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Supporting Information

Carbon Dioxide Mediated, Reversible Chemical Hydrogen Storage Using a Pd Nanocatalyst Supported on Mesoporous Graphitic Carbon Nitride

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Materials and Characterizations

Transmission electron microscope (TEM) images were obtained using a Philips, CM30, at 200 kV. In addition, high resolution transmission electron microscope (HRTEM) and scanning transmission electron microscope (STEM) images were obtained using a FEI Titan at 200 kV. Powder X-ray diffraction (XRD) was implemented using a Rigaku Mini Flex II with Cu K_α radiation ($\lambda = 1.54$ Å). Surface areas of catalysts were measured with an ASAP 2000, and listed in Table S1. ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker 300 MHz spectrometer and chemical shifts were given in δ ppm. ^1H NMR spectra were referenced to deuterium oxide (D_2O, 4.79 ppm) and ^{13}C NMR spectra were referenced to acetone as an internal standard ($(CH_3)_2CO$), 30.89 ppm). The FT-IR spectra of the catalysts were obtained on a Lamda FTIR-7600 in ATR mode. Gaseous products of FA dehydrogenation were analyzed using an IR spectrometer (Thermo Scientific Nicolet iS10) equipped with a gas cell and a MCT detector.

The XANES experiments for C and N K-edge spectra were performed using 10D XAS-KIST beamline with electron-beam energy of 3 GeV and a maximum stored current of 250 mA at Pohang Accelerator Lab. (PAL), Pohang, South Korea. The NEXAFS data of the C K-edge were collected in the total electron yield (TEY) mode by recording the sample drain current. The spectra were normalized by pre-edge background subtraction, incident beam intensity I0 and by keeping the area under the spectra in the energy range between 315 and 330 eV for the C K-edge and 440-455 eV for

N K-edge fixed. The base pressure of 5×10^{-8} Torr was used during measurements and temperature was kept at 300 K. All the chemical reagents were purchased from Sigma-Aldrich and used as received.

Experimental Procedures

Synthesis of mesoporous graphitic carbon nitride (mpg-C_3N_4)[14]

Cyanamide (5 g) was dissolved in an aqueous solution of silica dispersion (12.5 g, Ludox HS40), and the resulting solution was stirred at 80 °C for 6 h. The obtained white solid was then heated under N_2 atmosphere at 550 °C, for 4 h with a heating rate of 2 ^{o}Cmin^{-1}, yielding a yellowish-brown solid. This solid was ground and treated with a 4 M aqueous solution of NH_4HF_2 to remove silica particles from the template. Filtering and washing with copious amounts of water and ethanol followed by vacuum drying at 40 °C produced the desired mpg-C_3N_4 in the form of yellowish-brown powder (Fig. S1a).

Synthesis of Pd/mpg-C_3N_4

mpg-C_3N_4 (300 mg) was added to an aqueous solution (20 mL) of palladium nitrate (85 mg of $Pd(NO_3)_2 \cdot 2H_2O$; 32 mM). After stirring at room temperature for 2 h, reaction mixtures were filtered and washed with H_2O. The resulting orange-brown powders were dried at 40 °C under vacuum, followed by reduction with 10% H_2 at 250 °C for 2 h to give brown powders of Pd/mpg-C_3N_4 (Fig. S1b). For large-scale preparation, 3 g of mpg-C_3N_4 was added to 150 mL of aqueous solution containing 840 mg of Pd precursor.

Dehydrogenation of formic acid (Fig. 2)

A 1.0 M formic acid solution (10 mL) was added to a reaction tube containing 50 mg of catalyst (mpg-C_3N_4, Pd/mpg-C_3N_4 or Pd/C) and stirred under ambient conditions. Produced gaseous products were then measured using a gas burette connected to a real time recording system.

Dehydrogenation of formic acid at various concentrations (Fig. 3)

A desired formic acid solution (2.5 mL; 0.5-12 M) was added to a reaction tube containing 50 mg of Pd/mpg-C_3N_4 and stirred under ambient conditions. Produced gaseous products were measured using a gas burette connected to a real time recording system.

Dehydrogenation of formic acid at various temperatures (Fig. 4)

A 1.0 M formic acid solution (2.5 mL) was added to a reaction tube containing 50 mg of Pd/mpg-C_3N_4 at various temperatures (25, 35, 45, 55 °C) and stirred. Produced gaseous products were measured using a gas burette connected to a real time recording system.

