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## Covalent triazine framework-supported palladium as a ligand-free catalyst for the selective double carbonylation of aryl iodides under ambient pressure of CO<sup>+</sup>

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Carbonylation of aryl iodides with amines under atmospheric pressure of CO, catalyzed by Pd/CTFs (covalent triazine frameworks) without any specific additives, leads to the highly selective synthesis of  $\alpha$ -ketoamides.

Palladium-catalyzed carbonylations of aryl halides with carbon monoxide as the simplest C1 building blocks are considered to be a convenient method for forming regioselective carbonyl functional groups.<sup>1</sup> In particular, dicarbonylation of aryl halides provides a direct, selective, and valuable approach to the construction of  $\alpha$ -ketoamides, which serve as fundamental precursors in a variety of biologically active natural products and functional group transformations.<sup>2</sup> Although some elegant studies have shown great applicability of palladium-catalyzed double carbonylation in synthetic chemistry, most of them need either specific additives such as phosphine ligands and a nucleophilic amine base or high pressure of carbon monoxide and difficult-to-recycle metal catalysts, which limit their practical utilization.<sup>3</sup> The development of an efficient, easily synthesized, recyclable catalyst for this type of reaction under mild conditions is urgently required.

Covalent organic frameworks  $(COFs)^4$  and metal organic frameworks  $(MOFs)^5$  with a high surface area and tunable pore size have been widely studied in heterogeneous catalysis. COFs and MOFs can not only serve as templates to directly form nanoparticles within their pores to efficiently stabilize metal nanoparticles, but also exhibit promising applications in the storage of gases such as H<sub>2</sub>, CO<sub>2</sub> and CO, which are abundant, easily available and renewable resources in organic synthesis.<sup>6</sup> Recently, porous materials have been attracting considerable attention in the area of gas insertion reactions because of their good capacity for gas adsorption.<sup>7</sup> For example, COFs have been used as supports for metal nanoparticles in the hydrogenation of olefins.<sup>8</sup> Ag@MIL-101 has also achieved the capture and conversion of carbon dioxide.<sup>9</sup> The covalent triazine frameworks (CTFs) have been explored as sorbents for gas storage and solid supports for palladium nanoparticles in heterogeneous catalysis.<sup>10</sup> Herein, we choose the covalent triazine framework-supported palladium (Pd/CTFs) as the gasadsorption heterogeneous catalyst which can serve as a bifunctional material for both the capture of CO and the subsequent selective conversion of CO to  $\alpha$ -ketoamide. To the best of our knowledge, this is the first example of the Pd/CTF-driven double carbonylation of aryl iodides by a one-step reaction under atmospheric pressure of carbon monoxide without any specific additives or ligands.

The as-synthesized CTFs (ESI<sup>†</sup>) are impregnated into the N,N-dimethylformamide solution of palladium chloride for about 12 h and then the adsorbed PdCl<sub>2</sub> is reduced using NaBH<sub>4</sub> to obtain the Pd/CTFs catalyst.<sup>11</sup> Fourier transform infrared (FTIR) spectra of CTFs (Fig. S1, ESI<sup>†</sup>) show strong absorption signals at around 1500, 1360 and 800  $\text{cm}^{-1}$ , which indicate the presence of triazine. The content of Pd in the as-prepared Pd/CTFs is determined to be 2.05 wt% by inductively coupled plasma (ICP) spectrometry. The chemical state of Pd is determined by X-ray photoelectron spectroscopy (XPS) (Fig. S2, ESI<sup>†</sup>). The binding energy peaks of Pd 3d<sub>3/2</sub> and 3d<sub>5/2</sub> at 341.5 eV and 336.3 eV are indicative of the presence of metallic Pd(0). From the TEM images (Fig. 1a), we can clearly see that Pd nanoparticles (NPs) are sufficiently dispersed in CTFs and the average size of NPs is around 3 nm (Fig. 1a inset) on the surface of CTFs. High-resolution transmission electron microscopy (HRTEM) image (inset in Fig. 1b) shows the Pd(111) lattice planes with spacing d(111) = 0.228 nm, which matches well with the literature value for nanocrystalline Pd.<sup>12</sup> From Fig. 1b and Fig. S3 (ESI<sup>†</sup>), we can conclude that some small Pd NPs are located in the pores of CTFs. The SEM and TEM energy dispersive spectroscopy (EDS) mapping images (Fig. 1c-f and Fig. S4, ESI<sup>+</sup>) and the EDS spectrum (Fig. S5, ESI<sup>†</sup>) demonstrate that Pd NPs are

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**Fig. 1** (a–f) TEM images (a and b), SEM image and the corresponding mapping images (c–f) of Pd/CTFs; (g) CO adsorption isotherms of CTFs and Pd/CTFs at 298 K. The insets of (a) and (b) are the particle size distribution statistics and one of representative HRTEM image of Pd nanoparticles loaded on CTFs, respectively.

