

Supplementary Information

Highly Efficient Double-Carbonylation of Amines to Oxamides Using Gold Nanoparticle Catalysts

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Experimental

1) General

All organic reagents were purified before use. $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$ was obtained from N. E. Chemcat. Co., Ltd. Al_2O_3 (JRC-ALO-3), SiO_2 (JRC-SIO-6) and TiO_2 (JRC-TIO-4) were supplied by the Catalysis Society of Japan. GC-FID and GC-MS were performed on a Shimadzu GC-2014 instrument equipped with a UCW-98 column (3 m) and a Shimadzu GCMSQP5050A instrument equipped with a ULBON HR-1 capillary column (30 m \times 0.25 mm \times 0.25 μm), respectively. Inductively coupled plasma measurements were performed using a SII Nano Technology SPS7800 instrument. ^1H and ^{13}C -NMR spectra were recorded on a JEOL JNM-ESC400 spectrometer and a JNM-GSX270 spectrometer, respectively. Transmission electron microscopy (TEM) micrographs were obtained with a Hitachi HF-2000 microscope. Au L-edge X-ray absorption spectra were collected in the quick mode and recorded at room temperature in transmission mode at the facilities installed on the BL-01B1 line attached with a Si (311) monochromator at the SPring-8, Japan Atomic Energy Research Institute (JASRI), Harima, Japan. Data analysis was performed using the REX 2000 program, ver. 2.5.7 (Rigaku). Fourier transformation (FT) of the k^3 -weighted extended X-ray absorption fine structure (EXAFS) data was performed to obtain the radial structural function.

2) General reaction procedures

A typical procedure for the double-carbonylation of **1** using the Au/HT catalyst is as follows. Au/HT (0.10 g, 0.0045 mmol Au) was placed in a reaction vessel, followed by the addition of acetonitrile (5 mL) and **1** (0.5 mmol). The reaction mixture was vigorously stirred at 110 °C under 6 atm of mixed gases (5 atm of CO and 1 atm of air)

for 24 h. After the reaction, the Au/HT was removed by filtration, and naphthalene (0.25 mmol) was added as an internal standard. The obtained mixture was analyzed by GC and GC-MS.

3) Reuse experiments for the double-carbonylation of 1

After the hydrogenolysis of **1** under the above typical reaction conditions, Au/HT was separated by filtration and washed with 5% aqueous citric acid (2 x 10 mL) and 10% aqueous Na₂CO₃ (2 x 10 mL). Next, additional portions of **1** (0.2 mmol) and acetonitrile (5 mL) were added, followed by stirring under identical conditions. 91% yields of **2** were obtained in each run during the three recycling experiments.

4) Competitive reaction of 2-methyl and 4-ethyl piperidine using the Au/HT catalytic system or the homogeneous catalytic system reported in ref. 3c.

The competitive reaction between 2-methyl piperidine (0.5 mmol) and 4-ethyl piperidine (0.5 mmol) in acetonitrile (5 mL) using Au/HT (0.10 g, 0.0045 mmol Au) was carried out under 6 atm of mixed gases (5 atm of CO and 1 atm of air) at 110 °C for 24 h. The reaction using a homogeneous catalytic system was conducted in CH₃CN solvent (10 mL) in the presence of Pd(OAc)₂ (0.1 mmol) with KI (0.5 mmol) and K₂CO₃ (0.5 mmol) under 5 atm of CO and 1 atm of air at 110 °C for 24 h.

5) 10 mmol-scale double-carbonylation of 1 using Au/HT

Into a stainless steel autoclave with a Teflon inner cylinder (160 mL) were placed Au/HT (0.044 g, Au: 0.02 mmol), acetonitrile (20 mL) and **1** (10 mmol: 0.87 g). The reaction mixture was vigorously stirred at 150 °C under 20 atm of mixed gases (15 atm

of CO and 5 atm of air) for 100 h. After the reaction, the Au/HT was removed by filtration, and acetonitrile was evaporated. The residue was purified on a short column of silica gel (Wakogel C-200) using ethyl acetate and *n*-hexane (4:1) as an eluent to give 1.0 g of **2** (90% isolated yield) as a white solid.

