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Chem. Mater., Just Accepted Manuscript • DOI: 10.1021/acs.chemmater.7b00544 • Publication Date (Web): 03 Apr 2017

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# Tuning Synergistic Effect of Au-Pd Bimetallic Nanocatalyst for Aerobic Oxidative Carbonylation of Amines

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**ABSTRACT:** The activation and utilization of carbon monoxide (CO) is of crucial importance to the C<sub>1</sub> chemistry. Various catalytic transformation processes have been developed and studied in the last century, and oxidative carbonylation of amines was one of them. Catalysts that have been identified so far for the oxidative carbonylation of amines generally show relatively low activity and/or selectivity. Herein, a metal-organic framework (MOF), *i.e.*, MOF-253 prepared from AlCl<sub>3</sub>·6H<sub>2</sub>O and 2,2'-bipyridine-5,5'-dicarboxylic acid, was employed as a support of gold-palladium bimetallic nanoparticles (Au-Pd/MOF) for the oxidative carbonylation of amines under mild conditions. Compared to palladium or gold monometallic catalysts, higher catalytic activity (turnover frequency up to 2573 h<sup>-1</sup>) and selectivity in the carbonylation of amines were achieved by Au-Pd/MOF bimetallic catalysts through adjusting the molar ratio of gold and palladium within the framework. A breathing effect of Au-Pd/MOF in catalytic process was further observed from kinetic profiles and powder X-ray diffraction for the first time.

**KEYWORDS:** aerobic oxidative carbonylation, bimetallic catalyst, breathing effect, metal-organic frameworks, synergistic effect

#### INTRODUCTION

During the past few decades, many studies had shown that supported transition-metal nanoparticles could be effective catalysts in various chemical transformations.<sup>1-8</sup> Palladium (Pd)<sup>5</sup> and gold (Au)<sup>9-16</sup> are popular metals among these transition metals, due to their high activity demonstrated in carbon-carbon bond formation and aerobic oxidation reactions. After the concept of bimetallic nanoparticle catalysts was established in 1970's,<sup>17,18</sup> Au-Pd bimetallic catalysts have been raising as one of the most attractive systems in the catalysis research. As a new type of heterogeneous catalyst,19-39 the Au-Pd bimetallic nanoparticles have been investigated in the acetoxylation of ethylene,<sup>24</sup> synthesis of H<sub>2</sub>O<sub>2</sub>,<sup>34</sup> oxidation of alcohols,<sup>20,35</sup> and carbon monoxide (CO) oxidation.<sup>37,40</sup> However, the activation and utilization of CO in organic reactions catalyzed by Au-Pd bimetallic catalysts still remain unexplored, although it is an essential part of C<sub>1</sub> chemistry.

This work: Aerobic Oxidative Carbonylation

$R^{\mathrm{NH}_2}$	Au-Pd	H H	Selectivity: > 98 %
	<b>CO</b> /O <sub>2</sub>	R	TOF: up to 2573 h <sup>-1</sup>

**Scheme 1**. Au-Pd bimetallic catalysts for aerobic oxidative carbonylation.

Developing novel heterogeneous catalysts with higher efficiency and better selectivity is one of the primer goals in modern catalytic chemistry. Recently, we demonstrated that mesoporous silica framework supported single site Pd(II) is an efficient catalyst for the C-H olefination reactions, confirming that the ligand modified framework has distinctive capability to immobilize the Pd site and to remain its catalytic activity during the catalytic process.<sup>41</sup> Similar to mesoporous silica, metal-organic frameworks (MOFs) are a kind of crystalline porous materials containing organic linkers, metal clusters, and empty space in nanometer scale, having high surface area and porosity.<sup>42-44</sup> Owing to these unique properties, MOFs show considerable promise in catalysis.45-63 One of promising approaches is to use MOFs as the supports of metal sites (*i.e.*, metal complexes active or nanoclusters).<sup>27,51,54,56,64-69</sup> Based on these pioneering studies, we herein developed MOF supported Au-Pd bimetallic catalysts and investigated their catalytic performance in aerobic oxidative carbonylation reactions (Scheme 1). In this work, MOF-253 prepared from AlCl<sub>3</sub>·6H<sub>2</sub>O and 2,2'-bipyridine-5,5'-dicarboxylic acid was selected as the catalyst support owing to its high concentration of 2,2'-bipyridine unit and unique nanostructure. MOF-253 also showed good capability to immobilize and disperse the metal sites uniformly,67 demonstrating that it is an excellent support for heterogeneous catalysis.