Analysis of gas products resulting from formic acid dehydrogenation (Fig. S5)

A 1.0 M formic acid solution (10 mL) was added to a reaction tube containing Pd/mpg-C_3N_4 (50 mg) and stirred at room temperature. During the dehydrogenation reaction, the formed gases were transported into a gas cell in the FT-IR spectrometer. The reaction tube and the gas cell were pursed using N_2 to remove existing moisture and CO_2. The effluents were detected *in situ* by FT-IR spectroscopy, revealing the formation of only CO_2. To identify the exact position for CO stretching frequencies, a standard CO gas (30 ppm) was also employed.

Hydrogenation of CO_2 (Table 1)

The desired reactants, CO_2 and H_2, were added to a stainless steel reactor containing a mixture of D_2O (10 mL), triethylamine (2.5 mL), and Pd/mpg-C_3N_4 (50 mg). Reaction mixtures were heated to a desired temperature of either 100 °C or 150 °C and stirred for 24 h. After cooling the reactor, gases were slowly depressurized to air. The NMR spectra of the reaction mixture were collected using acetone (73 μL, 1.0 mmol) as an internal standard.

Computational Methods

Density functional theory (DFT) calculations were performed using the Gaussian 09 program package[S1] at Korea Institute of Science and Technology Information (KISTI). All ground-state geometries were fully optimized at the B3LYP/6-31G(d,p) level without any symmetry constraints. To identify the nature of stationary points, frequency analyses were conducted using the optimized geometries at the same level of theory. Natural bond orbital (NBO) analyses were employed to determine the atomic charge of the DFT-optimized geometries.

[S1] Gaussian 09, Revision A.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

Table S1. Surface area and pore diameter of mpg-C_3N_4 and Pd/mp-C_3N_4

	surface area (m^2g^{-1})	pore diameter (nm)
mpg-C_3N_4	151	9.4
Pd/mpg-C_3N_4	123	8.0

The obtained nitrogen adsorption/desorption isotherm curves of mpg-C_3N_4 and Pd/mpg-C_3N_4 exhibited typical type IV characteristics, which indicate the presence of mesoporous pores (Fig. S3). Incorporation of Pd NPs into mpg-C_3N_4 led to a slight decrease in surface area from 148 to 123 m^2g^{-1} (Table S1).

Calculation of turn over frequency

Initial TOF was calculated using amount of total gas ($H_2 + CO_2$) produced at 10 min by following equation.

$$moles\ of\ HCOOH\ reacted\ at\ 10\ min\ (n) = \frac{PV}{RT} = \left(\frac{1\ \times V_{gas}\ at\ 10\ min}{0.08206 \times temperature}\right) \times \frac{1}{2}$$

$$TOF\ (h^{-1}) = \frac{mols\ of\ HCOOH\ reacted\ at\ 10\ min}{mols\ of\ total\ \ metal\ used} * 6$$

Table S2. TOF values of FA dehydrogenation of reported catalysts without additives.

entry	catalyst	temperature	H_2+CO_2 at 10 min	TOF (h^{-1})	reference
1	Pd/mpg-C_3N_4	298 K	52 mL	144	this work
2	AgPd/C	298 K	80 mL	158	*Angew. Chem. Int. Ed.* **2013**, *52*, 3681.
3	CoAuPd/C	298 K	50 mL	49	*Angew. Chem. Int. Ed.* **2013**, *52*, 4406.
4	Pd/CN + *hv*	288 K	8 mL	64	*Angew. Chem. Int. Ed.* **2013**, *52*, 11822.
5	PdAu/C	298 K	30 mL	66	*Nanoscale* **2013**, *5*, 910-912.

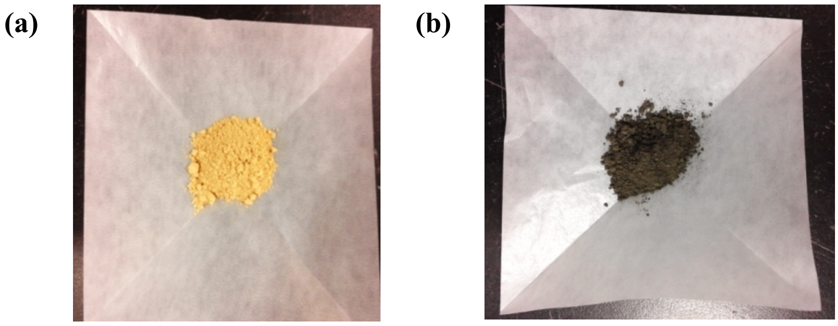

Fig. S1. Photographs of (a) mpg-C_3N_4 and (b) Pd/mpg-C_3N_4.