6) Product identification

The products were identified by GC, GC-MS and NMR analyses. Retention times (GC or GC-MS) and chemical shifts (^1H and ^{13}C -NMR) of the products were in agreement with those of the reported data and also with authentic samples.

NMR data for Table 2

Entry 1

N,N,N'N'-tetramethyl oxamide

CAS registry No. [1608-04-6], ^1H NMR (270 MHz, CDCl_3): δ 3.00 ppm (s, 12H); ^{13}C NMR (68 MHz, CDCl_3): δ 164.9, 37.0, 33.7 ppm. ^1H NMR and ^{13}C NMR were consistent with previously reported values. See Ref. 1S.

Entry 2

N,N,N'N'-tetraethyl oxamide

CAS registry No. [14288-05-2], ^1H NMR (270 MHz, CD_3OD): δ 3.24-3.47 (m, 8H), 1.08-1.28 ppm (m, 12H); ^{13}C NMR (68 MHz, CD_3OD): δ 166.1, 43.7, 39.6, 14.1, 12.7 ppm. ^1H NMR and ^{13}C NMR were consistent with previously reported values (Ref. 2S) and the authentic sample prepared by the reaction of oxalyl chloride with diethyl amine (Ref. 3S).

Entry 3

N,N'-dibutyl-*N,N'*-dimethyl ethane diamide

CAS registry No. [208943-08-2], ¹H NMR (270 MHz, CD₃OD): δ 3.30-3.35 (m, 2H), 3.10-3.21 (m, 2H), 2.86 (s, 6H), 1.44-1.55 (m, 4H), 1.15-1.31 (m, 4H), 0.81-0.90 ppm (m, 6H); ¹³C NMR (68 MHz, CD₃OD): δ 166.7, 51.1, 35.5, 31.0, 29.8, 21.0, 14.1 ppm. ¹H NMR and ¹³C NMR were consistent with the authentic sample prepared by the reaction of oxalyl chloride with *N*-methyl butyl amine. See Ref. 3S.

Entry 4

N,N'-bis(methoxy ethyl)-*N,N'*-dimethyl ethane diamide

CAS registry No. [182505-08-4], ¹H NMR (270 MHz, CD₃OD): δ 4.45-4.62 (m, 4H), 3.42-3.44 (m, 4H), 3.30 (s, 6H), 2.92-2.94 ppm (m, 6H); ¹³C NMR (68 MHz, CD₃OD): δ 165.3, 70.1, 58.8, 49.7, 46.0, 36.1, 32.3 ppm. ¹H NMR and ¹³C NMR were consistent with the authentic sample prepared by the reaction of oxalyl chloride with *N*-methyl-*N*-(2-methoxy ethyl) amine. See Ref. 3S.

Entry 5

N,N'-bis(2,2-dimethoxy ethyl)-*N,N'*-dimethyl ethane diamide

CAS registry No. [349121-48-8], ¹H NMR (400 MHz, CD₃OD): δ 4.44-4.51 (m, 2H), 3.41-3.47 (m, 2H), 3.27-3.33 (m, 14H), 2.91 ppm (s, 6H); ¹³C NMR (100 MHz, CD₃OD): δ 167.1, 104.3, 103.2, 55.5, 54.8, 52.8, 37.3, 36.7, 36.1, 34.0 ppm. ¹H NMR and ¹³C NMR were consistent with the authentic sample prepared by the reaction of oxalyl chloride with *N*-methyl aminoacetaldehyde dimethyl acetal. See Ref. 3S.

