



Short communication

# Efficient multicomponent synthesis of propargylamines catalyzed by copper nanoparticles supported on metal-organic framework derived nanoporous carbon



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## ABSTRACT

Cu nanoparticles were deposited on nanoporous carbon, MOF-5-C, which was fabricated by direct carbonization of MOF-5 without any additional carbon sources. The as-obtained catalyst (Cu@MOF-5-C) exhibited high catalytic activity due to the high surface area as well as hierarchical pores of MOF-5-C, and the synergetic interaction between the metal nanoparticles and support.

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## 1. Introduction

The challenge for green and sustainable development demands more efficient chemical transformation with no or less waste emission [1], so green chemistry based on the conception of atom economy has received considerable attention over the last few years. In this connection, lots of multicomponent reactions have been designed for the synthesis of various complex molecules, and these reactions have the fundamental advantages of minimizing chemical waste generation, lowering costs, increasing atom-economy, saving energy and time, and avoiding expensive purification processes [2–4]. The  $A^3$  coupling (the aldehyde-alkyne-amine reaction) is a typical example, where propargylamines are produced as the products [5,6].

Recently, propargylamines have gained considerable attention owing to their widely applications in drug discovery for the synthesis of various nitrogen-containing biologically active compounds, such as oxazoles,  $\beta$ -lactam, pyrrolidines [7–9]. Many methods including activation C–H bond of terminal alkynes using a wide range of metal-based (e.g. Cu, Ag, Au, Zn, etc.) catalysts have been developed for the synthesis of propargylamines over the last few years [10–12]. Unfortunately, in those systems, the homogenous catalysts are difficult to separate from the reaction products, which make the method not economical and environmentally attractive. In general, heterogeneous catalysts are

preferred due to easier recycling, which is crucial for cost effective industrial processes. Various types of heterogeneous catalysts (e.g. Au, Ag, Cu, etc.) have been developed in recent years for the synthesis of propargylamines [2,13–17]. Among the different metals, copper is considered as the most prominent and promising one for its versatility, low cost, and low toxicity [18]. Wang and co-workers have prepared an N-heterocyclic carbon silica supported complex with CuI for the synthesis of propargylamines [19]. Naeimi and co-workers have used MCM-41 silica to immobilize Cu metal for the synthesis of propargylamines [20]. Yang and co-workers prepared a new class heterogeneous IRMOF-3-GI-Cu catalyst by the covalent post-synthesis methodology and used to catalyze synthesis of propargylamines [21]. However, most of the supported catalysts involve some disadvantages such as tedious preparation of the catalyst, uneven distribution of the active sites, lower catalytic activity and so on. Therefore, exploring highly active and earth abundant non-noble metal-based heterogeneous catalysts for catalyzing  $A^3$  coupling reactions is highly desirable.

Very recently, using metal-organic-frameworks (MOFs) as sacrificial templates or precursors for the fabrication of porous carbon materials has gained particular attention [22]. MOF-derived porous carbon can be fabricated by direct carbonization of MOFs without any additional carbon sources, the organic ligands in the MOFs served as the carbon sources. The merits of MOF-derived porous carbon involve high specific surface area and porosity, diversified and tailorable porous structure, excellent thermal and chemical stability [23]. So MOF-derived porous carbons should be excellent supports or host for metal nanoparticles. The MOF-derived porous carbon materials have found widely

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applications in gas adsorbent [24], catalysis [25], energy storage [26], supercapacitors [27,28] and carriers for drug delivery systems [29]. However, the applications of MOFs-derived nanoporous carbons as catalyst carriers are still in its infancy. MOF-5 is a three-dimensional (3D) cubic porous framework with  $Zn_4O$ -clusters linked together through 1,4-benzenedicarboxylate-ligands [30], and it has large surface area, exceptional pore volume, relatively high thermal stability, which makes it a promising precursor or template to prepare porous carbon.

