Electronic Supplementary Material (ESI) for Green Chemistry

Supplementary Information

Gold Nanoparticle-Catalyzed Cyclocarbonylation of 2-Aminophenols

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Experimental

1) General

All organic reagents were purified before use. $HAuCl_4 \cdot xH_2O$ was obtained from Mitsuwa Chemicals Co., Ltd. Al_2O_3 (JRC-ALO-3), CeO_2 (JRC-CEO-1), 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 InertCap WAX-HT (30 m × 0.53 mm × 1.0 μm) and a Shimadzu GCMSQP5050A instrument equipped with a ULBON HR-1 capillary column (30 m × 0.25 mm × 0.25 μm), respectively. High performance liquid chromatography (HPLC) was performed on a Shimadzu LC-10ADvp: STR ODS-IV ($MeOH/H_2O$=70/30). 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 cyclocarbonylation of **1** using the Au/HT catalyst was as follows. Au/HT (0.10 g, Au: 0.0045 mmol) was placed in a reaction vessel, followed by the addition of DME (5 mL) and **1** (0.25 mmol). The reaction mixture was vigorously stirred at 110 °C under 50 atm of mixed gases (48 atm of CO and 2 atm of O_2) for 2 h. After the reaction, the Au/HT was removed by filtration, and naphthalene (0.2 mmol) was added as an internal standard. The obtained mixture was analyzed by GC and GC-MS.

3) Reuse experiments for the cyclocarbonylation of 1

After the cyclocarbonylation 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 Na_2CO_3 (2 x 10 mL). Next, additional portions of **1** (0.25 mmol) and DME (5 mL) were added, followed by stirring under identical conditions. 98% yields of **2** were obtained in the two reuse experiments.

4) 10 mmol-scale cyclocarbonylation of 1 using Au/HT

Into a stainless steel autoclave with a Teflon inner cylinder (160 mL) were placed Au/HT (0.1 g, Au: 0.0045 mmol), DME (10 mL) and **1** (1.09 g, 10 mmol). The reaction mixture was vigorously stirred at 130 ^{o}C under 50 atm of mixed gases (48 atm of CO and 2 atm of O_2) for 16 h. After the reaction, the Au/HT was removed by filtration, and DME was evaporated. The residue was purified by recrystallization using dichloromethane to give 1.24 g of **2** (92% isolated yield) as a white solid.

5) Product identification

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

Table 2, Entries 1-3

2-benzoxazolinone

CAS registry No. [59-49-4]. ^{1}H NMR and ^{13}C NMR were consistent with previously reported values. See Ref. 1S.

Entry 4

6-methyl 2-benzoxazolinone

CAS registry No. [22876-16-0]. ^{1}H NMR and ^{13}C NMR were consistent with previously reported values. See Ref. 1S.

Entry 5

4-methyl 2-benzoxazolinone

CAS registry No. [78258-80-7].

^{1}H NMR and ^{13}C NMR were consistent with previously reported values. See Ref. 2S.

Entry 6

5-methoxy 2-benzoxazolinone

CAS registry No. [40925-63-1]. ^{1}H NMR and ^{13}C NMR were consistent with previously reported values. See Ref. 3S.

Entry 7

6-fluoro 2-benzoxazolinone

CAS registry No. [2923-94-6]. ^{1}H NMR and ^{13}C NMR were consistent with the authentic sample obtained from Sigma Aldrich.

Entry 8

3H-naphth[2,3-d]oxazol-2-one

CAS registry No. [115164-17-5]. ^{1}H NMR and ^{13}C NMR were consistent with the authentic sample prepared by the reaction of 1,1'-carbonyldiimidazole with 3-amino-2-naphthol. See Ref. 1S.

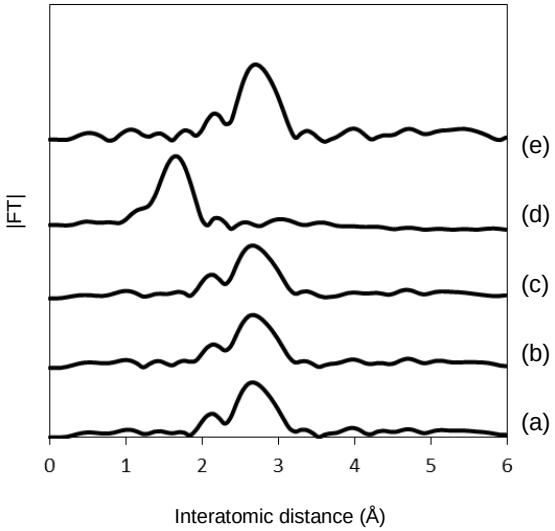
References

[1S] R. J. Nachman, *J. Heterocyclic Chem.*, 1982, **19**, 1545.

[2S] L. Quaranta, O. Corminboeuf and P. Renaud, *Org. Lett.*, 2002, **4**, 39.

[3S] Y. Lu and R. T. Taylor, *Heterocycles*, 2004, **62**, 869.