Entry 6

*N*¹,*N*¹,*N*²,*N*²-bis[2-(methyl amino)ethyl]-*N*¹,*N*²-dimethyl ethane diamide

CAS registry No. [500283-42-1], ¹H NMR (270 MHz, CD₃OD): δ 3.55 (t, 2H, *J*=6.9 Hz), 3.39-3.43 (m, 2H), 2.98-3.01 (m, 6H), 2.51-2.56 (m, 4H), 2.25-2.28 ppm (m, 12H); ¹³C NMR (68 MHz, CD₃OD): δ 166.7, 57.7, 56.5, 45.7, 45.0, 36.0, 35.9, 32.5, 32.2 ppm. ¹H NMR and ¹³C NMR were consistent with the authentic sample prepared by the reaction of oxalyl chloride with *N,N,N'*-trimethyl-ethylene diamine. See Ref. 3S.

Entry 7

N,N'-bis(2-propenyl)-*N,N'*-dimethyl ethane diamide

¹H NMR (400 MHz, DMSO): δ 5.71-5.84 (m, 2H), 5.17-5.25 (m, 4H), 3.95 (t, 2H, *J*=6.0 Hz), 3.79-3.83 (m, 2H), 2.77-2.92 ppm (m, 6H); ¹³C NMR (100 MHz, DMSO): δ 164.6, 164.3, 132.7, 132.0, 118.4, 117.6, 51.4, 47.3, 33.9, 30.6 ppm. ¹H NMR and ¹³C NMR were consistent with the authentic sample prepared by the reaction of oxalyl chloride with *N*-methyl allyl amine. See Ref. 3S. HRMS (EI) exact mass calcd for (C₁₀H₁₆O₂N₂) requires *m/z* 196.1212, found *m/z* 196.1211.

Entry 8

1,1'-Oxalyl-bis(4-methyl)-piperidine

CAS registry No. [3491221-21-7], ¹H NMR (400 MHz, CD₃OD): δ 4.37 (d, 2H, *J*=13.2 Hz), 3.53-3.58 (m, 2H), 3.14-3.19 (m, 2H), 2.76 (t, 2H, *J*=12.7 Hz), 1.72-1.91 (m, 6H) 1.10-1.18 (m, 4H), 0.99 (s, 6H); ¹³C NMR (100 MHz, CD₃OD): δ 164.8, 42.3, 35.5, 34.5, 32.1, 21.9 ppm. ¹H NMR and ¹³C NMR were consistent with the authentic sample

prepared by the reaction of oxalyl chloride with 4-methyl piperidine. See Ref. 3S.

Entry 9

1,1'-oxalyl dipiperidine

CAS registry No. [17506-94-4], ^1H NMR (400 MHz, CD_3OD): δ 3.46 (t, 4H, $J=5.4$ Hz), 3.65-3.67 (t, 4H, $J=5.4$ Hz), 1.42-1.60 ppm (m, 12H); ^{13}C NMR (100 MHz, CD_3OD): δ 164.8, 42.7, 27.3, 26.3, 25.2 ppm. ^1H NMR and ^{13}C NMR were consistent with previously reported values. See Ref. 4S.

Entry 10

1,1'-oxalyl dimorpholine

CAS registry No. [6432-78-6], ^1H NMR (400 MHz, CDCl_3) δ 3.45 (t, 4H, $J=4.8$ Hz), 3.66 (t, 4H, $J=4.8$ Hz), 3.71-3.74 ppm (m, 8H); ^{13}C NMR (100 MHz, CDCl_3): δ 162.8, 66.9, 66.6, 46.6, 41.5 ppm. ^1H NMR and ^{13}C NMR were consistent with previously reported values (Ref. 5S) and the authentic sample prepared by the reaction of oxalyl chloride with morpholine (Ref. 3S).

