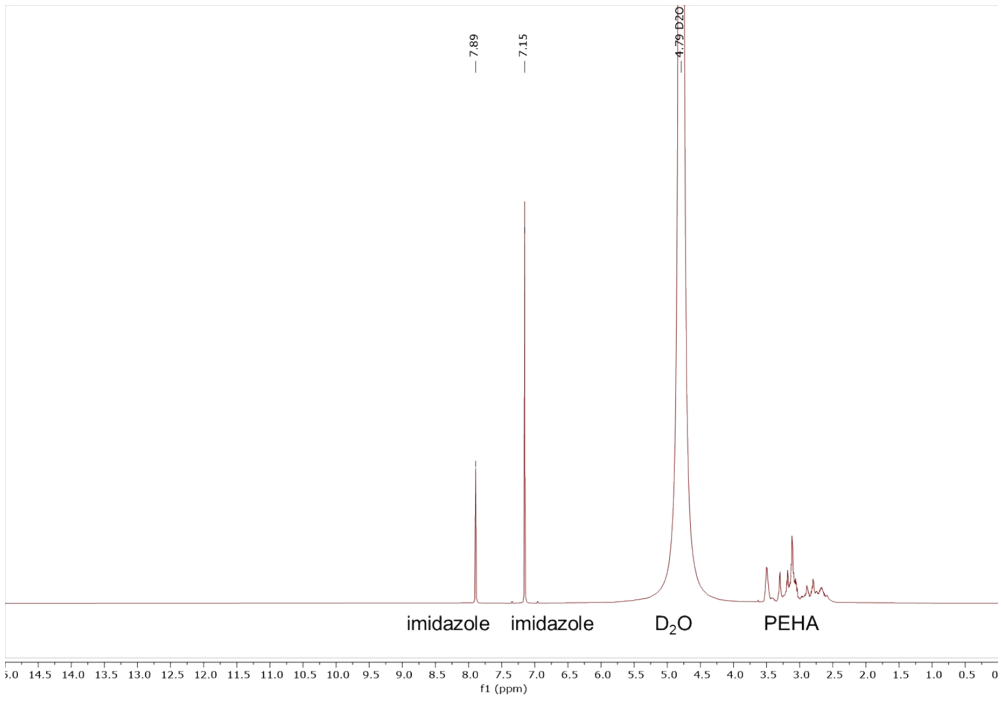

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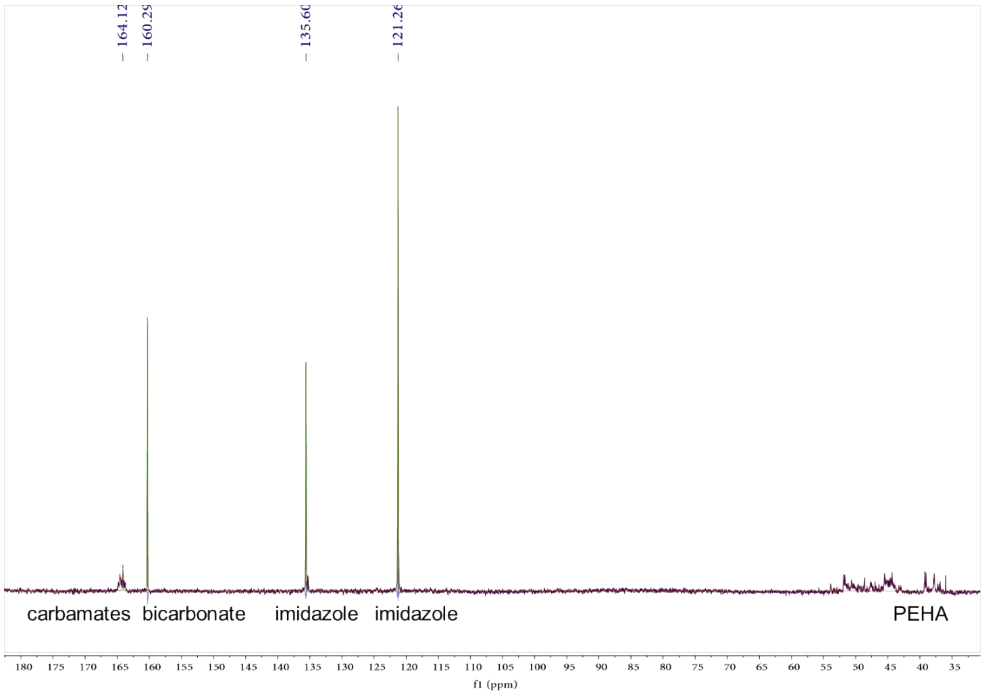

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168 ***Fig. S7.*** NMR spectra of 3.2 wt. % PEHA CO_2 capture solution (imidazole as an internal
169 standard). Above: ^{1}H NMR. Below: quantitative ^{13}C NMR.

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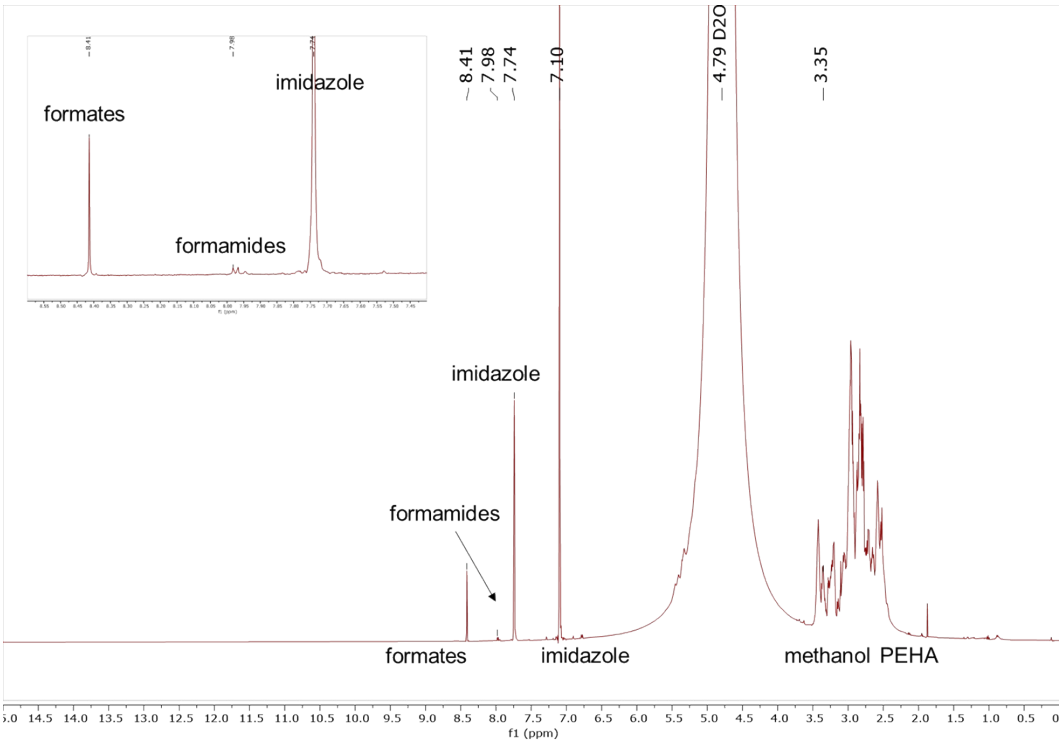