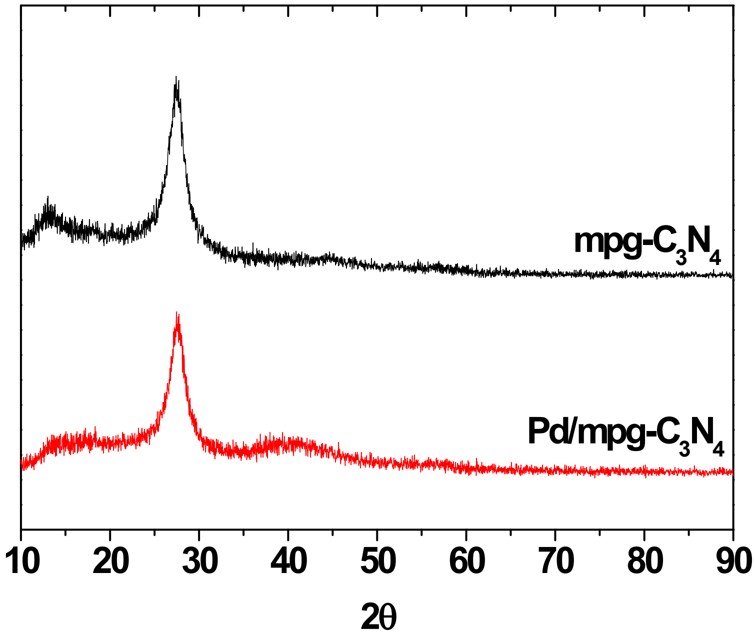

Fig. S2. XRD spectra of mpg-C_3N_4 and Pd/mpg-C_3N_4.

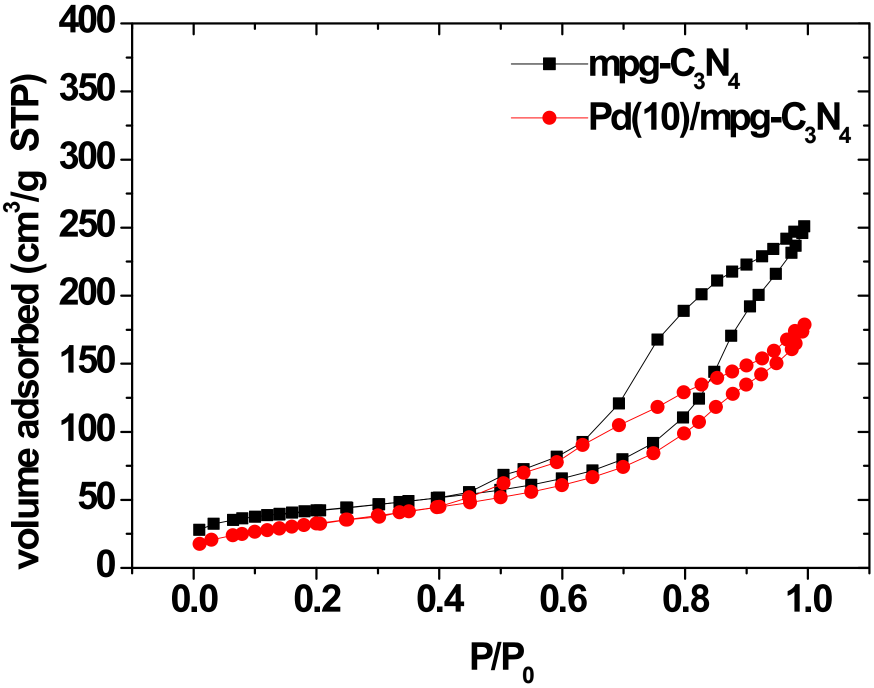

Fig. S3. Nitrogen adsorption/desorption isotherm plots of mpg-C_3N_4 and Pd/mpg-C_3N_4.