Entry 11

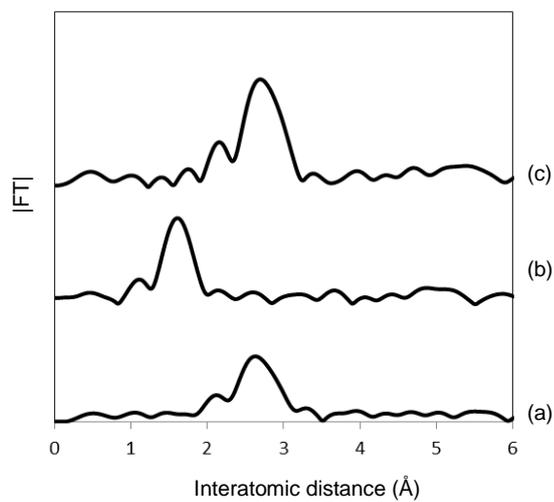
1,1-oxalyl bis(4-methyl)-piperadine

CAS registry No. [18799-35-0], ^1H NMR (400 MHz, DMSO): δ 3.48 (t, 4H, $J=5.0$ Hz), 3.27 (t, 4H, $J=5.4$ Hz), 2.29-2.32 (m, 8H), 2.19 ppm (s, 6H); ^{13}C NMR (100 MHz, DMSO): δ 162.6, 54.5, 53.7, 45.5, 45.2 ppm. ^1H NMR and ^{13}C NMR were consistent with the authentic sample prepared by the reaction of oxalyl chloride with 1-methyl piperadine. See Ref. 3S.

References

- [1S] E. Fritz, H. Langhals and C. Ruchardt, *Liebigs Ann. Chem.*, 1981, 1015.
- [2S] Y. Wakita, S. Noma, M. Maeda and M. Kojima, *J. Organomet. Chem.*, 1985, **297**, 379.
- [3S] B. H. Armbrecht, L. M. Rice, C. H. Grogan and E. E. Reid, *J. Am. Chem. Soc.*, 1953, **75**, 4829.
- [4S] Y. Imada, Y. Mitsue, K. Ike, K. Washizuka and S.-I. Murahashi, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 2079.
- [5S] M. Neveux, C. Bruneau, S. Lecolier and P. H. Dixneuf, *Tetrahedron*, 1993, **49**, 2629.

7) EXAFS analysis



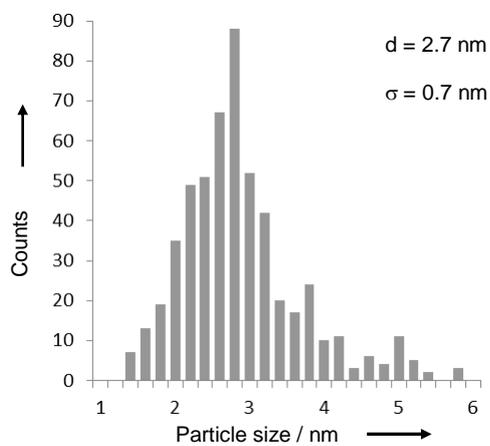
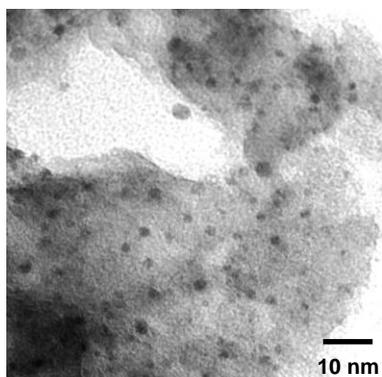
Curve fitting analysis of Au L-edge EXAFS

Sample	Coord. no. (CN)	Interatomic dis. (Å)	$\Delta\sigma/\sigma^2$
Au/HT (fresh)	8.7	2.82	0.0089
Au foil	12	2.88	-

Figure 1S. Fourier transformed k^3 -weighted Au L-edge EXAFS for (a) Au/HT, (b) Au₂O₃ and (c) Au foil.

8) TEM analysis

(a) Au/HT (fresh)



(b) Au/HT (after the reuse experiment)

