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Cite this: *Green Chem.*, 2013, **15**, 608

Received 21st November 2012,
Accepted 21st December 2012

DOI: 10.1039/c2gc36851j

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Gold nanoparticle-catalyzed cyclocarbonylation of 2-aminophenols†

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Gold nanoparticles supported on hydrotalcite acted as a highly efficient catalyst for the cyclocarbonylation of 2-aminophenols to 2-benzoxazolinones without any additives. After the cyclocarbonylation, the hydrotalcite-supported gold nanoparticles could be reused without loss of catalytic efficiency.

In recent years, green and sustainable organic synthesis using gold nanoparticle (Au NP) catalysts has attracted great interest.[1] In this context, the catalysis of Au NPs in liquid-phase organic transformations with CO remains quite rare,[2–5] whereas Au NP-catalyzed gas-phase reactions with CO have been widely studied.[6] The carbonylation of anilines to ureas and carbamates catalyzed by Au NPs has previously been demonstrated.[2] We also recently discovered that Au NPs supported on basic supports such as hydrotalcite [HT: $Mg_6Al_2CO_3(OH)_{16}$] and Al_2O_3 catalyzed the double-carbonylation of amines to oxamides.[3] In our continuing studies on the catalysis of Au NPs in liquid-phase reactions, we herein found that HT-supported Au NPs (Au/HT) could act as a highly efficient heterogeneous catalyst for the cyclocarbonylation of 2-aminophenols to 2-benzoxazolinones.

Cyclocarbonylations of 2-aminophenols to 2-benzoxazolinones are of significant importance because 2-benzoxazolinones and their derivatives are valuable compounds for extensive applications as intermediates for organic synthesis, fine chemicals, and pesticides.[7] Catalytic carbonylations are alternative green methods for traditionally stoichiometric reactions using toxic phosgene or its derivatives with 2-aminophenols, producing large amounts of HCl.[8] The cyclocarbonylations of 2-aminophenols have been carried out using Se metals with Et_3N[9] and homogeneous Pd complexes with additives such as iodides[10] and PPh_3.[11] These catalytic systems, however, have suffered from several drawbacks, such as the difficulty of separating the homogeneous metal species from the product, as well as the reuse of the catalysts. Despite heterogeneous catalysis having significant advantages in the above issues, there has been only one example of a heterogeneous catalyst for the cyclocarbonylation of 2-aminophenol using Pd/C with I_2.[10c]

The present Au/HT catalyst could efficiently promote the cyclocarbonylation of 2-aminophenols under non-flammable conditions. This catalyst system provided excellent yields of the corresponding 2-benzoxazolinones without any additives which have been necessary in previous cyclocarbonylations.[9–11] Moreover, the catalytic activity of Au NPs was found to be remarkably high among metal NPs, and the Au/HT catalyst could be reused without loss of its activity or selectivity.

The Au/HT catalyst was prepared according to the procedure in our previous work.[12] Briefly, HT was added to the aqueous solution of $HAuCl_4$. After the subsequent addition of NH_3 solution, the resulting mixture was further stirred. Then, the obtained slurry was filtered and washed with deionized water to afford HT-supported Au^{III} species. Treatment of the resulting solid with an aqueous solution of KBH_4 afforded the Au/HT as a reddish purple powder with a mean diameter of 2.7 nm.

Initially, the catalytic activity of Au/HT was tested in the cyclocarbonylation of 2-aminophenol (**1**) in 1,2-dimethoxyethane under 50 atm of CO/O_2 (48/2) at 110 °C, *i.e.*, the non-flammable condition.[13] Au/HT showed high catalytic activity in the cyclocarbonylation to afford 2-benzoxazolinone (**2**) in 99% yield without any formation of byproducts (Table 1, entry 1). The cyclocarbonylation did not proceed in the absence of O_2, which demonstrated the necessity of O_2 in the cyclocarbonylation (entry 2). When using Au/HT with different Au NP sizes, the size of Au NPs on HT affected the catalytic activity; the yield of **2** increased with decreasing mean particle size (d) of Au NPs (entries 1 and 3–6).[14] When Au/HT was removed from the reaction mixture at 40% conversion of **1**, further stirring of the resulting filtrate under similar reaction

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† Electronic supplementary information (ESI) available: Experimental details, EXAFS analysis and TEM images. See DOI: 10.1039/c2gc36851j