6) EXAFS analysis



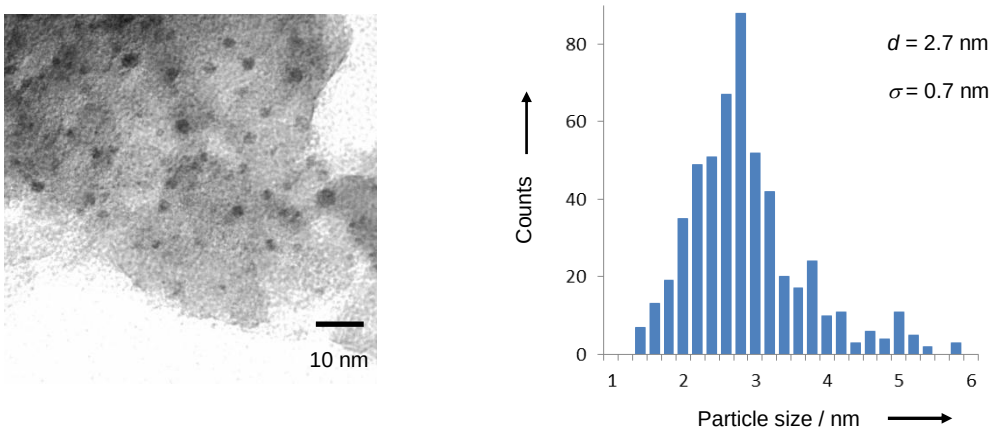
Curve fitting analysis of Au L-edge EXAFS

	Coord. no. (CN)	Interatomic dis. (ð)	$\Delta\sigma/ð^2$
Au/HT (fresh)	8.6	2.85	0.028
Au/HT (after reaction)	8.9	2.85	0.020
Au/HT (after two times reuse)	9.0	2.85	0.026
Au foil	12	2.88	-

Figure 1S. Fourier transformed k^3-weighted Au L-edge EXAFS for (a) Au/HT, (b) Au/HT after cyclocarbonylation of **1**, (c) Au/HT after being reused twice, (d) Au_2O_3 and (e) Au foil.

7) TEM analysis

(a) Au/HT (fresh)



(b) Au/HT (after reuse experiment)

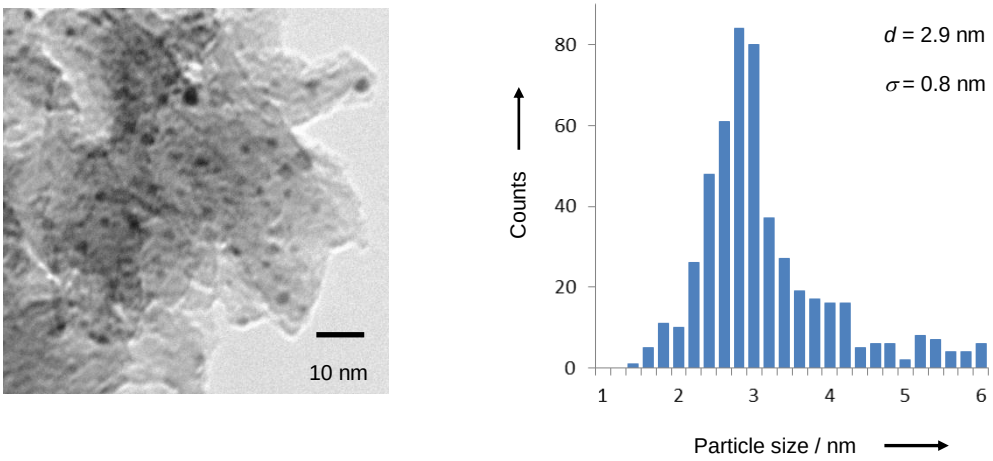
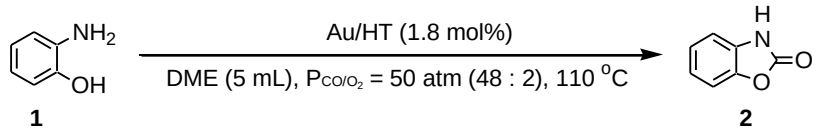


Figure 2S. Typical TEM images and size distribution diagrams (obtained by counting at least 500 particles) of (a) fresh Au/HT and (b) Au/HT after reuse.

8) Leaching test



1 **2**

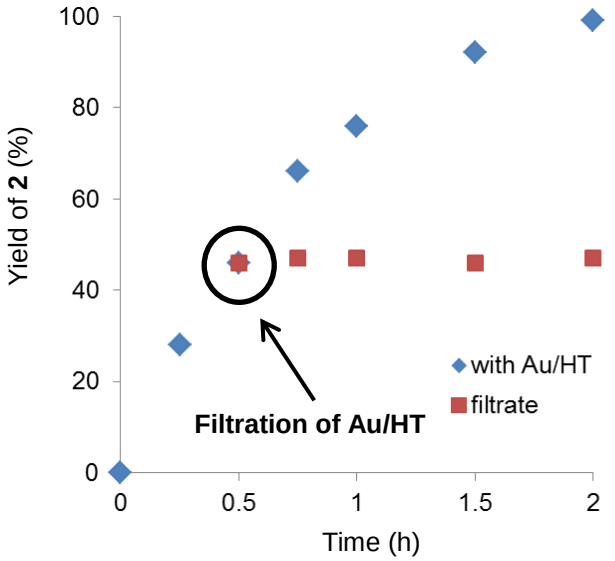


Figure 3S. Time profile for the cyclocarbonylation of **1** using Au/HT.