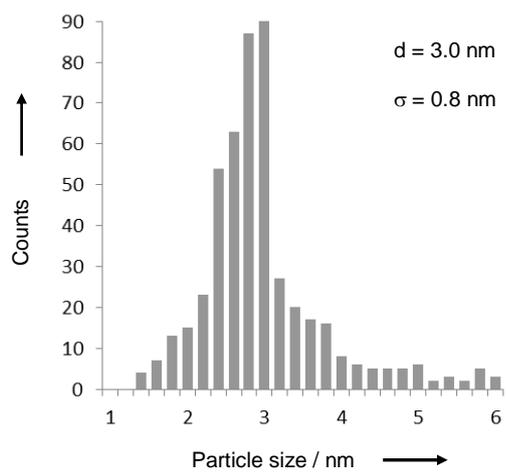
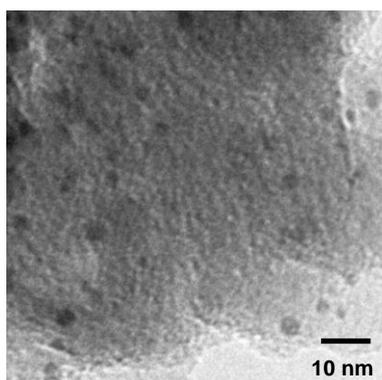


Figure 2S. Typical TEM images and size distribution diagrams (obtained by counting at least 500 particles) of (a) fresh Au/HT and (b) Au/HT after reuse.

9) Kinetic study for the Au/HT-catalyzed double-carbonylation

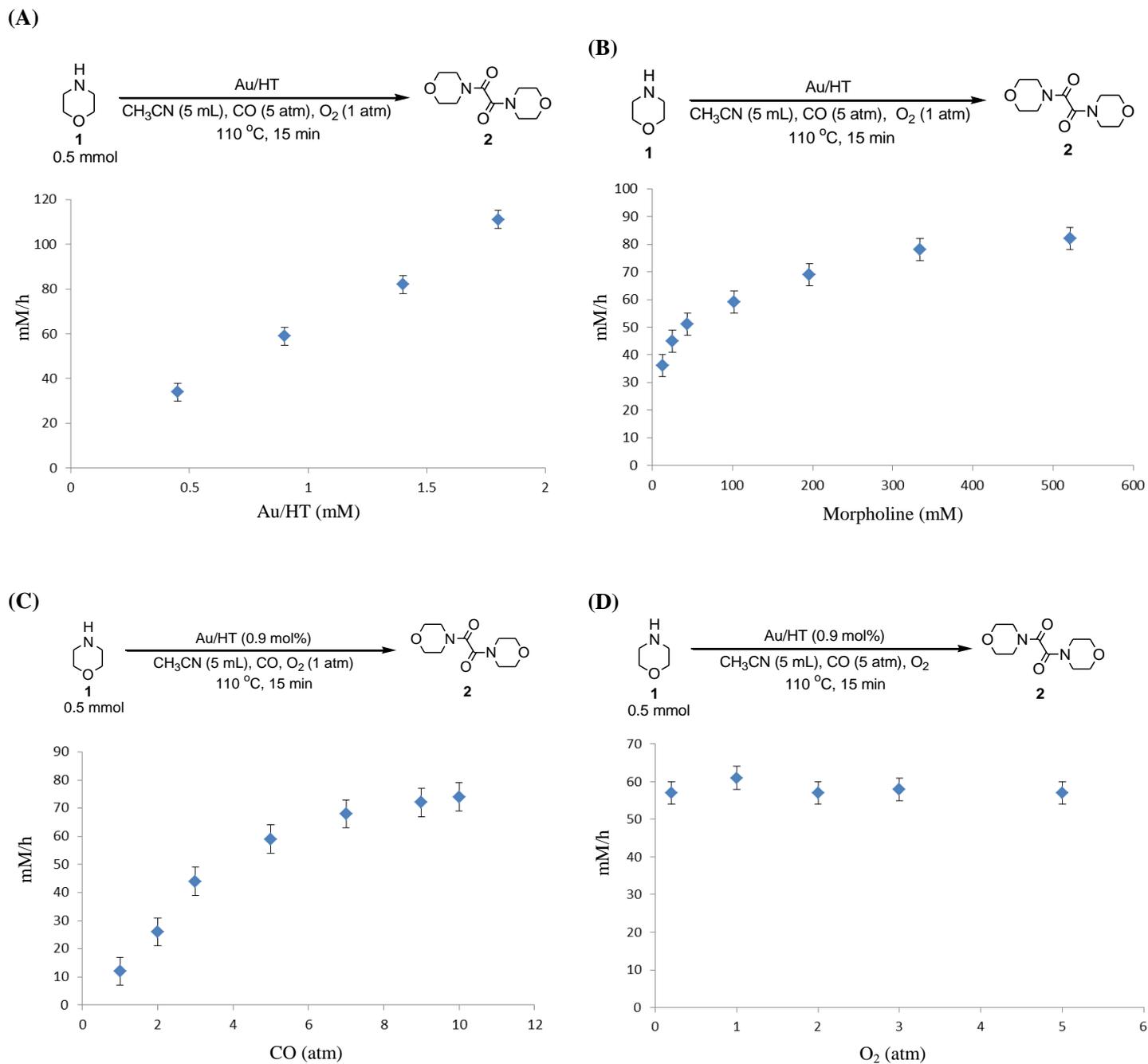
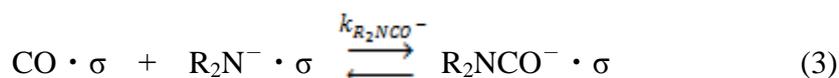