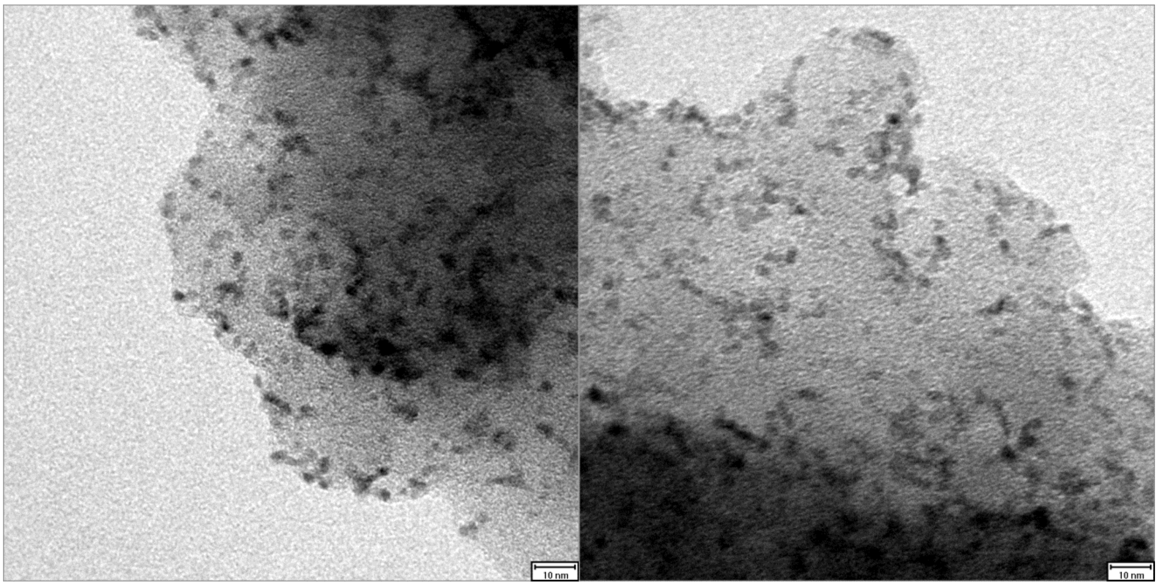

Fig. S4. TEM images of Pd/C (sigma-aldrich, 10% Pd), scale bars are 10 nm.

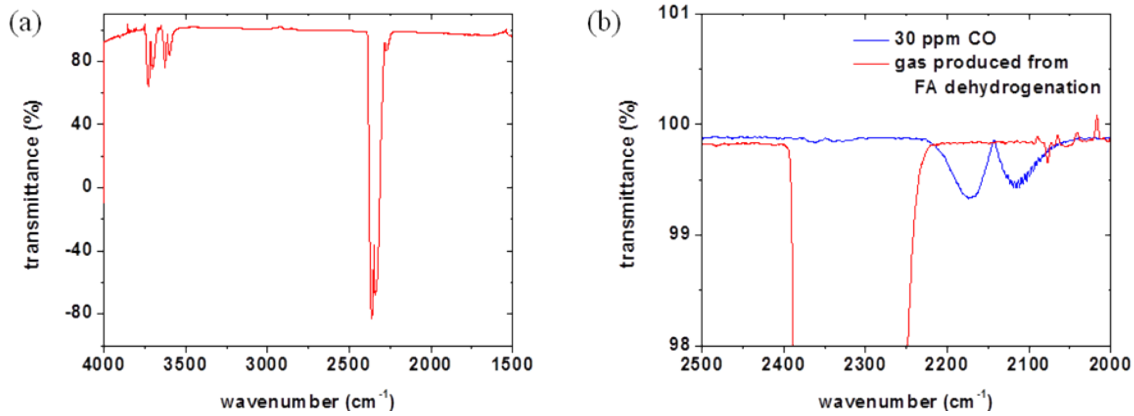

Fig. S5. (a) IR spectra of produced gas from FA dehydrogenation. (b) Expanded IR spectrum of produced gas from FA dehydrogenation and IR spectrum of 30 ppm CO standard gas.