In this work, nanoporous carbon was fabricated by direct carbonization of MOF-5 in nitrogen atmosphere without any additional carbon sources. The Cu nanoparticles were supported on the as-obtained porous carbon (MOF-5-C) by an impregnation method. The fabricated catalyst (Cu@MOF-5-C) was used to catalyze the  $A^3$  coupling reactions of aldehydes, alkynes, and amines. To the best of our knowledge, this is the first report about the application of MOF-derived porous carbon as catalyst support in the multicomponent synthesis of propargylamines. Due to the well dispersed Cu nanoparticles, high surface area as well as hierarchical pores of the MOF-5-C, and the synergetic interaction between the metal nanoparticles and the support, the Cu@MOF-5-C exhibited excellent catalytic activity for the  $A^3$  coupling reactions of aldehydes, alkynes, and amines.

## 2. Experimental

### 2.1. General procedure for the one-pot synthesis of propargylamines

The aldehyde (1.0 mmol), amine (1.0 mmol), alkyne (1.2 mmol), 3 mL of toluene and Cu@MOF-5-C catalyst (20 mg) were put in a round-bottomed flask under nitrogen atmosphere and extensively stirred at 110 °C for a desired reaction time. The progress of the reaction was monitored by thin layer chromatography. After completion of the reaction, the solid catalyst was separated by centrifugation and the solvent was evaporated in a rotary evaporator. The crude product was subjected to column chromatography with petroleum ether/ethyl acetate (9:1) as the eluent to afford the desired propargylamines. The products were characterized by  $^1H$  NMR and all gave satisfactory results. The recovered catalyst was washed with acetone (5 mL  $\times$  3), dried in vacuum and stored for another consecutive reaction run.

## 3. Results and discussion

### 3.1. Characterization of the catalyst

The nitrogen adsorption–desorption experiments were performed to examine the surface areas and pore properties of MOF-5-C and Cu@MOF-5-C (Fig. S1). The MOF-5-C exhibits a type I isotherm, and it steeply increases at low relative pressure, revealing the dominating micropore characteristic (Fig. S1A). Meanwhile, the slight hysteresis of the desorption curves and the durative small slope increase of the adsorption capacity at medium relative pressures illustrate the presence of mesoporosity. And the final almost vertical increase at the relative pressures near 1.0 points to the presence of macroporosity. During the carbonization process, ZnO is formed and can be reduced by carbon via  $ZnO + C/Zn(g) + CO$  at 900 °C [31]. Zn formed in the reduction process can be partially evaporated and highly porous carbon with a hierarchical pore structure can be formed. The BET surface area, total pore volume and total adsorption average pore width of MOF-5-C were 2524 m<sup>2</sup> g<sup>-1</sup>, 2.96 cm<sup>3</sup> g<sup>-1</sup> and 4.69 nm, respectively. The large surface area and pore volume will offer more sites for active metal. As shown in Fig. S1B, the nitrogen adsorption desorption isotherm of Cu@MOF-5-C has similar characteristic with that of MOF-5-C, which demonstrated that the pore properties of MOF-5-C was mostly maintained in Cu@MOF-5-C catalyst. The BET surface area, total pore volume and total adsorption average pore width of Cu@MOF-5-C were 2039 m<sup>2</sup> g<sup>-1</sup>, 1.86 cm<sup>3</sup> g<sup>-1</sup> and 3.64 nm, respectively. The lower surface area and pore volume of Cu@MOF-5-C could be ascribed to the fact that a certain

amount of Cu nanoparticles were embedded in the surface and the pores of MOF-5-C during the fabrication process, the pore entrances were plugged by the Cu nanoparticles, and the differences in the mass fraction of porous MOF-5-C between MOF-5-C and Cu@MOF-5-C (the later containing non-porous Cu). Besides, the surface area of Cu@VXC72 and Cu@AC were 253 and 1800 m<sup>2</sup> g<sup>-1</sup>, respectively, which were lower than that of Cu@MOF-5-C. The copper content in Cu@MOF-5-C was determined by means of ICP-AES and amounted to 9.7 wt%. The SEM image of MOF-5-C was shown in Fig. 1A, from which hierarchical porosity structures can be seen. It can be clearly seen from Fig. 1B that Cu@MOF-5-C still remains the porosity structures. High specific surface area and porosity of MOF-5-C is favourable for efficient loading and well dispersing of Cu nanoparticles, which can greatly enhance the catalytic activity efficiently. The TEM of Cu@MOF-5-C (Fig. 1C) clearly shows that Cu nanoparticles were well dispersed on the surface of MOF-5-C and particle size of Cu nanoparticles was about 8–12 nm. Well-defined lattice fringes of Cu particles (Fig. 1D) are continuously extended to the whole particle, indicating its single crystalline nature.