Figure 3S. Dependence of initial reaction rate on (A) the amount of catalyst, (B) the concentration of morpholine, (C) CO pressure and (D) O₂ pressure.

10) Kinetic study for the double-carbonylation of 1 using Au/HT

The proposed reaction scheme based on the Langmuir–Hinshelwood model for the present system is as follows;



where \cdot and σ indicate the adsorbed species and a vacant active catalyst site, respectively. k_i and k_{-i} represent adsorption and desorption rate constants, respectively.

We assume the rate-determining step is the surface reaction of the coupling of the R_2NCO^- species represented in eq. (4). Under steady-state conditions, the rate of adsorption can be equated to the rate of desorption.

From the above assumptions, the following kinetic equation can be obtained.

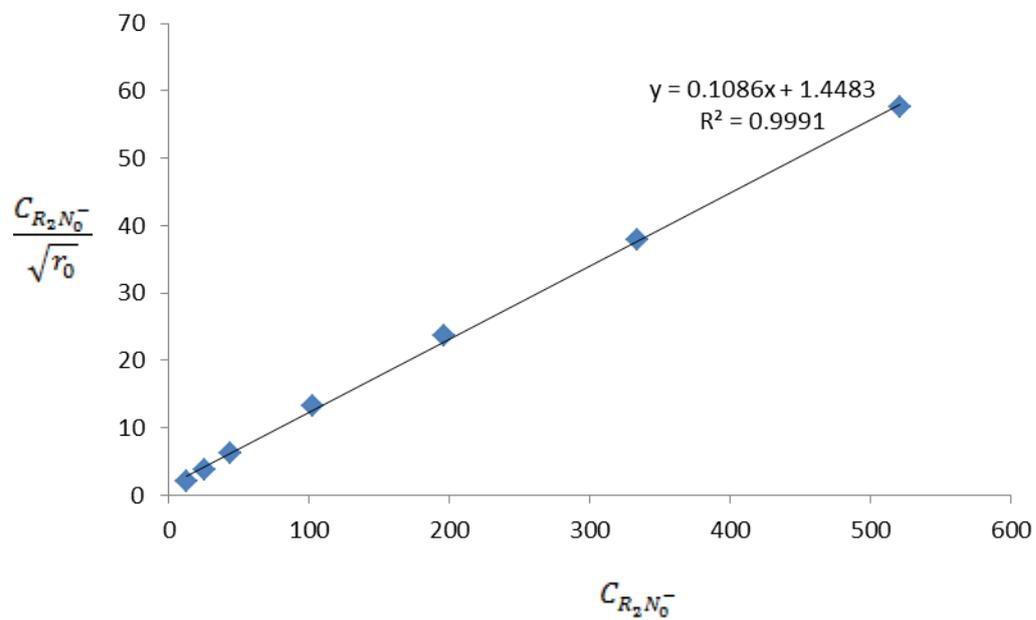
$$r = \frac{\vec{k}(K_{\text{CO}}K_{\text{R}_2\text{N}^-}K_{\text{R}_2\text{NCO}^-}C_{\text{CO}}C_{\text{R}_2\text{N}^-})^2}{\left(1 + K_{\text{CO}}C_{\text{CO}} + K_{\text{R}_2\text{N}^-}C_{\text{R}_2\text{N}^-} + K_{\text{CO}}K_{\text{R}_2\text{N}^-}K_{\text{R}_2\text{NCO}^-}C_{\text{R}_2\text{N}^-}C_{\text{CO}} + \frac{C_{(\text{R}_2\text{NCO})_2}}{K_{(\text{R}_2\text{NCO})_2}}\right)^2} \quad (6)$$