homogeneously distributed throughout the CTFs. The diffraction peak of Pd species from powder X-ray diffraction (PXRD) (Fig. S6, ESI†) cannot be found, which suggests that the particles are highly dispersed on the support with the size of NPs in pores of CTFs being smaller than the detection limit.<sup>10c,13</sup> The N<sub>2</sub> adsorption–desorption isotherms show (Fig. S7, ESI†) that the surface area of Pd/CTFs samples (607 m<sup>2</sup> g<sup>-1</sup>) is lower than that of pure CTFs (784 m<sup>2</sup> g<sup>-1</sup>), which should be due to the incorporation of the Pd NPs into the pores and the location on the framework surface of CTFs. The average pore diameter of CTFs is about 1.2 nm (Fig. S8, ESI†). The CO uptake of the Pd/CTFs are measured up to 1 atm at 298 K, which show good adsorptive properties of CO (Fig. 1g), which is important for the subsequent conversion of CO into  $\alpha$ -ketoamides.

The catalytic activities of Pd/CTFs are investigated by the double carbonylation of aryl iodides with amines under atmospheric pressure of CO to afford α-ketoamides with good chemoselectivity. In our initial investigation, we select 4-iodoanisole and morpholine as model substrates to explore the optimal reaction conditions (Table 1). Firstly, the reaction is performed employing 4-iodoanisole and morpholine as reactants at 70 °C in DMF in the presence of Pd/CTFs and K2CO3 under atmospheric pressure of CO for 24 h. We were delighted to find that the double carbonylation reaction indeed occurred. Then to optimize the reaction conditions, we screened various bases on this catalytic system, and K<sub>2</sub>CO<sub>3</sub> was verified to be a superior base in comparison with an organic base (DABCO, Et<sub>3</sub>N) and a strong inorganic base (KOH). It is noteworthy that when the solvent is changed to CH<sub>3</sub>CN under otherwise identical conditions, the yield is increased to 84% indicating that CH<sub>3</sub>CN is a superior solvent. The influence of various equivalents of amine on double

 Table 1
 Optimization of reaction conditions<sup>a</sup>

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					Yield <sup>c</sup> (%)	
Entry	Cat. (mg)	Base	Solvent	Conv. (%)	3aa	4aa
1	30	$K_2CO_3$	DMF	90	74	8
2	30	K <sub>2</sub> CO <sub>3</sub>	Toluene	80	49	26
3	30	$K_2CO_3$	CH <sub>3</sub> CN	91	84	11
4	30	$K_2CO_3$	THF	84	41	24
5	30	$K_2CO_3$	1,4-Dioxane	60	45	15
6	30	KOH	$CH_3CN$	60	34	11
7	30	$K_3PO_4$	$CH_3CN$	79	72	7
8	30	Et <sub>3</sub> N	$CH_3CN$	10	6	4
9	30	DABCO	$CH_3CN$	36	13	23
10	15	$K_2CO_3$	$CH_3CN$	68	63	4
11	25	$K_2CO_3$	$CH_3CN$	82	74	8
12	30	_	CH <sub>3</sub> CN	37	29	8
$13^{b}$	30	$K_2CO_3$	$CH_3CN$	Trace	Trace	Trace

 $^a$  Reaction condition: **1a** (0.2 mmol), **2a** (0.8 mmol), base (0.4 mmol) and CO (balloon pressure) in 1 mL solvent at 70  $^\circ C$  for 24 h.  $^b$  Room temperature for 48 h.  $^c$  Determined by <sup>1</sup>H MNR spectroscopy of the crude mixture.

carbonylation is assessed (Table S1, ESI<sup>†</sup>), and we find that four equivalents of amine are optimal. More interestingly, we screen the reaction temperature and find that double carbonylation is greatly influenced by temperature (Fig. S9, ESI<sup>†</sup>). When the reaction is carried out at 100 °C, a satisfactory yield and high selectivity of mono carbonylation is obtained. And the results show that the double carbonylation reaction display the maximum yield and excellent selectivity when we use  $K_2CO_3$  as the base and  $CH_3CN$  as the solvent in the presence of 30 mg Pd/CTFs at 70 °C; however, the mono carbonylation products are the main products at 100 °C under otherwise identical conditions (Fig. S9, ESI<sup>†</sup>).

Having identified the optimal reaction conditions, we explore the substrate scope of this double carbonylation reaction with various aryl iodides and amines, as listed in Table 2. The yields and selectivity of the di-carbonylation reactions are better for the substrates bearing electron-donating groups (Table 2, entries 1-5). In contrast, the substrates with electron-withdrawing groups on the aryl ring give rise to the products in slightly lower yields and poor selectivity (Table 2, entries 7 and 8). The dissatisfactory results may be due to the negative nucleophilicities caused by the electron-deficient groups. Additionally, other amines including piperidine, pyrrolidine, diethylamine, and n-propylamine are all amenable to the standard reaction conditions to generate the desired products in good yields and selectivity (Table 2, entries 9-12). Furthermore, the 1-naphthalene iodide is also selected as the substrate (Table 2, entries 13 and 14); however, lower yields and poor selectivity of the products are obtained, which may be due to the fact that the large steric hindrance which makes it difficult for the reacting agents to enter into the pores of the Pd/CTFs and the carbonylation of Ar-I occurs only at the surface of the catalysts. We also explored the substrate scope of the mono-carbonylations of aryl iodides with amines under the best conditions (Table S2, ESI<sup>+</sup>) and found that