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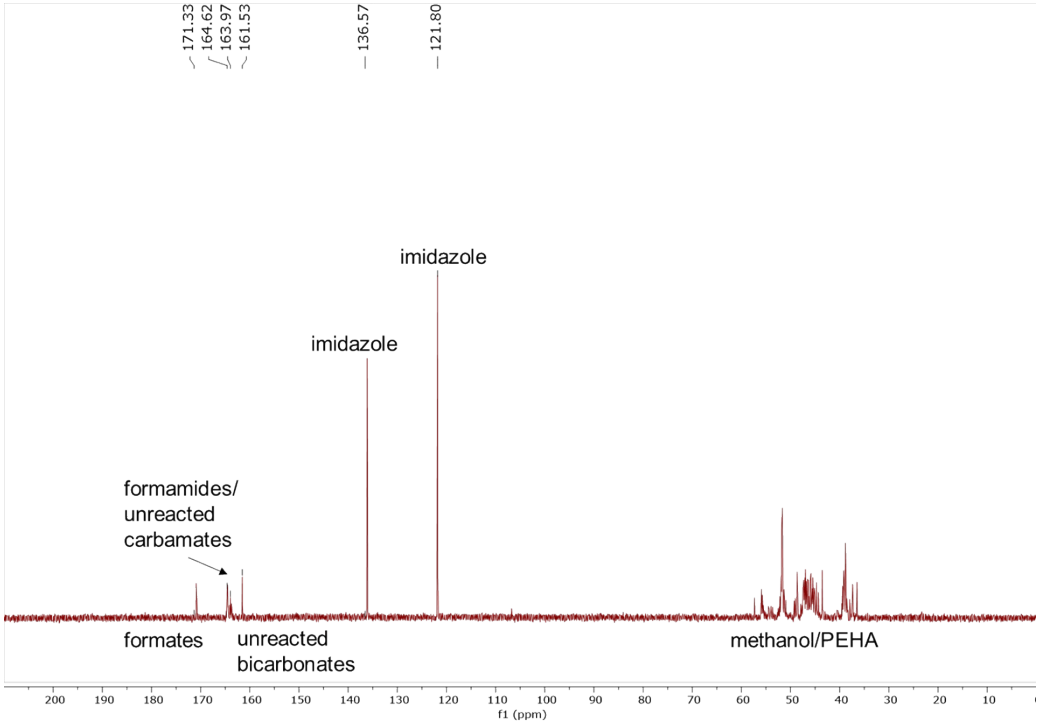

173 ***Fig. S8.*** NMR spectra of 3.2 wt. % PEHA CO_2 capture solution after hydrogenation

174 (imidazole as an internal standard). Above: ^{1}H NMR. Below: non-quantitative ^{13}C NMR.

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5. GC-TCD analysis of gas phase

Gas phase after the hydrogenation was collected by a Tedlar® gas sampling bag. Specifically, the outlet of the Biotage® Endeavor™ Catalyst Screening System and a vacuum pump were connected to the gas sampling bag via a 3-way line connector valve. Firstly, the gas sampling bag and all the linings were vacuumed; secondly, the gas inside the high-pressure reactor was released into and gathered by the gas sampling bag; excess gas was evacuated as soon as the gas sampling bag was full by switching the 3-way valve.

Blank (no gas injection), 1 ml of the gas phase after hydrogenation, and 0.5 ml of various gas standards (lab air, CO_2, H_2, CO, CH_4, O_2, N_2) were analyzed by GC-TCD respectively. Each sample was repeated at least twice.

Table S2 shows the retention time of gas standards, as well as to-be-determined peaks presented in the gas phase after the hydrogenation. Fig. S9 shows the GC-TCD of the gas phase after the hydrogenation. CO_2, O_2, N_2 were from air trapped in the needle of the gas sampler syringe. H_2 was one of the reactants. CO was not detectable using this instrument and sampling method. Based on the limit of detection (LOD) and limit of analysis (LOA) (Section 6 Table S3), we conclude that the CO in the gas phase after the hydrogenation, if assuming it existed, should be below 0.05 ml.

Table S2. **Retention time of various samples in GC-TCD**

A. Gas standards*

Component	**CO_2**	**Noise**	**H_2**	**O_2**	**N_2**	**Noise**	**CH_4**	**CO**
Retention Time/min	6.2	9.1	13.3	14.2	14.9	15.6	16.2	17.1

B. Gas phase after hydrogenation**

Component	**P1**	**P2**	**P3**	**P4**	**P5**	**P6**
Retention Time/min	6.1	9.1	13.0	14.0	14.8	15.4

*The two noises are attributed to leaks in the injector and valve switch, appearing whenever an injection happens.

**Reaction condition: 600 µL 3.2 wt. % PEHA CO_2 capture solution, 1 mL H_2O containing 5.29 mg Au/SiO_2 and boric acid (1 mol % corresponding to the amount of

PEHA presented in the CO_2 capture solution), and 16 bar H_2 (25 °C). The entire system was stirred at 500 rpm, 100 °C for 36 hours.