The XRD pattern in Fig. S2A showed the crystalline structure of the MOF-5-C and the Cu@MOF-5-C samples. The three well defined peaks around 43°, 50° and 74° can be assigned to (111), (200) and (220) crystal planes of Cu, respectively. It is obvious that Cu basically existed in its zero oxidation state.

In order to determine the electronic state of the atom, Cu@MOF-5-C was analyzed by XPS (Fig. S2). Fig. S2B showed the survey spectra of the Cu-MOF-5-C, from which we can see that elemental Cu, Zn, O and C coexisted in the samples. The two peaks at 1021.8 and 1044.9 eV can be attributed to Zn2p<sub>3/2</sub> and Zn2p<sub>1/2</sub>, respectively (Fig. S2C), which were in good agreement with the values for zero-valent Zn and Zn<sup>2+</sup> in ZnO. The Cu2p peaks at 932.6 and 952.5 eV (Fig. S2D) can be attributed to the binding energy of Cu2p<sub>3/2</sub> and Cu2p<sub>1/2</sub>, respectively, which was in accord with the values of zero-valent Cu. The satellite peak at 942.9 eV is typically associated with copper in the bivalent binding energy state, which can be assigned to Cu<sup>2+</sup> in CuO species [32]. Based on the results of the XRD and XPS, it can be reasoned that Zn, ZnO, Cu and CuO coexisted in the Cu@MOF-5-C sample.

### 3.2. Three-component coupling reaction catalyzed by Cu@MOF-5-C

To evaluate the catalytic performance of the catalyst and optimize the reaction conditions, our investigation firstly focused on the effect of type of solvents on the model  $A^3$ -coupling reaction of benzaldehyde, phenylacetylene, and piperidine. The  $A^3$ -coupling reactions were carried out in chloroform, DMF, glycol, methanol and toluene, respectively, using Cu@MOF-5-C as catalyst at 110 °C. The results were summarized in Table 1. It is evident that chloroform, DMF and toluene are suitable reaction solvents for  $A^3$ -coupling reaction (Table 1, entries 1, 2 and 5), whereas glycol and methanol afforded lower yields (Table 1, entries 3 and 4). Although chloroform and DMF afforded good yields, they are high toxicity solvents. Therefore, all the  $A^3$ -coupling reactions were performed with toluene as solvent. The effects of reaction temperature on the model  $A^3$ -coupling reactions were also investigated. When the reactions were attempted at 50 °C and 80 °C, the yields are not as excellent as that at 110 °C (Table 1, entry 5). As a result, all the  $A^3$ -coupling reactions were performed at 110 °C in all the subsequent experiments. By increasing the reaction time from 2 h to 8 h, the catalytic performance can be significantly enhanced from 46% to 97%. So we chose 6 h as the suitable reaction time.

It was observed that only trace amount of product was obtained when the reaction was carried out at 110 °C in toluene for 6 h in the absence of catalyst (Table 1, entry 8), which indicated that the catalyst is absolutely necessary for this transformation. For comparison, nano copper was prepared according to the reported method [33] and used to catalyze the coupling reaction. The result showed that the yield was only 52% (Table 1, entry 9). Besides, only trace of product was observed