To the best of our knowledge, this is the first report of aerobic oxidative carbonylation reaction catalyzed by Au-Pd bimetallic catalyst. Carbonylation reaction is an important reaction in organic chemistry and C1 chemistry. Both Au and Pd could be used as catalysts in this reaction, but there are some activity and/or selectivity issues associated by using only single metal catalysts. On the other hand, the present Au-Pd bimetallic catalyst shows an amazing potential in the activation of O2 and C0, making it highly unique for further developments.

#### EXPERIMENTAL SECTION

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General information. All the chemicals including nonaqueous tetrahydrofuran (THF), MeOH and dimethyl sulfoxide (DMSO) were purchased from Sigma Aldrich and used as received. All non-aqueous reactions and manipulations were performed in a N<sub>2</sub> atmosphere using standard Schlenk techniques. The catalyst amount in each reaction was weighted on a microbalance (Mettler Toledo XS3DU). NMR spectra were recorded on Bruker spectrometer at 300 MHz (<sup>1</sup>H NMR) and 75 MHz (<sup>13</sup>C NMR), or a Bruker spectrometer at 400 MHz (<sup>1</sup>H NMR) and 100 MHz (<sup>13</sup>C NMR). Tetramethylsilane (TMS) was used as an internal standard. All <sup>1</sup>H NMR spectra were reported in delta ( $\delta$ ) units, parts per million (ppm) downfield from the internal standard. Coupling constants were reported in Hertz (Hz). Brunauer–Emmett–Teller (BET) surface areas were obtained using a Micromeritics ASAP 2020M automated sorption analyzer. High-angle annular darkfield scanning transmission electron microscope (HAADF-STEM) images and cross-sectional compositional line profiles were obtained using a JEOL 2100. Powder X-ray diffraction (PXRD) measurements were performed on a SHIMADZU XRD-6000 Labx diffractometer at 40 kV and 30 mA using Cu K $\alpha$  radiation ( $\lambda = 1.5418$  Å) over 2 $\theta$  range of 2.5° - 40° at room temperature. X-Ray photoelectron spectroscopy (XPS) was referenced to the carbon species with C 1s at the binding energy of 284.8 eV. The metal loading was determined by inductively coupled plasma mass spectrometry (ICP-MS) using Agilent 7700. All catalytic reactions were carried out in an autoclave and monitored by thin-layer chromatography (TLC), NMR and gas chromatography (GC). The yield and selectivity data in catalyst scanning reactions were determined by GC with dodecane as the internal standard. The concentration of the product in kinetic profiles was determined by Bruker 400 MHz NMR with 1,3,5-trimethoxybenzene as the internal standard.

Synthesis of 2,2'-bipyridine-5,5'-dicarboxylic acid. 2,2'-Bipyridine-5,5'-dicarboxylic acid was synthesized following our previous work.<sup>41</sup> To a stirred solution of potassium permanganate (4383 mg, 27.7 mmol) in water (60 mL), 5,5'-dimethyl-2,2'-bipyridine (786 mg, 4.3 mmol) was added. The mixture was heated in an oil bath to reflux for 5 h. Subsequently, the mixture was cooled down to room temperature followed by filtration. Then, the filtrate was washed by  $Et_2O$  (100 mL) for three times. After the pH value of the water phase was adjusted to 2, white floc solid appeared. The mixture was filtered and white solid was obtained. The solid was dried at 50 °C under vacuum overnight. 2,2'-Bipyridine-5,5'-dicarboxylic acid (684 mg, 2.8 mmol, 66 % yield) was obtained as a white solid. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz):  $\delta$  = 13.57 (br. s., 2 H), 9.20 (s, 2 H), 8.57 (d, *J* = 8.3 Hz, 2 H), 8.42 - 8.47 ppm (m, 2 H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 101 MHz):  $\delta$  = 166.5, 157.8, 150.8, 138.9, 127.6, 121.6 ppm.