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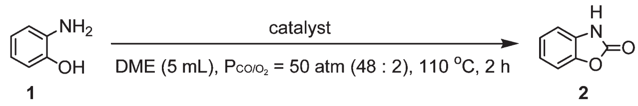
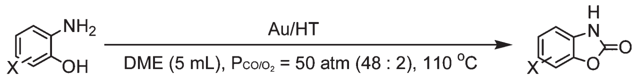
Table 1 Cyclocarbonylation of **1** to **2** using various catalysts[a]

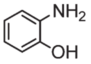
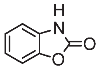
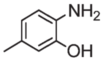
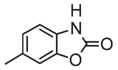
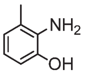
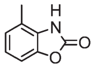
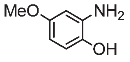
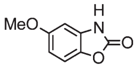
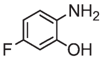
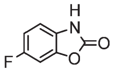
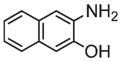
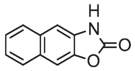


Entry	Catalyst	*d* (nm)	Conv.[b] (%)	Yield[b] (%)
1	Au/HT	2.7	99	99
2[c]	Au/HT	2.7	<1	<1
3	Au/HT	5.8	95	95
4	Au/HT	7.9	88	86
5	Au/HT	12	81	81
6	Au/HT	20	59	56
7	Rh/HT		10	7
8	Pd/HT		12	6
9	Pt/HT		5	3
10	Ru/HT		3	0
11	Ag/HT		3	0
12	Cu/HT		4	0
13	Au/Al_2O_3	3.6	97	97
14	Au/CeO_2	3.8	92	92
15	Au/TiO_2	3.7	87	82
16	Au/HAP	3.0	75	72
17[d]	Au/HAP + Na_2CO_3	3.0	91	87
18	Au/SiO_2	2.2	63	62

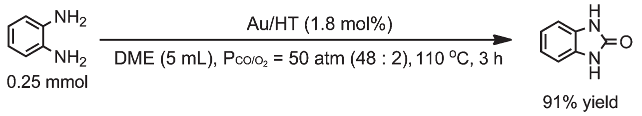
[a] Reaction conditions: catalyst (1.8 mol%), **1** (0.25 mmol). [b] Determined by GC using an internal standard technique. [c] In the absence of O_2. [d] 1.0 mmol of Na_2CO_3 was added.

Table 2 Cyclocarbonylation of various 2-aminophenols with Au/HT[a]

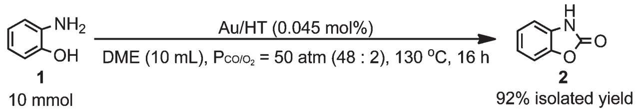


Entry	Substrate	Product	Time (h)	Conv.[b] (%)	Yield[b] (%)
1			2	99	99
2[c]			2	99	98
3[d]			2	99	98
4			3	99	99
5			3	97	96
6			6	99	97
7			4	99	96
8			6	99	95

[a] Reaction conditions: Au/HT (0.10 g, Au: 1.8 mol%), substrate (0.25 mmol). [b] Determined by GC or HPLC using an internal standard technique. [c] Reuse 1. [d] Reuse 2.



Scheme 1 Cyclocarbonylation of 1,2-phenylenediamine with Au/HT.



Scheme 2 10 mmol-scale cyclocarbonylation of **1** using Au/HT.

conditions did not afford **2** (see Fig. 3S in ESI†). From the ICP analysis, no leaching was confirmed in the filtrate (detection limit: <0.1 ppm). These results indicated that the cyclocarbonylation of **1** proceeded on the solid surface of Au/HT.

Next, a series of metal NPs was supported on HT and then tested under similar reaction conditions (entries 7–12).[4b] In contrast to the result using Au/HT, platinum group metals such as Rh, Pd, Pt, and Ru NPs on HTs gave extremely low yields of **2** (entries 7–10)[15] and coinage metals of Ag and Cu NPs did not have any catalytic activity (entries 11 and 12). These results highlighted the fact that Au NPs have remarkably high and unique catalytic activity for the cyclocarbonylation among metal NPs. The effect of supports on the Au NP-catalyzed cyclocarbonylation was further investigated using Au NPs deposited on various inorganic supports such as SiO_2, TiO_2, Al_2O_3, CeO_2 and hydroxyapatite (HAP). Basic supports such as Al_2O_3 and CeO_2 as well as HT were found to be effective (entries 13 and 14). The use of non-basic supports of TiO_2, HAP and SiO_2 resulted in lower yields of **2** (entries 15, 16 and 18). Notably, addition of Na_2CO_3 to the Au/HAP catalyst system enhanced the yield of **2**, confirming that bases have a positive effect on the cyclocarbonylation (entry 16 *vs.* entry 17).