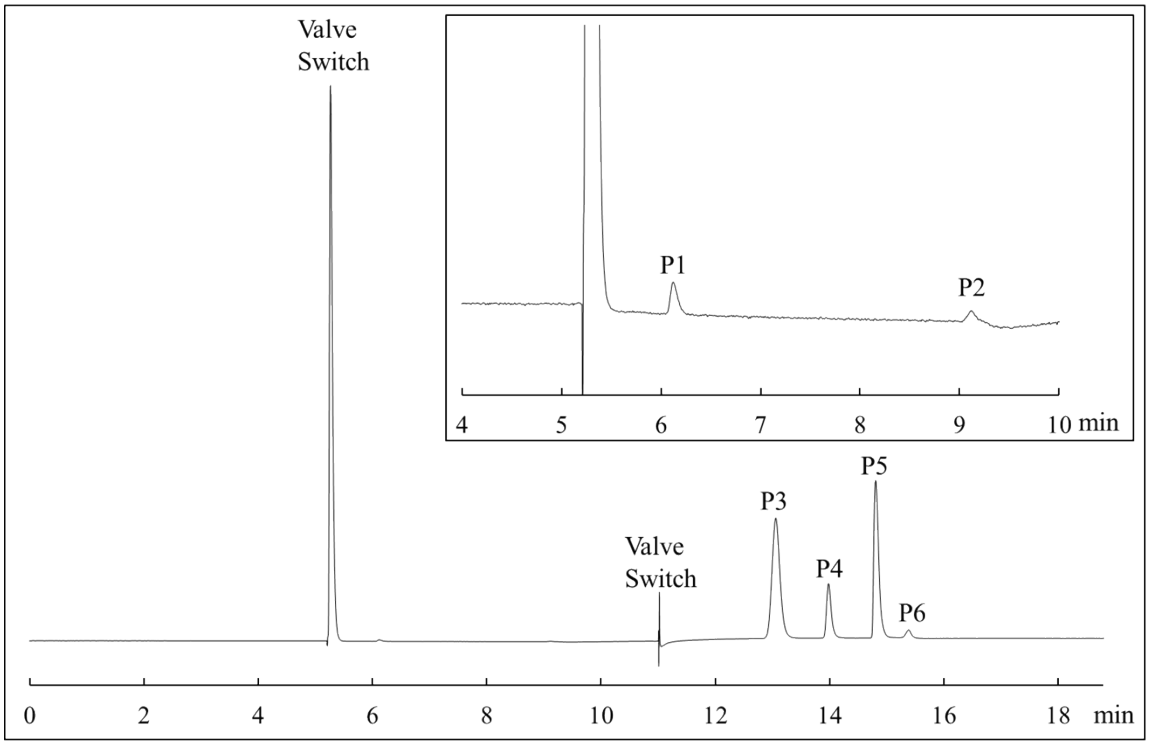


Fig. S9. GC-TCD of the gas phase after a typical hydrogenation reaction. The insert chromatograph is the zoom-in section of retention time= 4-10 min. According to *Table S2*, P1-P6 are identified to be CO_2, noise, H_2, O_2, N_2, and noise.

6. Limit of detection (LOD) and limit of analysis (LOA) determination on GC-TCD

In order to determine the LOD and the LOA, the GC was "injected" with a "blank sample" ten times.

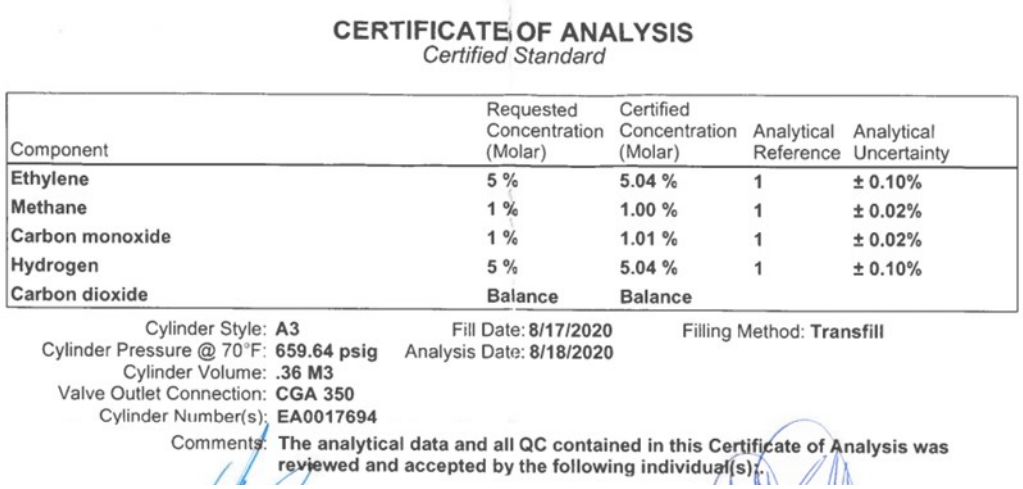
The blank was the run initiated without a volume of gas introduced. The peak height was measured at the base corresponding to a gas analyte. The mean and standard deviation was determined. The LOD was three times the standard deviation at the point where the analyte peak should have occurred. The LOA was ten times the limit of detection. The signal was validated by the injection of a pure gas sample at the limit of detection.

Two gases, nitrogen and oxygen were excluded because of a constant leak from the switch valve.

The gas standard used in calibration is a certificated gas mixture purchased from Praxair Canada Inc. The gas components and their molar concentrations can be found in Fig. S10.

Table S3. **Limits of detection (LOD) and limits of analysis (LOA) (ml) of gas standard**

Gas	LOD (ml)	LOA (ml)
CO_2	0.005	0.01
H_2	0.005	0.01
CO	0.05	0.1



CERTIFICATE OF ANALYSIS
Certified Standard

Component	Requested Concentration (Molar)	Certified Concentration (Molar)	Analytical Reference	Analytical Uncertainty
Ethylene	**5 %**	**5.04 %**	**1**	**± 0.10%**
Methane	**1 %**	**1.00 %**	**1**	**± 0.02%**
Carbon monoxide	**1 %**	**1.01 %**	**1**	**± 0.02%**
Hydrogen	**5 %**	**5.04 %**	**1**	**± 0.10%**
Carbon dioxide	**Balance**	**Balance**		

Cylinder Style: **A3**
Cylinder Pressure @ 70°F: **659.64 psig**
Cylinder Volume: **.36 M3**
Valve Outlet Connection: **CGA 350**
Cylinder Number(s): **EA0017694**
Fill Date: **8/17/2020**
Analysis Date: **8/18/2020**
Filling Method: **Transfill**
Comments: **The analytical data and all QC contained in this Certificate of Analysis was reviewed and accepted by the following individual(s):**

Fig. S10. Certificate of the gas standard used in the calibration curves and the determination of LOD and LOA.