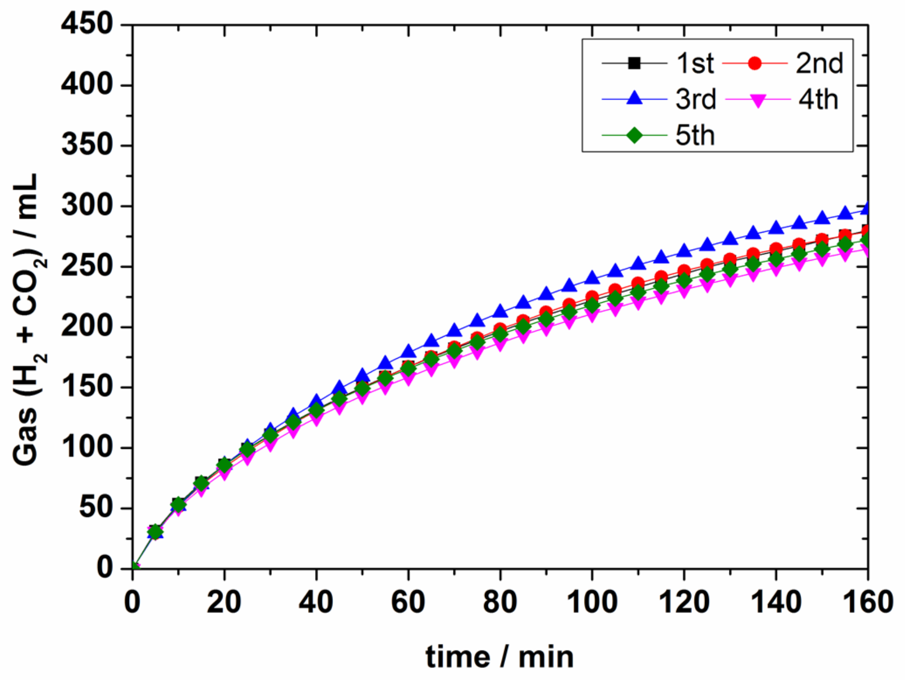

Fig. S6. Catalyst recycle experiments. 10 mL of FA (1.0 M) was dehydrogenated with 50 mg of Pd/mpg-C_3N_4 at 25 ^oC.

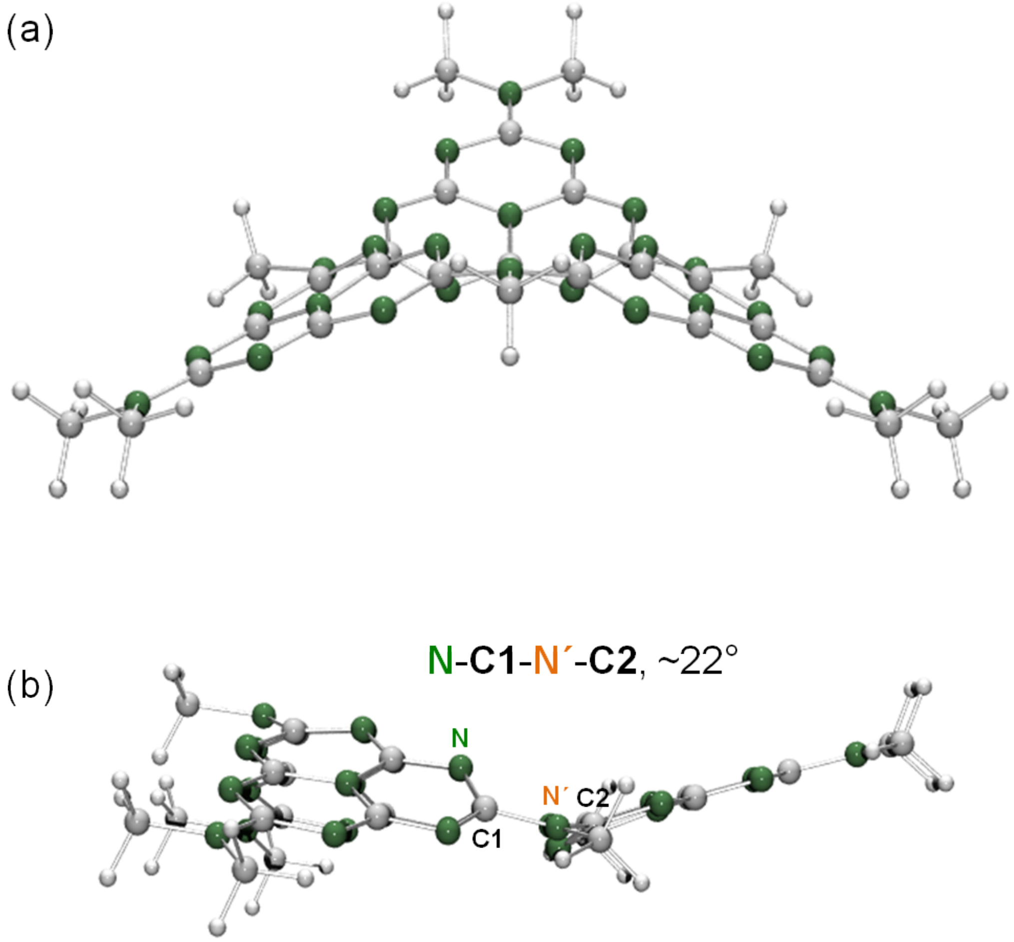

Fig. S7. The DFT-optimized structure (**1**): (a) side view and (b) side view from a different angle.