The cyclocarbonylation of 2-aminophenol derivatives using Au/HT was investigated under the optimized reaction conditions. 2-Aminophenols with electron donating and withdrawing substituents were successfully transformed to the corresponding 2-benzoxazolinones in high yields (Table 2, entries 1 and 4–7). Au/HT also efficiently catalyzed 3-amino-2-naphthol to the corresponding 2-oxazolinone (entry 8). Furthermore, 1,2-phenylenediamine could be applied in the present carbonylation system, converting to the cyclic urea 2-benzimidazolinone in high yield (Scheme 1).

Au/HT also worked well under preliminary scale-up conditions; a 10 mmol-scale cyclocarbonylation of **1** proceeded to afford **2** with high efficiency (Scheme 2). In this reaction, the turnover number reached up to 2000.[16] In the present Au/HT catalyst system, the obtained 2-benzoxazolinone products were easily isolated from the reaction mixture and purified by recrystallization due to the absence of additives. Moreover, the used Au/HT could be easily recovered by simple filtration after the reaction and reused without loss of its catalytic efficiency (Table 2, entries 2 and 3).

Taking into consideration the positive effect of bases in the cyclocarbonylation of **1** (*vide supra*), a plausible reaction mechanism is proposed in Scheme 3. Initially, CO adsorbs on the

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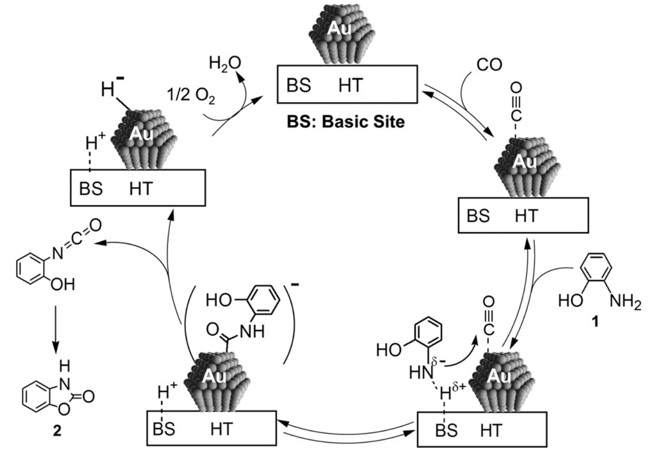

Scheme 3 Plausible reaction mechanism.

surface of Au NPs on HT. Then, nucleophilic attack of the N atom of **1** toward CO on the Au NPs occurs, affording a [Au-carbamoyl]$^-$ and H$^+$ through the activation of N–H of **1** by a basic site of HT.[17] Subsequent β-elimination of the [Au-carbamoyl]$^-$ gives a [Au–H]$^-$ and an isocyanate intermediate,[18] followed by intramolecular attack of the hydroxyl group of **1**, yielding **2**.[19] The resulting [Au–H]$^-$ and H$^+$ react with O_2 to form water, regenerating the catalyst.

In conclusion, hydrotalcite-supported Au NPs showed high catalytic activity for the cyclocarbonylation of 2-aminophenols to 2-benzoxazolinones under non-flammable conditions. The present Au NP-catalyzed system did not require any additives such as PPh_3 and I_2 that have been necessary in previously reported cyclocarbonylations. The significantly unique catalysis of Au/HT with high activity was also disclosed. Moreover, the solid Au/HT was easily recovered by simple filtration and reusable with no decrease in catalytic activity. This study also clearly showed that the cooperative contribution of small Au NPs with basic supports was important to achieve highly efficient cyclocarbonylation of 2-aminophenols.

This work was supported by a Grant-in-Aid for Young Scientists (A) (23686116) from the Japan Society for the Promotion of Science (JSPS). We thank Dr Uruga, Dr Tanida and Dr Nitta (SPring-8) for XAFS measurements. One of the authors A. N. thanks the JSPS Research Fellowships for Young Scientists. The TEM experiments were carried out at a facility of the Research Center for Ultrahigh Voltage Electron Microscopy, Osaka University.

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