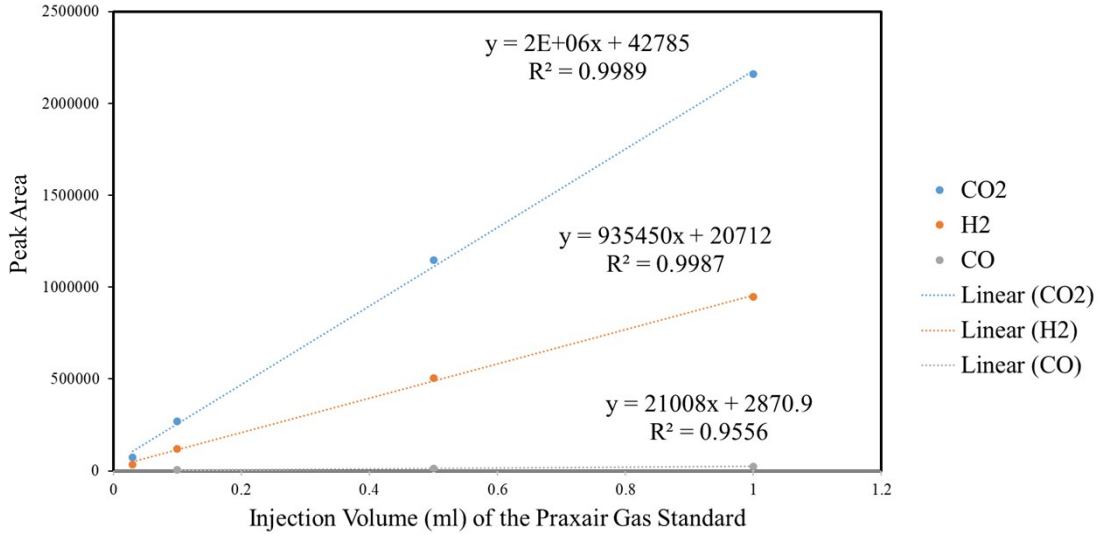
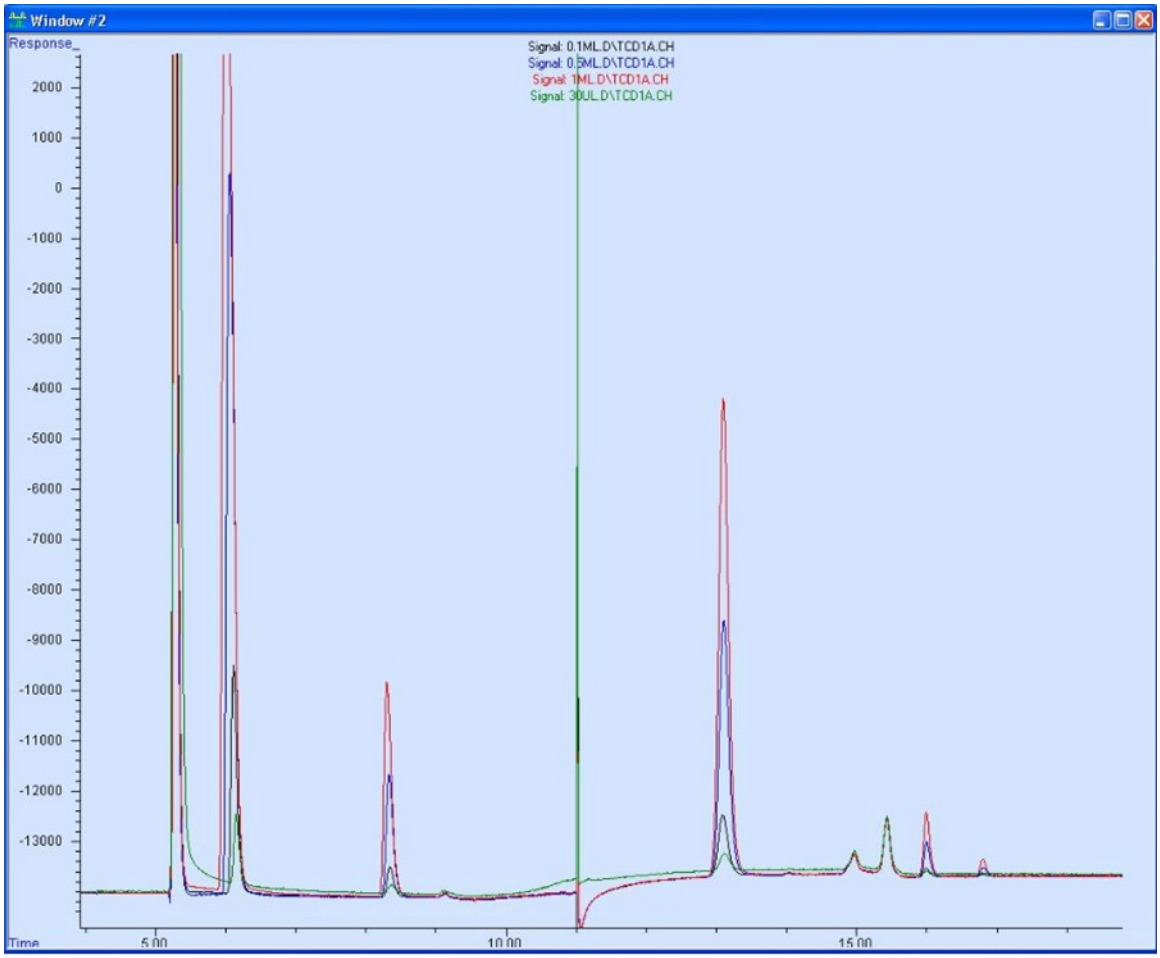


Fig. S11. Calibration curves. The injection volumes (ml) of the Praxair gas standard were 0.03, 0.1, 0.5, and 1.



227 ***Fig. S12.*** Gas chromatographs of the gas standard with various injection volumes.

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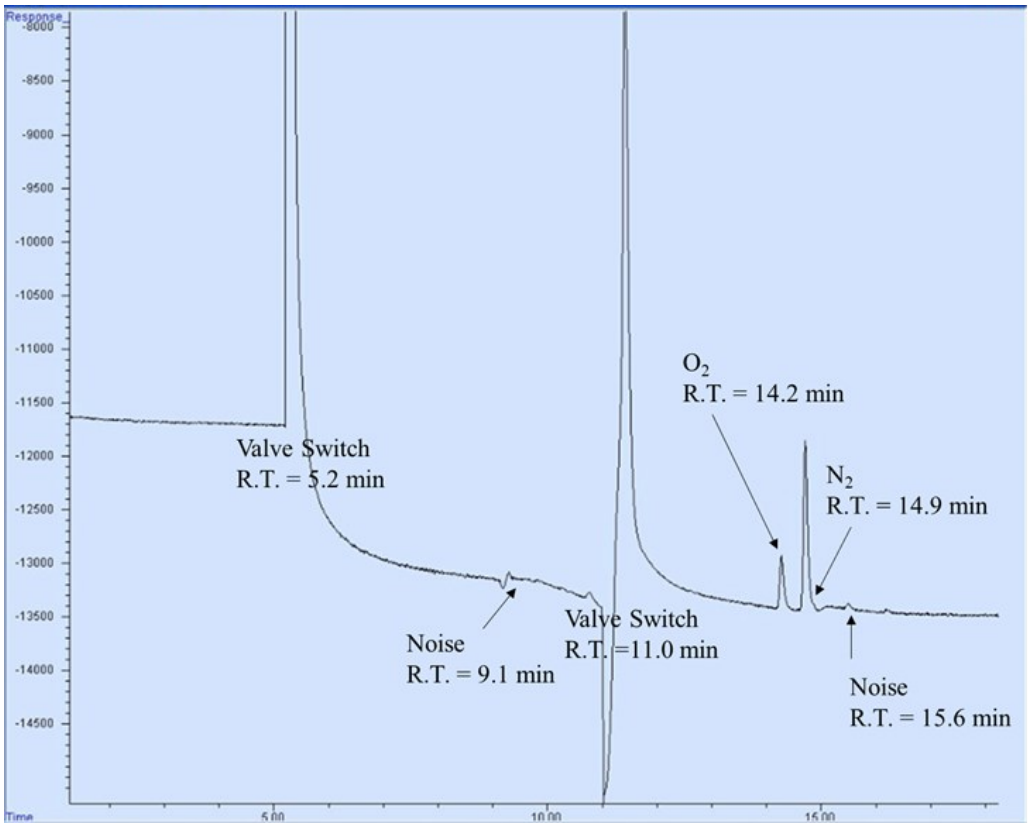