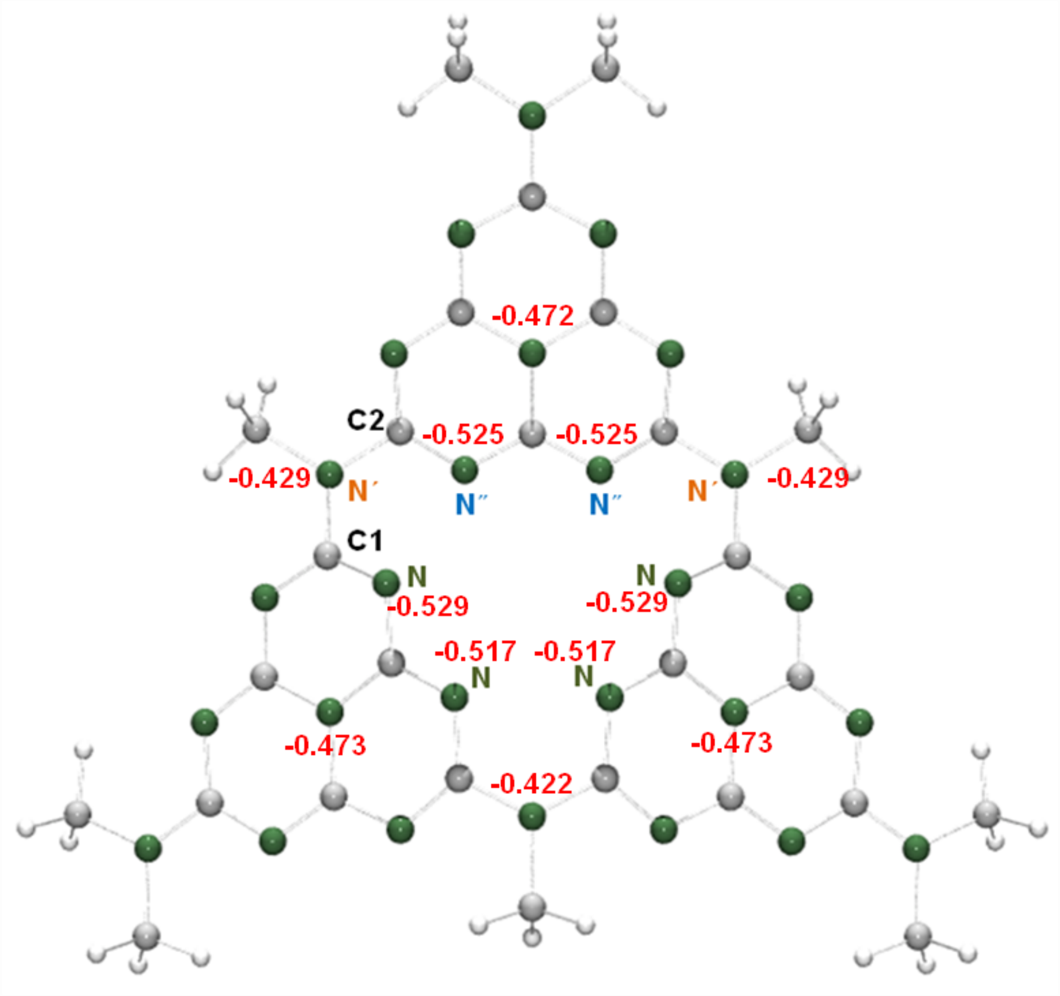

Fig. S8. The calculated NBO charges of nitrogen atoms in the three melm unit.