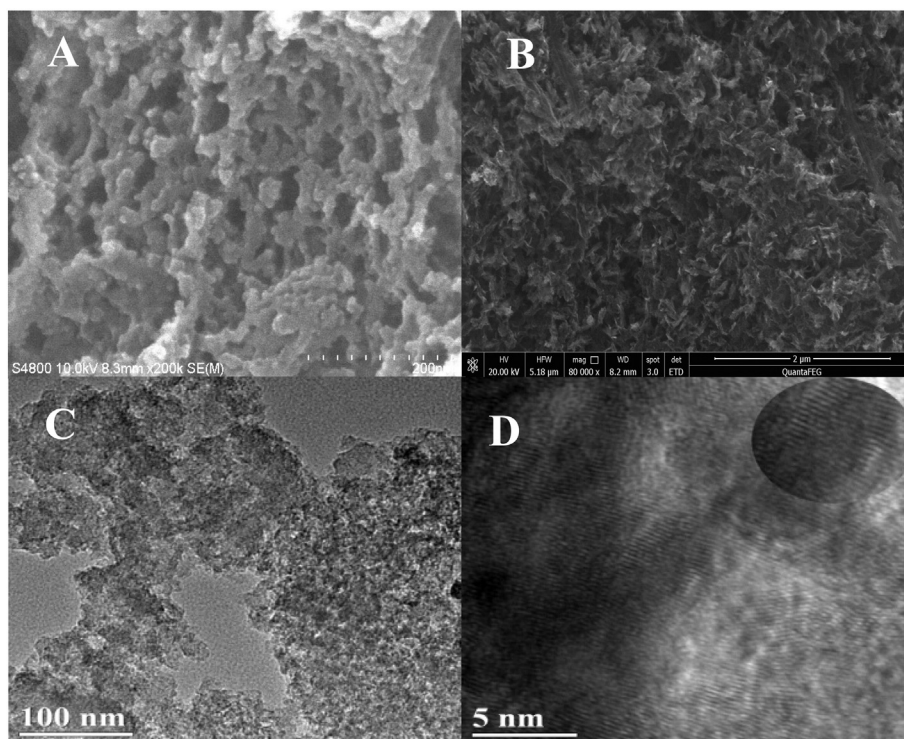


Fig. 1. The SEM images of MOF-5-C (A), Cu@MOF-5-C (B) and TEM of Cu@MOF-5-C (C, D).

using MOF-5-C as catalyst (Table 1, entry 10). The results also showed that under air conditions the product afforded only in very poor yields (Table 1, entry 11), which can be attributed to the fact that terminal alkynes can produce Glaser-type oxidative coupling products in the presence of copper salts and oxygen of air [34], so inert atmosphere is essential for protecting the reactive reagents from oxidation. Moreover, we observed that the yields were obviously affected by the dosage of

Table 1

Effect of temperature, inert atmosphere, catalyst dosage and reaction time on the  $A^3$ -coupling reactions.<sup>a</sup>

Entry	Solvents	Temperature(°C)	Catalyst dosage(mg)	Reaction time(h)	Yield <sup>b</sup> (%)
1	chloroform	110	20	6	78
2	DMF	110	20	6	71
3	glycol	110	20	6	47
4	methanol	110	20	6	57
5	toluene	110	20	6	96
6	toluene	50	20	6	18
7	toluene	80	20	6	70
8	toluene	110	0	6	trace
9	toluene	110	2	6	52 <sup>c</sup>
10	toluene	110	20	6	trace <sup>d</sup>
11	toluene	110	20	6	51 <sup>e</sup>
12	toluene	110	5	6	84
13	toluene	110	10	6	89
14	toluene	110	30	6	98
15	toluene	110	20	6	62 <sup>f</sup>
16	toluene	110	20	6	73 <sup>g</sup>
17	toluene	110	20	2	46
18	toluene	110	20	4	74
19	toluene	110	20	8	97
20	toluene	110	20	6	49 <sup>h</sup>

<sup>a</sup> Reaction conditions: benzaldehyde (1.0 mmol), piperidine (1.0 mmol), phenylacetylene (1.2 mmol), solvent (3 mL), Cu@MOF-5-C as catalyst, nitrogen, 6 h. <sup>b</sup> Isolated yield based on column chromatography. <sup>c</sup> nano copper as catalyst. <sup>d</sup> MOF-5-C as catalyst. <sup>e</sup> under air reaction conditions. <sup>f</sup> Cu@VXC72 as catalyst. <sup>g</sup> Cu@AC as catalyst. <sup>h</sup> The catalyst was removed after 2 h, the filtrate was stirred for another 4 h.