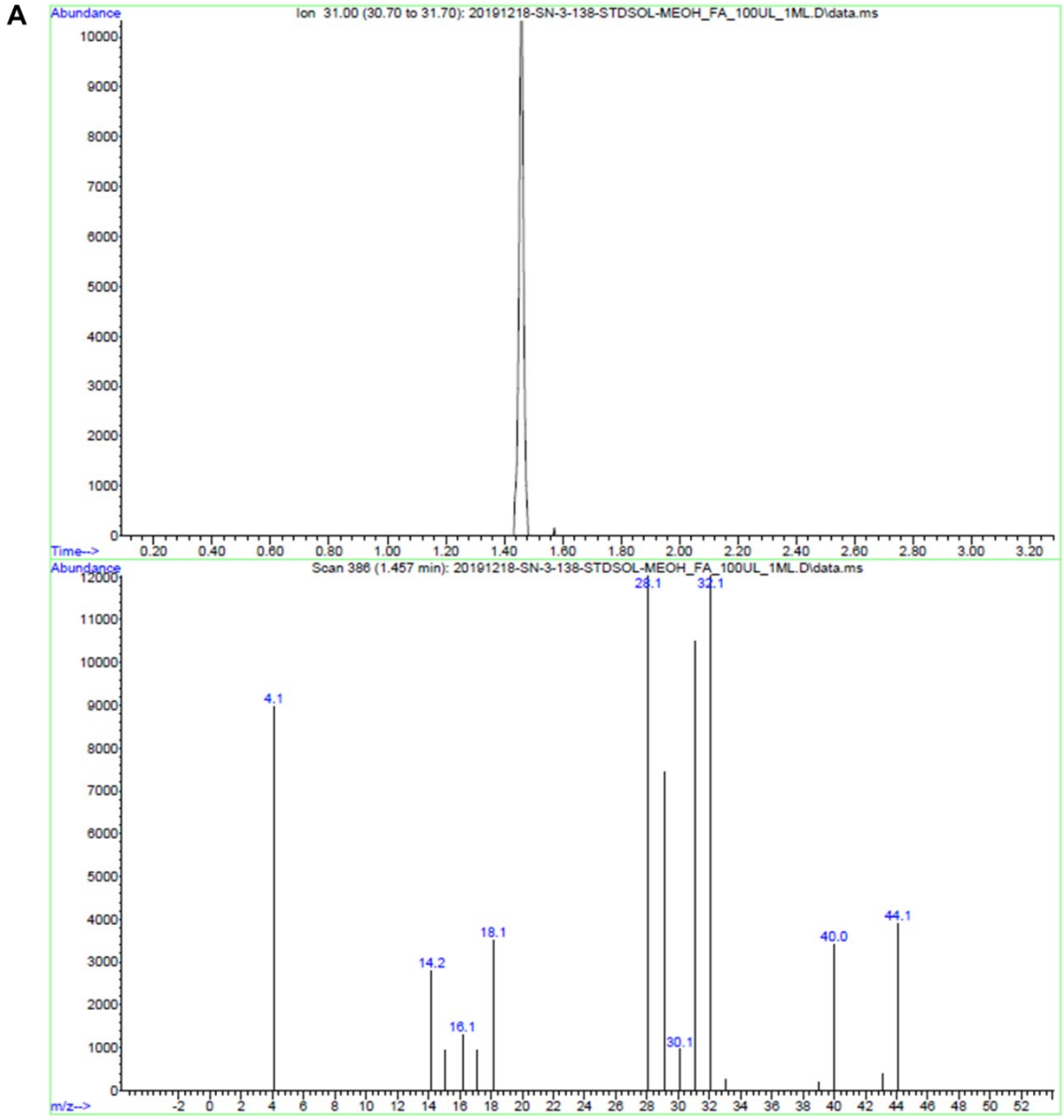
Fig. S13. Gas chromatographs of the blank (no gas injection).

7. GC-MS identification and quantification of MeOH

The signal of MeOH is within the regions of PEHA -CH_2- in ^{1}H NMR. Sometimes, due to low MeOH concentrations in reaction mixtures, it was difficult to quantify the yield of MeOH depending on ^{1}H NMR. Thus, an additional step of GC-MS characterization was used to identify and quantify the MeOH in the hydrogenated products.

The large quantities of salts (formate and unreacted bicarbonates) presented in the product mixture made a direct injection of our liquid sample into a GC-MS unlikely. An alternative sample injection method was thus developed. 100 μL sample was injected into a pre-vacuumed chamber, resulting in the evaporation of volatile chemicals (like MeOH) but not the salts. 1 mL gas sample was then taken from the chamber and injected into GC-MS.

Compared to a standard aqueous solution containing MeOH, the reaction mixture had a similar peak with identical retention time and MS spectrum (Fig. S14). These are consistent with the presence of MeOH in the hydrogenation products.



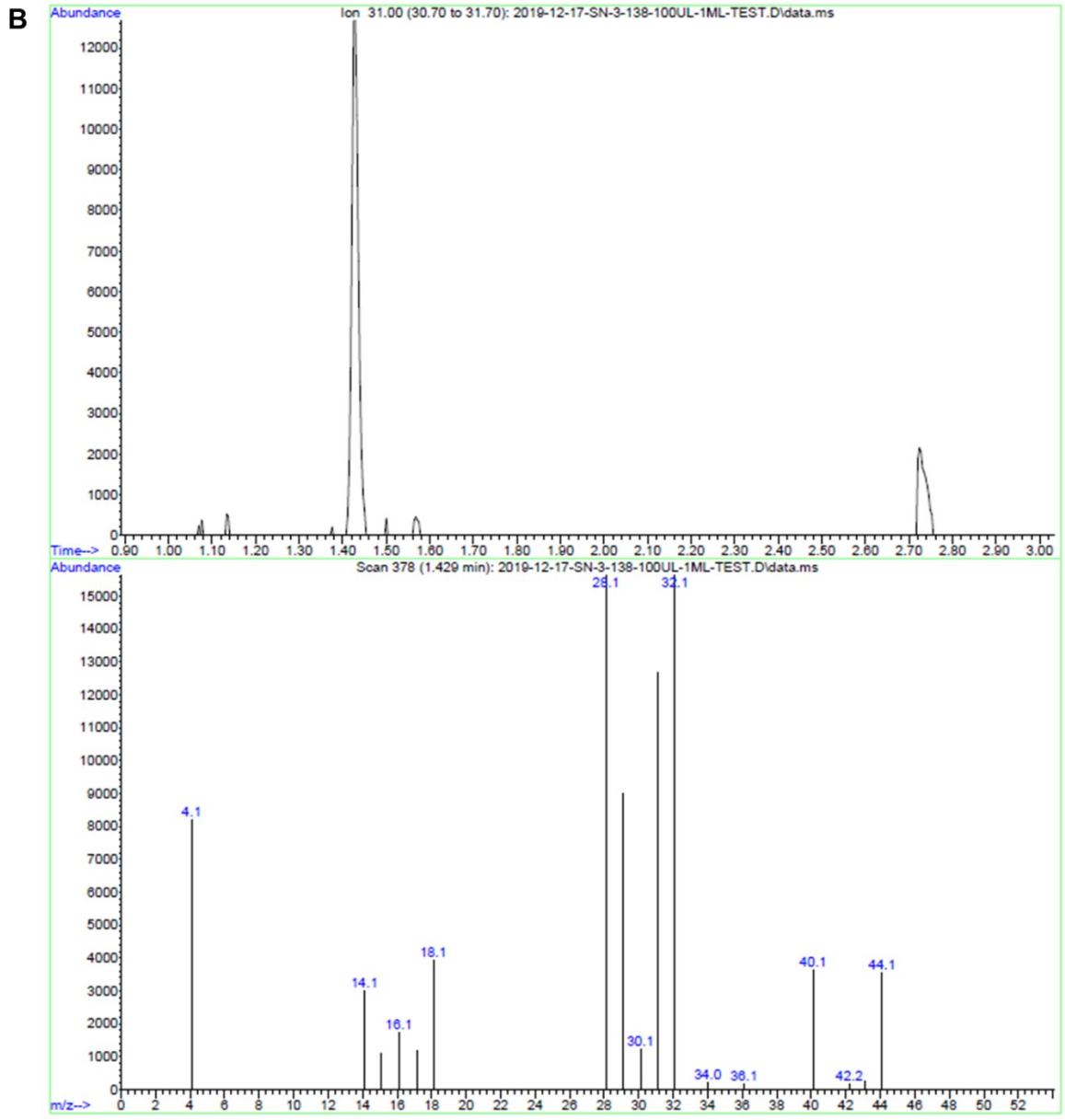


Fig. S14. GC-MS.