Synthesis of MOF-253. MOF-253 was synthesized as the reported method with slight modifications.<sup>68</sup> A solution of AlCl<sub>3</sub>·6H<sub>2</sub>O (151 mg, 0.625 mmol) and glacial acetic acid (859 µL, 15.0 mmol) in N,N'-dimethylformamide (DMF, 10 mL) was added to a Teflon-capped 20 mL scintillation vial containing 2,2'-bipyridine-5,5'-dicarboxylic acid (153 mg, 0.625 mmol). The mixture was heated on an oven at 120 °C for 24 h. The resulting white microcrystalline powder was then filtered and washed with DMF. The powder was extracted with methanol via soxhlet extraction for 72 h, after which the powder was collected by filtration and heated at 250 °C under dynamic vacuum on a Schlenk line for 12 h. The N<sub>2</sub> adsorption isotherm (Figure S1 in the Supporting Information) and pore size distribution (Figure S2) of the prepared MOF-253 were determined, showing a pore size of about 1.2 nm. Its pore size determined by PXRD was from 1.2 nm to 1.3 nm.

**Preparation of catalysts**. All the catalysts were prepared via an impregnation method using AuCl<sub>3</sub> solution in MeOH and/or Pd salt solution in dry DMSO. The loaded metal species were reduced by hydrogen to obtain the metal particles. The detailed preparation procedure employed is described below. All the metal concentrations used in following catalytic experiments were obtained from ICP-MS tests.

**Preparation of Au/MOF**. To a mixture of MOF-253 (40 mg) in MeOH (3 mL), an appropriate amount of AuCl<sub>3</sub> solution in MeOH was added. The mixture was stirred and refluxed for 3 days. After centrifugation and washing by plenty of MeOH, the retaining solid was dried under vacuum for two days. Then, the gold immobilized MOF-253 (Au/MOF) catalyst was obtained after treating the solid under hydrogen at 80 °C for 2 h.

**Preparation of Pd/MOF**. To a mixture of MOF-253 (40 mg) in dry DMSO (3 mL), an appropriate amount of palladium salt (PdCl<sub>2</sub>, Pd(OTFA)<sub>2</sub> or Pd(OAc)<sub>2</sub>) solution in DMSO was added. The mixture was stirred at room temperature for 1 day. After centrifugation and washing by plenty of MeOH, the retaining solid was dried under vacuum for two days. Then, the palladium immobilized MOF-253 (Pd/MOF) catalyst was obtained after treating the solid under hydrogen at 80 °C for 2 h.

**Preparation of Au-Pd/MOF**. To a mixture of gold immobilized MOF-253 (40 mg, before the treatment by hydrogen) in dry DMSO (3 mL), an appropriate amount of palladium salt (PdCl<sub>2</sub>, Pd(OTFA)<sub>2</sub> or Pd(OAc)<sub>2</sub>) solution in DMSO was added. The mixture was stirred at room temperature for two days. After centrifugation and washing by plenty of MeOH, the retaining solid was dried under vacuum for two days. The Au-Pd immobilized MOF-253 (Au-Pd/MOF) catalyst was obtained after treating the solid under hydrogen at 80 °C for 2 h.