Cu@MOF-5-C. With increasing catalyst dosage from 5 mg to 20 mg, the yield of the product increased from 84% to 96% (Table 1, entries 12, 13 and 5). However, when the amount of the catalyst was larger than 20 mg, the yield of propargylamine no longer increased greatly (Table 1, entry 14). So 20 mg Cu@MOF-5-C was chosen as the optimal catalyst dosage. To confirm the role of hierarchical pores of MOF-5-C, commercial available active carbon with similar surface area with MOF-5-C and VXC72 carbon were used as the catalyst support. Compared with Cu@MOF-5-C catalyst, Cu@VXC72 and Cu@AC exhibited low catalytic activity (Table 1, entry 15, 16). The high catalytic activity of Cu@MOF-5-C can be ascribed to high surface area, hierarchical pores of MOF-5-C, and the synergetic interaction between the metal nanoparticles and support.

After optimizing the reaction conditions, the catalytic activity of Cu@MOF-5-C for the  $A^3$ -coupling reactions was further explored on different combinations of aldehydes and alkynes to examine the scope of the three-component coupling reactions. In this study, we used various electronically diverse aldehydes (e.g. benzaldehyde, isovaleraldehyde) and alkynes (phenylacetylene, cyclopropyl acetylene), and piperidine as the reactants. All reactions were performed with 20 mg Cu@MOF-5-C catalyst at 110 °C in toluene, and all the substrates produce the desired propargylamines with excellent yields. The results were depicted in Table 2.

The initial reaction set involved reacting benzaldehyde and piperidine with a variety of alkynes including 4-ethylphenylacetylene, 4-butylphenylacetylene, 3-methylphenylacetylene, 4-methoxyphenylacetylene, 4-chlorophenylacetylene and 4-fluorophenylacetylene. It is interested to note that the aromatic alkyne containing electron donating groups gave a slightly higher yield (entries 3, 4, 5, 7) than those containing electron withdrawing groups (entries 8, 9). It was observed that aliphatic alkyne (entry 6) also give well productiveness with correspondingly propargylamine derivatives. In addition, we explored our methodology for the synthesis of propargylamine derivatives by coupling phenylacetylene, piperidine with different aromatic aldehydes. In the case of aldehydes containing an electron donating

**Table 2**  
Three-component coupling of aldehyde, alkyne and amine for the synthesis of propargylamines.<sup>a</sup>

Entry	Alkyne	R <sup>1</sup> CHO	R <sup>2</sup> NHR <sup>3</sup>	Aldehydes	Amines	Products	Yield <sup>b</sup> (%)
1							96
2							76
3							87
4							97
5							99
6							75
7							96
8							85
9							76
10							92
11							93
12							89
13							99
14							98
15							90

<sup>a</sup> Reaction conditions: aldehyde (1.0 mmol), amine (1.0 mmol), alkyne (1.2 mmol), Cu@MOF-5-C catalyst: 20 mg, toluene: 3 mL, temperature: 110 °C, time: 6 h. protected by N<sub>2</sub>. <sup>b</sup> Isolated yield based on column chromatography.

group e.g. 2-methoxybenzaldehyde, 2-hydroxybenzaldehyde and 4-methylbenzaldehyde (entries 10, 11, 12), it was observed that they gave slightly lower yields compared with those aldehydes containing electron withdrawing groups (entry 13). A high yield was also obtained with the aliphatic aldehydes 3-methylbutanal (entry 14). Among the different amines studied, morpholine gave excellent yield (entry 15).

#### 4. Conclusion

In summary, we fabricated nanoporous carbon from a low-cost, facile and high porous MOF – 5, and it was served as the carrier material for copper nanoparticles. The obtained Cu@MOF-5-C showed excellent catalytic activity for the three-component coupling reaction, which

can be ascribed to high surface area, hierarchical pores of MOF-5-C, and the synergetic interaction between the metal nanoparticles and support. The present research might highlight the development of high catalytic activity heterogeneous catalysts by using MOF-derived porous carbon as hosts for ultrafine metal nanoparticles.

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# Electronic supplementary information (ESI) available: material and methods, preparation of Cu@MOF-5-C, the nitrogen adsorption-desorption isotherms and XRD pattern of the catalysts, the comparison with other reported catalyst and hot filtration test, the recyclability of the catalyst, a tentative reaction mechanism, and analytical data of the products.

### Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.catcom.2016.10.030>.

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