A. A standard aqueous solution containing MeOH and formic acid.

B. A reaction mixture after hydrogenation.

Both samples were treated with the same sample preparation/injection method. MeOH has a retention time of 1.4 min in both A and B. The fragments from air were visible in both MS spectra of A and B, because the dead volume in the gas sampler syringe made air being also injected into the GC-MS.

8. Mechanistic studies: ^{18}O isotope study

To further understand the role of Pathways I and II in the generation of methanol, formamide was hydrogenated in $H_2{}^{18}O$. After the reaction, a portion of the reaction mixture was analyzed by ^1H NMR with imidazole as an internal standard, to obtain the total quantity of methanol present. Another portion of the reaction mixture was analyzed by the procedure described in the previous section, *GC-MS identification and quantification of MeOH,* to identify $Me^{18}OH$ and quantify $Me^{16}OH$ (Fig. S15, B).

A methanol ($Me^{16}OH$) standard solution in GC-MS establishes that methanol has a retention time of 1.205 min under the experimental conditions. This retention time was less than the one shown in Fig. S14, because approximately 1 m of the column was removed (cut) between these two experiments. This removal was necessitated by maintenance of the GC-MS. Fig. S15, B demonstrates the presence of $Me^{18}OH$ and $Me^{16}OH$, with the former being dominant. It is notable that m/z=33.1 and m/z=34.1 occur naturally (Fig. S15 A), but with low abundances. Given the dramatic contrast between Fig. S15, A and B in terms of the abundances of these two ion fragments, we are confident in assigning the two ion fragments in B to $Me^{18}OH$. A new ion fragment m/z=35.1 further establishes the existence of $Me^{18}OH$.

Semi-quantification methodology explanation

One of the standard methods to quantify a chemical of interest is to build a calibration curve on the peak area of a primary ion fragment in ion fragment chromatogram, for example, m/z=29 or 31 in the case of methanol. (*J. Chromatogr. A 1017 (2003) 151–159*)

Nevertheless, this approach is not applicable in our case. On the one hand, the peak area of the m/z=31 in the ion fragment chromatogram of Fig. S15, B corresponds to two species: $Me^{18}OH$ and $Me^{16}OH$. On the other hand, the peak area of m/z=29 is not usable either, given the primary interference from N_2 and the minor interference from formic acid. Although only 0.74% compared to the m/z=28 in the relative abundance (NIST Standard Reference Database 69: *NIST Chemistry WebBook*), the m/z=29 from N_2 arises as primary background noise in our case. Use of a methodology based on peak areas in an

ion fragment chromatogram to analyze Fig. S15, B will result in a peak area of m/z=29 consisting of N_2, $Me^{16}OH$, and formic acid.

Considering the above, we decided to quantify $Me^{16}OH$ based on the abundance of the m/z=29 in mass spectra at 1.205 min, the retention time of methanol. Similar methods are used in label-free quantitative proteomics (*Current Genomics, 2008, 9, 263-274*). The limited accuracy of this methodology is sufficient for this semi-quantification purpose, because this study is interested in which category the ratio of $Me^{18}OH$ to $Me^{16}OH$ falls into: 0, between 0 and 1, or ≥ 1. The credibility of this method is based on:

a) the negligible presence of formic acid at 1.205 min;

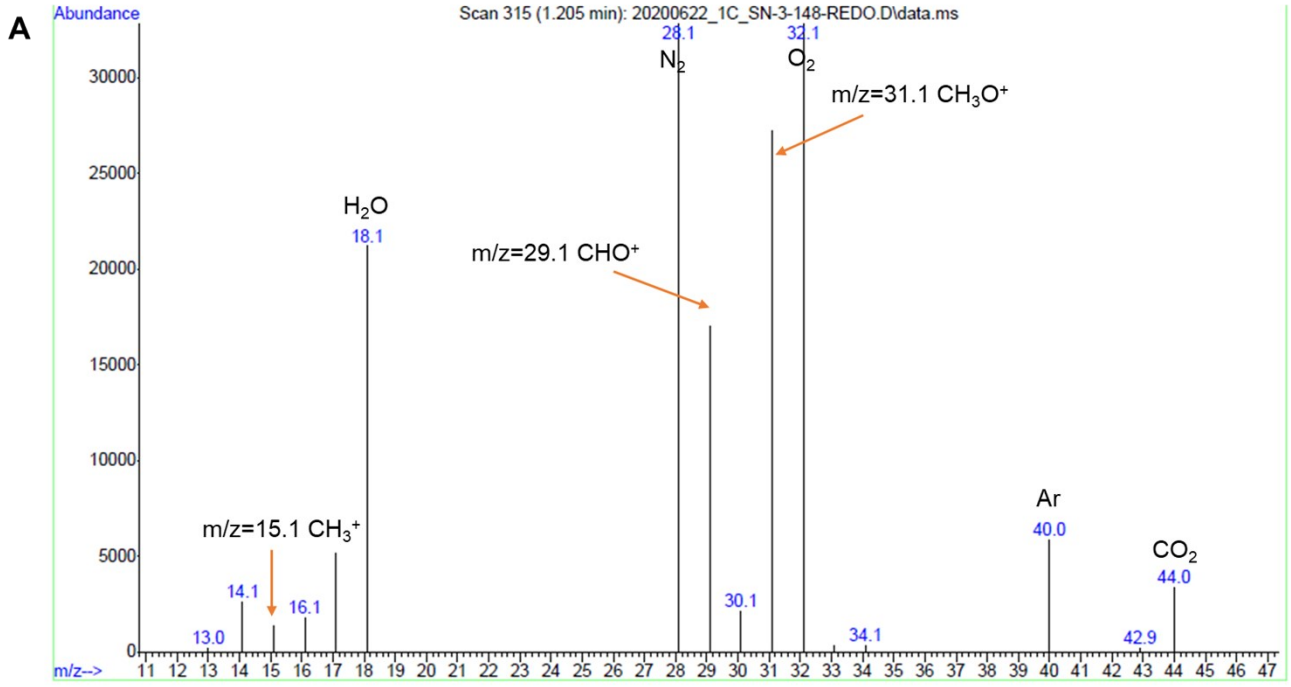
b) the nearly identical retention time of $Me^{18}OH$ and $Me^{16}OH$;

c) the ability to quantify the exact N_2 contribution to m/z=29 at 1.205 min via running a blank solution;

d) the assumption that the chromatography peaks of $Me^{18}OH$ and $Me^{16}OH$ are symmetrical with nearly identical half peak widths.