**General catalytic procedures.** A test tube was added with catalyst (Au/MOF, Pd/MOF, Au-Pd/MOF or a mixture of Au/MOF and Pd/MOF), as well as THF and amine (4 mL). The mixture was treated by ultrasonication to disperse the

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catalyst. The resulting solution was sealed in a 600 mL Parr reactor and purged by 10 atm of CO gas for five times, and then the reactor was filled by CO (6 bar) and O<sub>2</sub> (2 bar). After stirring the mixture at 90 °C for 20 h, the reactor was cooled down to room temperature and the excess gas was released slowly. After dodecane was added as an internal standard, the residue was analyzed by GC to obtain the yield and selectivity data. The turnover number (TON) and turnover frequency (TOF) data were further calculated in the basis of total metal concentration.

**Procedures for kinetic experiments.** To a 1.5 mL vial was added Au-Pd/MOF (0.3 mg), cyclohexanamine (0.014 mmol), 1,3,5-trimethoxybenzene (about 0.2 mg) and THF- $d_8$  (0.25 mL). The mixture was treated by ultrasonication to disperse the catalyst. The resulting solution was sealed in a Norell heavy wall NMR tube and filled by the mixture gases of CO and O<sub>2</sub> (5 bar, CO:O<sub>2</sub> = 3:1). Then, the mixture was heated to 90 °C and monitored by <sup>1</sup>H NMR.

#### Table 1. Comparison of catalytic activity for oxidative carbonylation of cyclohexanamine using different supported catalysts.

a1	IH <sub>2</sub> Cat., CO, O2			N,N'-dicyclohexylo and N-cyclohexylforr	oxalamide mamide
Entry	Cat. <sup>a</sup>	Au/Pd	TON	Selectivity	Yield
		molar		(%) <sup>b</sup>	(%) <sup>b</sup>
_		ratio			
1	MOF-253	0:0	None	None	None
2	Au/MOF	1:0	545	36	6
3	Pd/MOF <sup>c</sup>	0:1	2841	73	23
4	Au-Pd/MOF <sup>c</sup>	0.20:0.80	9786	88	46
5	Au-Pd/MOF <sup>c</sup>	0.27:0.73	14128	98	54
6	Au-Pd/MOF <sup>c</sup>	0.69:0.31	1941	38	8
7	Au/MOF,	0.55:0.45	2575	75	40
	Pd/MOF <sup>c</sup>				
8	Au/MOF,	0.25:0.75	2325	71	45
	Pd/MOE <sup>c</sup>				

Reaction conditions: cyclohexylamine (**a1**, 4.3 mmol), CO (6 bar),  $O_2$  (2 bar), THF as the solvent (4.0 mL), 90 °C, 20 h. TON was calculated in the basis of the total metal. (a) The catalyst mass was around 0.3 mg. The metal concentrations in catalysts were obtained from ICP-MS measurements. (b) The yield and selectivity were determined by GC with dodecane as the internal standard. (c) Pd(OTFA)<sub>2</sub> was used as the Pd precursor.

#### **RESULTS AND DISCUSSIONS**

To achieve desirable catalytic activity and selectivity, a series of MOF-253 supported Au-Pd bimetallic catalysts (Au-Pd/MOF) were synthesized, and their catalytic performance was tested in a model reaction (Table 1). Under eight bar of gas mixture consisting of CO and O<sub>2</sub> (3 to 1), no product was found in the blank reaction by employing only MOF-253 as the catalyst (Table 1, entry 1). To examine the catalytic efficiency of MOF-253 supported monometallic catalysts in carbonvlation of cyclohexanamine, Au/MOF and Pd/MOF were also synthesized by an impregnation method. Both of Au/MOF and Pd/MOF could produce carbonylation product a2