where K_i represents the adsorption equilibrium constant for species i , which can be defined as the ratio of k_i to k_{-i} . According to equation 6, the initial reaction rate r_0 is given by

$$\frac{C_{\text{R}_2\text{N}_0^-}}{\sqrt{r_0}} = \frac{1 + K_{\text{CO}}C_{\text{CO}_0} + K_{\text{R}_2\text{N}^-}(1 + K_{\text{CO}}K_{\text{R}_2\text{NCO}^-}C_{\text{CO}_0})C_{\text{R}_2\text{N}_0^-}}{\sqrt{\vec{k}K_{\text{CO}}K_{\text{R}_2\text{N}^-}K_{\text{R}_2\text{NCO}^-}C_{\text{CO}_0}}} \quad (7)$$

where C_{CO_0} and $C_{\text{R}_2\text{N}_0^-}$ represent initial concentrations of CO and R_2N^- , respectively.

A plot of $\frac{C_{R_2N_0^-}}{\sqrt{r_0}}$ versus $C_{R_2N_0^-}$ showed linear proportionality, supporting the proposed reaction scheme.



11) FT-IR absorption spectra of 1-(H)- or 1-(D)-morpholine on Au/HT

FT-IR data were collected on a JASCO FT-IR 410 spectrometer equipped with a MCT detector. Self-supporting pellets were prepared from the sample powders and treated directly in the IR cell, which allowed for thermal treatments under a controlled atmosphere. Au/HT was pretreated at 423 K under outgassing for 1 h, then treated under 3 mbar of 1-(H)- or 1-(D)-morpholine at 353 K (Figure 4S).

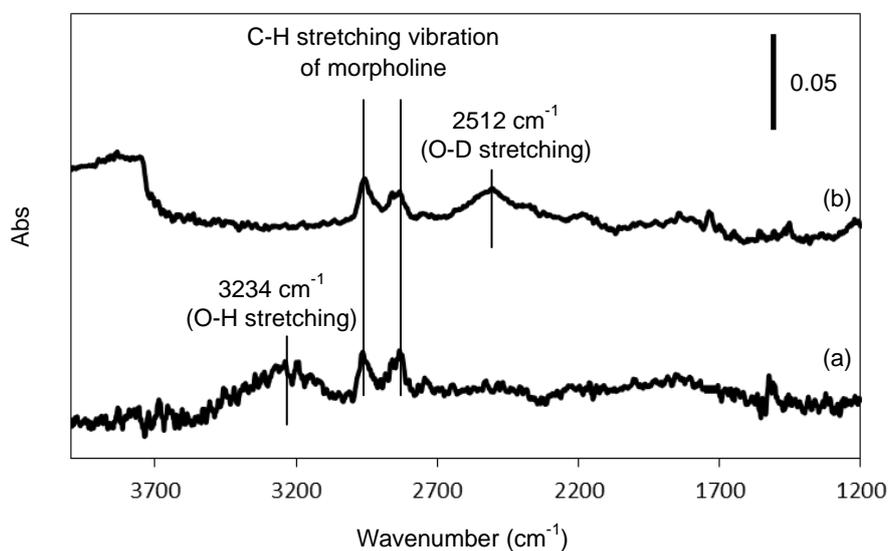


Figure 4S. FTIR spectra of Au/HT after absorption of (a) 1-(H)-morpholine and (b) 1-(D)-morpholine at 353 K.