Calibration curve and calculation of the ratio of $Me^{18}OH$ to $Me^{16}OH$

In order to mimic the product distribution in typical CO_2 hydrogenation catalyzed by our Au(0) catalyst, we prepared the stock solution by adding 6 μL formic acid (88%) and 6 μL methanol to 6 mL water. We diluted this stock solution into standard solutions, while the blank was water. The calibration curve and original data are shown in Fig. S16**.** Finally, we determined the mole ratio of $Me^{18}OH$ to $Me^{16}OH$ to be 3.5:1.



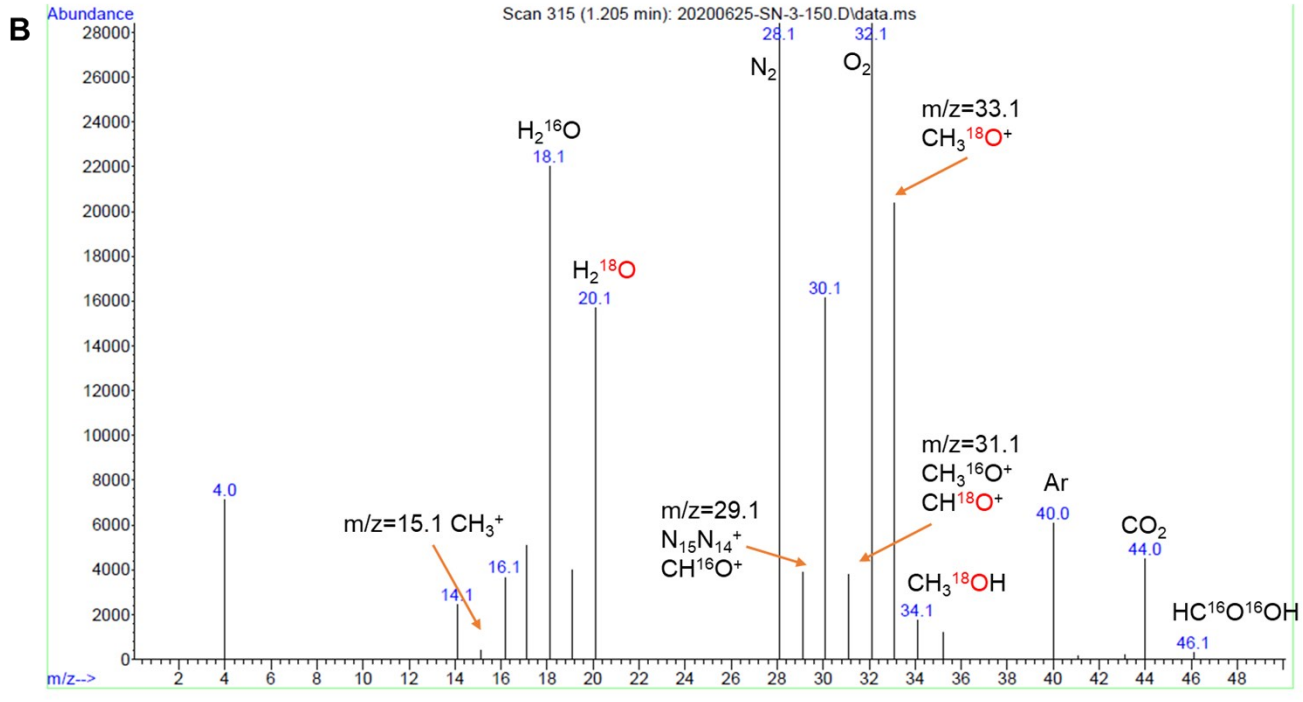


Fig. S15. Mass spectra.

A. A standard solution containing $Me^{16}OH$ and formic acid.

B. The reaction mixture after formamide hydrogenation in $H_2{}^{18}O$. It is worth noticing that the normalized abundance (after subtracting the N_2 background) of m/z=29 is 2127, about

half in the abundance of m/z=31, which is in agreement with a typical MS pattern of $Me^{16}OH$ where m/z=31 is higher than m/z=29.

A

[MeOH]/mol/L	Abundance of m/z=29	Normalized abundance of m/z=29
0.00617	9011	7242
0.00308	5289	3520
0.00154	3388	1619
0.000771	2778	1009
0	*1769	0
Formamide hydrogenation in ^{18}O-water	3896	2127

B

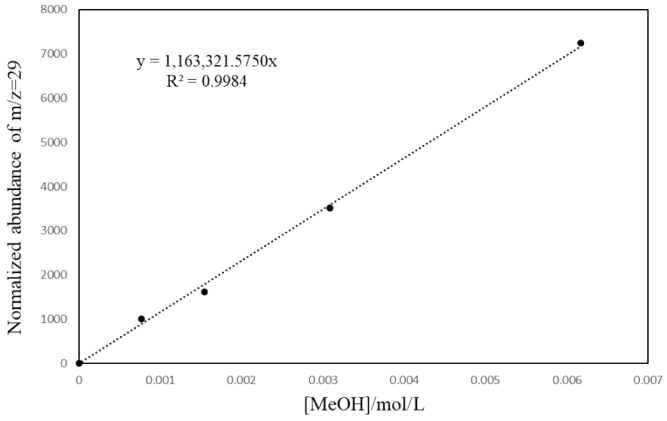


Fig. S16. Calibration curve.

A. Raw data showing the abundance of m/z=29 at retention time=1.205 min. *The m/z=29 signal in the blank is from M+1 of N_2, constant background as the amount of N_2 presented in all the samples should be identical, given that the same sample preparation method, injection method, and injection syringe were used every time.

B. Calibration curve.

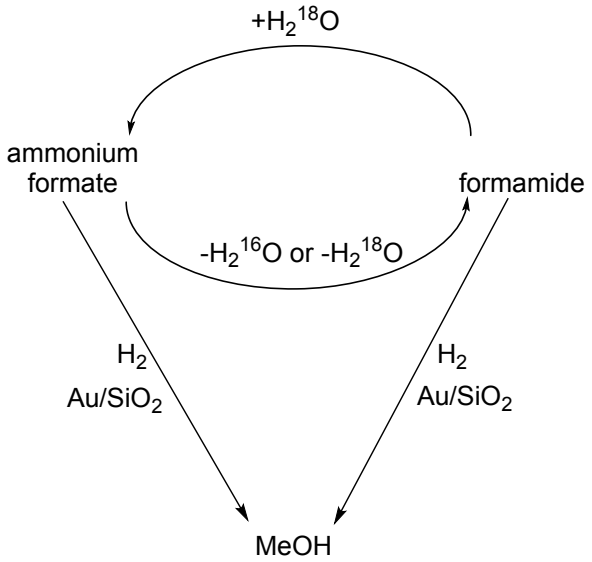


Fig. S17. Potential transformations in the isotopic studies.