(Table 1, entries 2 and 3). The carbonylation of reactant **a1** in the presence of Au/MOF led to lower selectivity (36 %, entry 2) with N-cyclohexylformamide as a side product. A relatively higher selectivity (73 %, entry 3) was obtained in the presence of Pd/MOF as the catalyst, having dicarbonylation as the main byproduct. Significantly, the catalytic efficiency by using Au-Pd/MOF bimetallic catalyst was improved dramatically through tuning the molar ratio of Au and Pd (entries 4-6). Compared to Au/MOF monometallic catalyst, the TON of Au-Pd/MOF (molar ratio of Au and Pd = 0.27/0.73) increased by almost 26 times (entry 5), and the selectivity rose to 98 %. When Pd(OTFA)<sub>2</sub> was used as the Pd precursor and the Au molar ratio was adjusted to 27 %, the TON increased to five times higher than that of Pd/MOF monometallic catalyst (entry 5). Furthermore, when Au/MOF and Pd/MOF were physically mixed together under two different ratios and then used as catalysts in the model reaction (entries 7 and 8, molar ratio of Au and Pd = 0.55/0.45 and 0.25/0.75), the catalytic activity and selectivity were similar to Pd/MOF monometallic catalyst. These results indicate that the catalytic efficiency was enhanced by Au-Pd bimetallic nanoparticles rather than the separated gold and palladium nanoparticles.



**Figure 1.** Effect of Au/Pd molar ratio on Au-Pd/MOF catalyzed oxidation carbonylation of cyclohexanamine. Reaction conditions: cyclohexylamine (4.3 mmol), CO/O2 (8 bar, 3:1), THF as the solvent (4.0 mL), 90 °C, 20 h. The metal contents in catalysts were obtained from ICP. The yield and selectivity were determined by GC with dodecane as the internal standard. TOF was calculated in the basis of total metal. PdCl<sub>2</sub> was used as the palladium precursor for the synthesis of Au-Pd/MOF.

Then, we investigated Au-Pd/MOF with different metal molar ratios in order to achieve the most effective catalyst (Table S1 and Figure S3). As shown in Figure S3a, Au was not an active metal for this reaction by itself, but the combination of Au and Pd could enhance the product selectivity as compared with the Pd/MOF monometallic catalyst. Better catalytic efficiency was reached when the Au molar percentage was adjusted to 20~30 %. Similar results were revealed when switching the Pd precursor to Pd(OAc)<sub>2</sub> (Figure S3b), and the highest selectivity was observed when 30 mol % of Au was used in Au-Pd/MOF.

We further studied the Au-Pd/MOF bimetallic catalyst using PdCl<sub>2</sub> as the Pd precursor (Figure 1). The best product selectivity and catalytic efficiency were achieved at the same time when the Au:Pd molar ratio in Au-Pd/MOF was adjusted to 26/74, and this catalyst (named as Au<sub>26</sub>-Pd<sub>74</sub>/MOF) was chosen for further investigations. These data demonstrate a clear synergistic effect between Au and Pd in Au-Pd/MOF bimetallic catalyst, which could influence the catalytic performance in oxidative carbonylation of amine.

Further investigation on Au<sub>26</sub>-Pd<sub>74</sub>/MOF bimetallic catalyst was carried out through high-resolution transmission electron microscopy (HR-TEM). Fine metal clusters from Au<sub>26</sub>-Pd<sub>74</sub>/MOF bimetallic catalyst were observed in HAADF-STEM images (Figure 2a and Figure S4c). These clusters fall in the range of 0.7 to 2.0 nm in diameter, and intermediate particles were 1.2 nm in size (Figure 2b), matching well with the pore size of MOF-253. Due to the interference of porous framework, the crystalline lattice of Au-Pd bimetallic nanoparticles was only observed on some larger nanoparticles (Figure 2c). Corresponding fast Fourier transformation (FFT) patterns (Figure 2d) further support the structure of the metal nanoparticles with body-centered cubic (BCC) morphology that was same to the reported Au-Pd bimetallic nanoalloy and different to the Pd-only and Au-only alloy (facecentered cubic, FCC).<sup>70-72</sup> The cell length was about 0.40 nm, which also matches to pervious reports.68