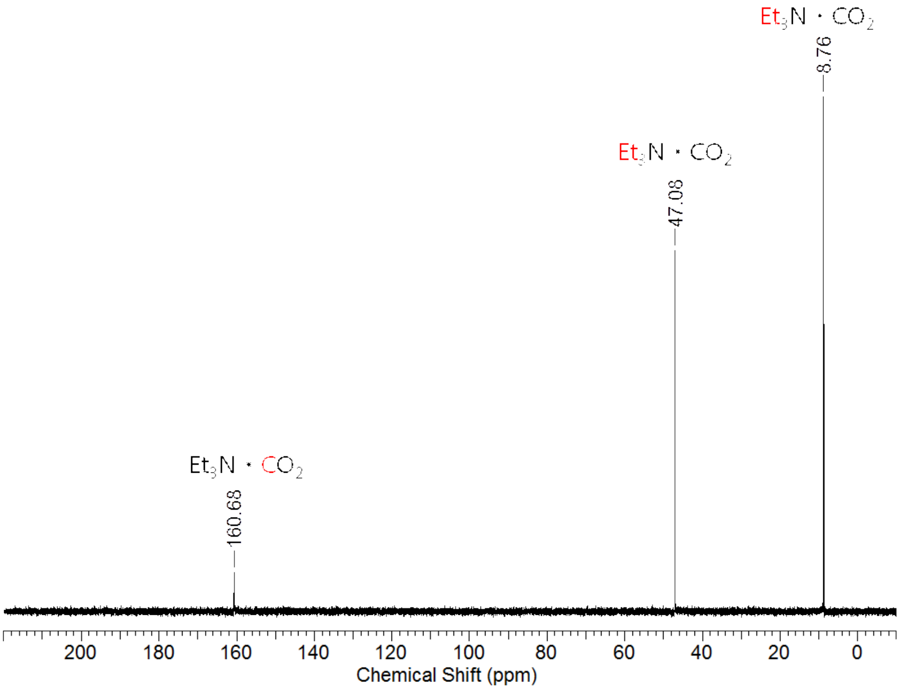

Fig. S9. ^{13}C NMR spectra of $Et_3N{\cdot}CO_2$ adduct.

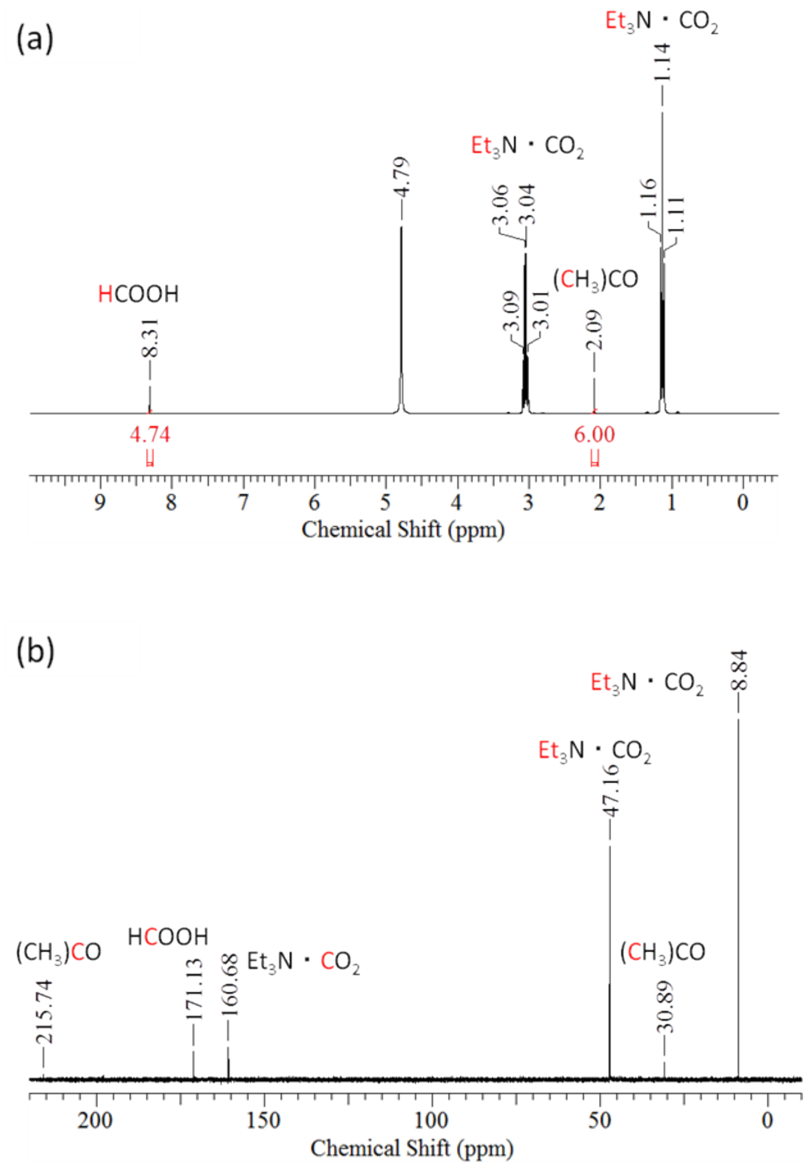

Fig. S10. NMR spectra of a reaction mixture after CO_2 reduction: (a) ^{1}H NMR and b) ^{13}C NMR.