9. Additional studies

Table S4. Recently reported systems of amine-captured CO_2 hydrogenation to C1 products in (partially) aqueous conditions similar to this work

Catalyst	Temp/°C	Base	Solvent	P(H_2/CO_2)/ bar	Time/ h	Products	Conversion/ %	No. of cycles before catalysts lost 20% activity	Ambient air as CO_2 source: studied	Ref.
AuNP/SiO_2	100	PEHA	H_2O	16/3	48	formate, formamide, MeOH	80	> 4	Yes	This work
AuNC[a]/SiO_2-Schiff	90	NEt_3	H_2O/MeOH (v:v =1:4)	50/30	12	formate	-[b]	1	No	[1]
Au/TiO_2	40	NEt_3	Neat	90/90	72	formate, CO	29	> 12	No	[2]
Ru-MACHO-BH	145	PEHA	H_2O/2M-THF (v:v =3:5)	80/1	72	formate, formamide, MeOH	95	>4	Yes	[3]

a. AuNC stands for gold nanoclusters (d = ~1.5 nm). b. The yield or the conversion was not given.

Reference:

1. Q. Liu, X. Yang, L. Li, S. Miao, Y. Li, Y. Li, X. Wang, Y. Huang and T. Zhang, *Nature Communications*, 2017, **8**, 1407.

2. D. Preti, C. Resta, S. Squarcialupi and G. Fachinetti, *Angewandte Chemie International Edition*, 2011, **50**, 12551-12554.
3. S. Kar, R. Sen, A. Goeppert and G. K. S. Prakash, *Journal of the American Chemical Society*, 2018, **140**, 1580-1583.

Table S5. Study of CO_2 hydrogenation in dilute PEHA solutions

Entry	wt % of PEHA in water	CO_2 capture			Hydrogenation[b]			
					Product distribution			Conversion(%)[c]
		Mole ratio of carbamate: bicarbonate[a]	CO_2 capacity[a] (mmol of CO_2/(g of PEHA))	CO_2 capacity[a] (mmol of CO_2/(ml of capture solution))	Formate (%)[c]	Formamide (%)[c]	MeOH (%)[c]	
1	3.2	1:1	14.45	0.49	55	44	1	68
2	1.6	1:2	8.06	0.26	38	54	8	16
3	0.8	1:5	12.54	0.10	24	54	22	40

Notes: a. The CO_2 capacity, identification and quantification of carbamate and bicarbonate were determined by quantitative ^{13}C NMR with imidazole as an internal standard. b. Hydrogenation reaction conditions: 600 μL CO_2 capture solution, 1 mL H_2O containing 5.29 mg Au/SiO_2 and boric acid (1 mol % corresponding to the amount of PEHA presented in the CO_2 capture solution), and 16 bar H_2 (25 °C). The entire system was stirred at 500 rpm, 100 °C for 36 hours. c. The selectivity and overall conversion were based on ^1H NMR with imidazole as an internal standard.

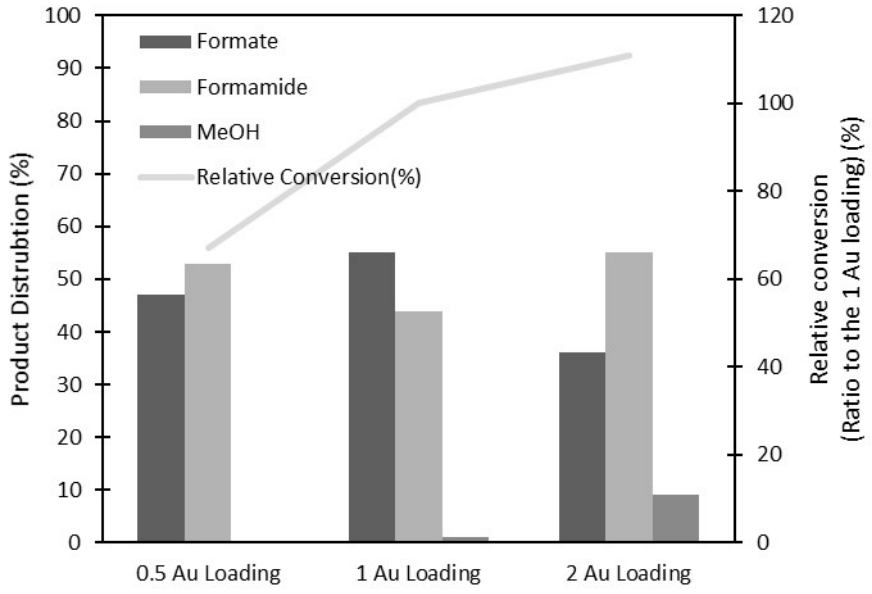


Fig. S18. Catalytic activities with different Au loadings. 1 Au loading meant 5.29 mg Au/SiO_2; 2 Au loading meant 10.58 mg Au/SiO_2, etc. Reaction conditions: 600 μL 3.2 wt. % PEHA CO_2 capture solution, 1 mL H_2O containing Au/SiO_2 and boric acid(1 mol % corresponding to the amount of PEHA presented in the CO_2 capture solution), and 16 bar H_2 (25 °C). The entire system was stirred at 500 rpm, 100 °C for 36 hours.

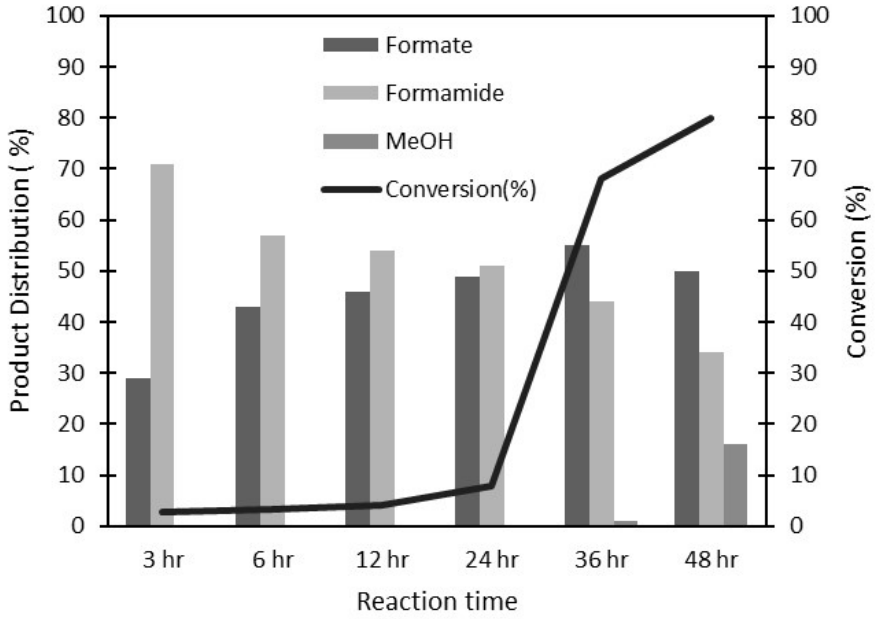


Fig. S19. Product distribution and conversion with various reaction times. Reaction conditions: 600 μL 3.2 wt. % PEHA CO_2 capture solution, 1 mL H_2O containing 5.29 mg Au/SiO_2 and boric acid(1 mol % corresponding to the amount of PEHA presented in the CO_2 capture solution), and 16 bar H_2 (25 °C). The entire system was stirred at 500 rpm, 100 °C.