Pd/CTFs, K<sub>2</sub>CO<sub>3</sub> Amines co Amines Amines CH3CN, 70°C, 24h 0 (1atm) 2 3 Yield<sup>b</sup> [%](3/4) Entry 1 2 3 ò 84 (88/12) 1 3ba 79 (79/21) 2 3 75 (86/14) 4 90 (95/5) 60 (70/30) 5 71 (76/24) 6 7 43 (49/51) 8 32 (35/65) 9 72 (79/21) 70 (77/23) 10 2c 11 76 (77/23) 3ad 79 (91/9) 12 35 (43/57) 13 2b 18 (18/82) 14 3ib

Table 2 Double carbonylation reaction of aryl iodides with various  $\operatorname{amines}^a$ 



various aryl iodides with different amines could afford the desired products at high temperatures.



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Fig. 2 Yields (%) as a function of time in double carbonylation of aryl iodides with amines at 70  $^\circ \rm C.$ 

To prove the high catalyst activity of Pd/CTFs, we draw a time course of evoluted *a*-ketoamide of the model reaction under the optimized conditions over Pd/CTFs, 5 wt% Pd/C (HEOWNS) and Pd nanoparticle networks (Pd NNs, Fig. S14, ESI<sup>†</sup>) (Fig. 2). After 6 h, Pd/CTFs and Pd/C exhibit remarkably high activity compared to Pd NNs, and Pd/CTFs show a higher activity than Pd/C. These results suggest that the enhanced catalytic activity and the high selectivity of Pd/CTFs can be ascribed to the CO adsorption of CTFs and the improvement concentration of CO around the catalytic centers. On the other hand, CTFs can provide a microreactor through its pores and the framework which accelerates the catalytic process.9 Furthermore, the recyclability and recoverability of Pd/CTFs are investigated. There are good regeneration properties without obvious change in activity at the second recycling run. However, from the third to the fifth recycling run, the yields of  $\alpha$ -ketoamide decrease from 84% to 65% (Fig. S11, ESI<sup>†</sup>). After each recycle, the concentration of leaching palladium species in the reaction mixture is detected using ICP-MS (Fig. S12, ESI<sup>†</sup>). It is noteworthy that the leaching Pd amount is negligible and no double carbonylation activity is detected using the supernatant liquid after the isolation of the solid catalyst. The TEM investigation shows the aggregation Pd nanoparticles on the surface of CTF (Fig. S13, ESI<sup>+</sup>), which may be an important reason for the decrease of catalyst activity. We also carried out Hg(0) poisoning test<sup>3e</sup> and found that the carbonylation reaction was inhibited completely, suggesting that palladium nanoparticles are the real active catalyst. However, the Pd/C catalyst showed poor circulation in double carbonylation catalysis systems.<sup>14</sup> These results confirm that the Pd/CFTs are highly active and stable for the highly selective synthesis of  $\alpha$ -ketoamides by carbonylation of aryl iodides with amines under atmospheric pressure of CO.

The well-accepted oxidative addition/reduction elimination mechanism is always involved in Pd-catalyzed carbonylations of aryl halides with CO and amines.<sup>3,15</sup> Firstly, the oxidative addition of aryl halide to Pd(0) generates an organopalladium halide species, and there is a subsequent migratory insertion of a coordinated carbon monoxide to form the Pd acyl intermediate. The acylpalladium halide species is further coordinated with carbon monoxide at 70 °C and then attacked by the nucleophilic amine at a terminal CO to yield  $\alpha$ -ketoamide (double carbonylation product). But at a high temperature of 100 °C, acylpalladium

halide species reacts directly with a nucleophile (amine) and the base to form the amide (mono carbonylation product). We speculate that lower temperatures are favourable for absorbing more CO in the pore canals, and the increased concentration of CO is prone to coordinate to the Pd species.<sup>3c,16</sup> Such speculations are proved by our experimental results.

In summary, we have reported a facile preparation of the hybrid Pd/CTFs catalyst using the impregnation-reduction method. This is the first example that porous material simultaneously captures and converts CO for one-step selective double carbonylations of Ar–I with amines under atmospheric pressure of CO without the assistance of any ligands. The synergetic effect of palladium nanoparticles (catalytic center) and high porosity of CTFs (gas adsorption) led to the accomplishment of this reaction at atmospheric pressure instead of high pressure. Wide substrate scopes, promising yields and selectivities, and low loading and good recyclability of the catalysts demonstrate the effectiveness of Pd/CTFs. Therefore, this work will be of help in the design of a highly active and stable catalyst for gas insertion reactions *via* such synergistic effects of gas capture substrates and active catalysts.

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