Cartesian coordinates

1 (Fig. 4b)

C	-2.70740900	-2.25850100	-0.43566900
C	-4.69837300	-1.21739200	-0.06401900
C	-2.65930400	-0.00001600	-0.61469500
C	-4.69840100	1.21729600	-0.06398000
C	-2.70746200	2.25846300	-0.43560200
C	-6.60293300	-0.00007500	0.27319900
N	-4.01101100	-0.00003800	-0.21800400
N	-4.00892300	-2.35979200	-0.13475200
N	-5.99859700	-1.20763800	0.17704700
N	-2.03810600	-1.15880800	-0.79497200
N	-5.99862300	1.20750400	0.17709000
N	-2.03813200	1.15879600	-0.79493200
N	-4.00897900	2.35971500	-0.13468200
C	3.43890200	-5.53255400	-0.38753700
C	1.35709800	-4.59172700	-0.31659000
C	3.35783900	-3.37906900	0.37539500
C	1.16561300	-2.37385000	0.66676400
C	3.07289300	-1.23196600	1.10143700
C	-0.63398800	-3.49596800	-0.13254700
N	1.96139700	-3.43950200	0.21759000
N	2.10739100	-5.63903000	-0.61485500
N	0.03941500	-4.58356200	-0.53611200
N	4.08996100	-4.44052600	0.07783200
N	-0.15242900	-2.45793200	0.55707700
N	3.91067300	-2.23651600	0.78781800
N	1.74500100	-1.29539900	1.17604200
C	3.07287200	1.23203400	1.10144400
C	1.16556500	2.37388900	0.66681300
C	3.35777200	3.37913200	0.37537300

C	1.35699900	4.59175900	-0.31656900
C	3.43878800	5.53261300	-0.38757600
C	-0.63406700	3.49597200	-0.13247600
N	1.96132500	3.43954500	0.21760500
N	1.74498100	1.29545500	1.17609900
N	-0.15248000	2.45794900	0.55715000
N	3.91063100	2.23658800	0.78778600
N	0.03931000	4.58357400	-0.53606000
N	4.08987300	4.44059600	0.07778400
N	2.10726900	5.63907000	-0.61486100
N	-1.99774800	-3.46218400	-0.42568900
N	3.70015900	0.00003800	1.34615500
N	-1.99783200	3.46216300	-0.42559700
N	4.19416800	-6.62253600	-0.66447200
N	-7.93888900	-0.00009400	0.49602900
N	4.19403200	6.62260300	-0.66453600
C	-8.70198000	1.23341700	0.62618300
H	-8.03537200	2.08607300	0.52199200
H	-9.47927000	1.27471400	-0.14772500
H	-9.19244700	1.26554600	1.60752400
C	-8.70195300	-1.23362700	0.62614200
H	-9.19246600	-1.26576800	1.60745800
H	-9.47920300	-1.27494700	-0.14780400
H	-8.03531500	-2.08626400	0.52198200
C	3.61535100	-7.85641700	-1.17767100
H	2.54095700	-7.73441500	-1.29173600
H	4.06460800	-8.10219600	-2.14845500
H	3.82227800	-8.68225700	-0.48482000
C	5.63756200	-6.63377800	-0.47129300
H	5.91193800	-7.41709800	0.24702000
H	6.13820900	-6.85071200	-1.42362400
H	5.96234700	-5.66519800	-0.09899900
C	-2.74547400	-4.71618800	-0.60042100

H	-3.44832500	-4.60966800	-1.42803000
H	-2.02599600	-5.50241400	-0.81770300
H	-3.31047200	-4.95298900	0.30577900
C	5.16999400	0.00005000	1.46382400
H	5.46899700	-0.89621000	2.00291100
H	5.65180200	0.00003800	0.48199400
H	5.46898500	0.89633000	2.00288400
C	-2.74558800	4.71615200	-0.60030000
H	-3.44842300	4.60964300	-1.42792600
H	-3.31060700	4.95290800	0.30589800
H	-2.02612700	5.50240400	-0.81754600
C	3.61518600	7.85647200	-1.17773200
H	4.06441600	8.10224700	-2.14853000
H	2.54079100	7.73445500	-1.29177000
H	3.82212000	8.68232100	-0.48489500
C	5.63743100	6.63386500	-0.47139600
H	5.96223700	5.66529700	-0.09909000
H	6.13805200	6.85078300	-1.42374500
H	5.91181800	7.41720300	0.24689300