The XPS spectra of Au<sub>26</sub>-Pd<sub>74</sub>/MOF also confirmed the presence of Pd, and only weak signal of Au was found due to the low concentration of Au in the catalyst (Figure S5). A negative shift (0.3-0.5 eV) of Pd 3d in Au<sub>26</sub>-Pd<sub>74</sub>/MOF was observed as compared to that of Pd/MOF, further supporting the conclusion that the Au-Pd nanoalloy was formed in the catalyst. Relatively high binding energy of Pd 3d in the catalyst may be due to small particle size of the metals.<sup>27,34</sup> In addition, a peak splitting of N 1s was found after the loading of metals in Au<sub>26</sub>-Pd<sub>74</sub>/MOF (Figure S6). No significant peak change was found through FT-IR analysis (Figure S7). The compositional line profiles (Figure S8) further indicate the presence of both Au and Pd in a nanocluster, implying that the two metal precursors were reduced into bimetallic clusters by H<sub>2</sub> during the preparation.

In order to investigate the synergistic effect of Au<sub>26</sub>-Pd<sub>74</sub>/MOF catalyzed oxidative carbonylation of amines, more control experiments were designed and carried out based on the model reaction. As shown in Scheme S1 and Table S2 in the Supporting Information, no product was found by GC when using different concentrations of N-cyclohexylformamide instead of CO. In addition, no dicarbonylation product was observed when N-cyclohexylformamide was reacted with O<sub>2</sub> in the presence of the Au<sub>26</sub>-Pd<sub>74</sub>/MOF catalyst. When employing CO instead of the CO/O<sub>2</sub> mixture, no product was detected in the reaction mixture. When the model reaction was tested using Au-Pd loaded TS-1 zeolite catalyst prepared under a similar method, only a trace amount of product was found by GC.

Basically, there are three interpretations of the synergetic effect, *i.e.*, bifunctional mechanism, electronic effect and geometric ensemble effect.<sup>37</sup> Above results indicate that this bimetallic catalyst does not work as a kind of "bifunctional" catalyst in this model reaction, confirming the synergistic effect in Au<sub>26</sub>-Pd<sub>74</sub>/MOF catalyzed oxidative carbonylation reaction. The study about the electronic and geometric effect generated from the Pd–Au interfaces in the catalyst in terms of an increase or decrease of Pd–Pd and Au–Au bond lengths in Pd-Au/MOF as compared with that of Au/MOF and Pd/MOF should be useful for better understanding the mechanism. We will try to address the detailed synergetic mechanism in our future research.

The kinetic investigation was then carried out. As shown in the first hour from curve *a* in Figure S9a, an induction period was observed. However, no induction period was observed when the Au<sub>26</sub>-Pd<sub>74</sub>/MOF catalyst was immersed into THF-*d*<sub>8</sub> for 20 h before the kinetic experiments (curve *b* in Figure S9a). This observation indicates that the induction period was not caused by the pre-activation of metal species inside the MOF-253 support. Only possible explanation is the breathing effect induced by the flexibility of MOF-253, which may restrict the diffusion process of the reactants and products. The breathing effect of a MOF is its ability to exhibit displacive phase transition behavior, where the unit cell volume of the MOF varies in response to an external stimulus.<sup>73,74</sup>



**Figure 2.** (a) HAADF-STEM image of Au<sub>26</sub>-Pd<sub>74</sub>/MOF bimetallic catalyst, (b) size distribution of Au-Pd nanoclusters in Au<sub>26</sub>-Pd<sub>74</sub>/MOF, (c) crystalline lattice of Au-Pd nanoclusters in Au<sub>26</sub>-Pd<sub>74</sub>/MOF, and (d) corresponding FFT patterns of these Au-Pd nanoclusters.

To further confirm whether the distinct induction period in kinetic profiles of dry Au<sub>26</sub>-Pd<sub>74</sub>/MOF is resulted from the structural change of MOF-253 or not, PXRD measurements of dry and wet Au<sub>26</sub>-Pd<sub>74</sub>/MOF samples were carried out (Figure S9b). The diffraction shifts in PXRD between Au<sub>26</sub>-Pd<sub>74</sub>/MOF and MOF-253 may be caused by the filling of Au and Pd metals in the MOF pores, leading to a slight change of the framework. The PXRD pattern of wet sample is in a good agreement with that of the simulated structure having larger pores, while that of the dry sample matches well with the calculated structure having smaller pores. The pore sizes of the framework under two states were further simulated (Figure S10). For the dry sample, the Al–Al–Al angle ( $\theta$ ) in the framework is 64°. Comparatively, the angle ( $\theta$ ) increased to 80° when the sample was changed to the wet state (Figure S10a), and the ID (inner diameter) of the pores increased to nearly 13 Å. Combining the changes of the ID and the molecular sizes of cyclohexylamine and product (Figure S10b), it is obvious that the porous framework shall have a notable confinement to the diffusion process, specifically

to the product. The breathing effect of the catalyst can be accounted for the structural flexibility of MOF-253 (Figure S9c). While the breathing effect of MOFs has been extensively reported in adsorption, separation, conductivity and sensor,<sup>75-78</sup> this phenomenon has not been observed in catalytic process so far.



**Figure 3.** Au<sub>26</sub>-Pd<sub>74</sub>/MOF catalyzed oxidation carbonylation of different amines. 2 % NH<sub>3</sub> aqueous solution was used in the urea generation test, and no additional solvent was employed.

In addition, a preliminary study on the reusability of Au<sub>26</sub>-Pd<sub>74</sub>/MOF for the model reaction over five runs was carried out, showing that both of the reaction yield and selectivity dropped slightly after five cycles (Figure S11). The recycled Au-Pd/MOF was tested by PXRD. As shown in Figure S12, those peaks in the recycled Au-Pd/MOF were weaker than the peaks from original catalyst, indicating its relatively low stability after five cycles. Finally, the substrate scope was investigated in the presence of Au<sub>26</sub>-Pd74/MOF under the optimized conditions. As shown in Figure 3, cyclohexanamine and 1-adamantylamine could be converted into corresponding products in good yields of 96 % (a2) and 92 % (c2), respectively. The reaction of benzylamine under the standard condition gave an isolated yield of 81 % (b2). In the case of ethylenediamine, only trace product was found by mass spectrometry, and no reaction was observed when using aniline and ammonia as the reactants.

## CONCLUSIONS

In conclusion, the present catalytic study shows that the integration of Au with Pd in Au-Pd/MOF bimetallic catalyst could be beneficial to the product selectivity and catalyst efficiency for the carbonylation reaction of amines. The best Au/Pd molar ratio for oxidative carbonylation of amine was 26:74. A clear synergistic effect of Au-Pd/MOF bimetallic catalyst was revealed from the catalytic results. Compared to Au and Pd monometallic catalysts, the TOF of Au<sub>26</sub>-Pd<sub>74</sub>/MOF increased by 95 and 16 times, respectively. Moreover, the breathing effect of MOF-253 has been identified from the kinetic profiles for the first time. Thus, this newly developed MOF-253 supported Au-Pd bimetallic catalyst could offer an effective catalytic protocol to aerobic oxidative carbonylation of amines. Further mechanistic and kinetic investigations as well as studies on the electronic and geometric effect generated from the Pd-Au interface in the catalysts are currently undergoing in our laboratory, and will be reported in due course.

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

N<sub>2</sub> adsorption and pore size distribution, Au/Pd loading molar ratio and ICP results, additional catalytic results of Au-Pd/MOF, effect of Au/Pd molar ratio on Au-Pd/MOF catalyzed oxidation carbonylation, HAADF-STEM image, XPS spectra, N 1s spectra, FT-IR spectra, control catalytic experiments, schematic presentation for the breathing effect of Au-Pd/MOF, catalytic performance in five cycles, PXRD, and NMR data of carbonylation products (PDF).

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#### Author Contributions

<sup>§</sup>These authors contributed equally to this work.

#### Notes

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The authors declare no competing financial interests.

#### ACKNOWLEDGMENT

This work is supported by the Singapore Academic Research Fund (RG112/15 and RG19/16). We thank Dr. Steve Heald and Dr. Tianpin Wu from Argonne National Laboratory for helpful discussions.

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