Contents lists available at SciVerse ScienceDirect

# ELSEVIER





journal homepage: www.elsevier.com/locate/catcom

#### Short Communication

## Postsynthetic modification of metal–organic framework as a highly efficient and recyclable catalyst for three-component (aldehyde–alkyne–amine) coupling reaction

### Jin Yang <sup>a</sup>, Pinhua Li <sup>a</sup>, Lei Wang <sup>a,b,\*</sup>

<sup>a</sup> Department of Chemistry, Huaibei Normal University, Huaibei, Anhui 235000, PR China

<sup>b</sup> State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, PR China

#### ARTICLE INFO

Article history: Received 9 May 2012 Received in revised form 16 June 2012 Accepted 19 June 2012 Available online 28 June 2012

#### Keywords: Cu(I)–MOF catalyst Metal–organic framework Postsynthetic modification Heterogeneous catalyst

#### 1. Introduction

Metal–organic frameworks (MOFs), are hybrid solids with infinite network structures building from organic bridging ligands and inorganic connecting points [1–3]. Due to possessing high porosity, MOFs have been constructed from designer building blocks to impart unique properties for a wide range of potential applications including nonlinear optics [4], gas storage [5–7], sensing [8], and catalysis [9–11].

In recent years, a series of porous metal–organic frameworks (MOFs) has aroused great interest for their potential application as heterogeneous catalysts. The uniformity of their pore and channel size account for much of their catalytic selectivity [12–14]. Yaghi's group firstly reported an amine-functionalized porous MOF, IRMOF-3, with a cubic structure having amino groups that do not take part in the formation of 3D framework structure [15], after that, a large number of successful attempts to chemically transform the free amine in IRMOF-3 through postsynthetic modification techniques have been reported [16–20]. Cohen's group initiated a systematic investigation on the postsynthetic modification of IRMOF-3 with linear alkyl anhydrides and cyclic anhydrides [21–24]. Furthermore, the postsynthetic modification of various porous MOFs, such as UMCM-1-NH<sub>2</sub> [25], DMOF-1-NH<sub>2</sub> [23,26],

#### ABSTRACT

A MOF-supported Cu(I) catalyst bearing *N*,*O*-chelating ligand was prepared through postsynthetic modification of IRMOF-3 and used as an efficient heterogeneous catalyst for three-component coupling reaction of aldehyde, alkyne, and amine. The catalyst exhibited both high catalytic activity and stability for the reaction and the framework of Cu(I) catalyst was mainly maintained after the catalyst was reused for four times.

© 2012 Elsevier B.V. All rights reserved.

UiO-66-NH<sub>2</sub> [27], and MIL-53(Al)-NH<sub>2</sub> [28] with anhydrides and other reagents were also investigated. Lin's group reported that the postsynthetic modifications of iron-carboxylate nanoscale metal-organic frameworks MIL-101(Fe)-NH<sub>2</sub> for imaging and drug delivery [29]. Rosseinsky's group developed the postsynthetic modification of a microporous MOF [Cu<sub>2</sub>(L-asp)<sub>2</sub>(bipy)]·(Guest) with HCl and that the as-synthesized material can afford Brönsted acid sites in the cavies [30,31]. Recent works have also revealed that chemical functionalization of MOFs by the postsynthetic modification technique can generate catalytically active sites effectively [32-37]. For instance, Lin's group pioneered the post-synthetic route to catalytically active 3D homochiral MOFs by utilizing orthogonal functionalities within the backbones of BINOL-derived bridging ligands, the dihydroxy substituents are not involved in coordinative interactions and are therefore accessible for further chemical functionalization. The MOF was treated with Ti(OiPr)<sub>4</sub>, a complex known to coordinate to BINOL and its derivatives to produce Lewis-acid catalysts [38]. Corma's group described the post-functionalization of IRMOF-3 with an Au(III) Schiff base complex, the novel MOF material showing high catalytic activity for the domino coupling and cyclization reactions [32]. Ahn's group described onestep post-functionalization of IRMOF-3 with Mn(acac)<sub>2</sub> complex and the resultant material can be used as a heterogeneous catalyst for the epoxidation of alkenes [33]. MOFs therefore appear to be excellent candidates for catalysis, with the understanding of their potential still largely in its infancy.

Herein, in a parallel approximation, a new modified IRMOF-3 with open metal sites was prepared by the covalent post-synthesis methodology and was selected as a new heterogeneous catalyst to demonstrate this new nanoporous material to be excellent candidate for catalysis.

<sup>\*</sup> Corresponding author at: Department of Chemistry, Huaibei Normal University, Huaibei, Anhui 235000, PR China. Tel.: + 86 561 3802 069; fax: + 86 561 3090 518. *E-mail address*: leiwang@chnu.edu.cn (L. Wang).

<sup>1566-7367/\$ –</sup> see front matter 0 2012 Elsevier B.V. All rights reserved. doi:10.1016/j.catcom.2012.06.023



Scheme 1. Post-synthesis modification procedure.

#### 2. Experimental

#### 2.1. General

The chemicals were purchased from commercial suppliers and were used without purification prior to use except where otherwise indicated. All <sup>1</sup>H and <sup>13</sup>C NMR were performed in CDCl<sub>3</sub> and recorded on a Bruker Avance 400 NMR spectrometer. IR were recorded with KBr pellets using Perkin-Elmer Instrument. Elemental analyses were performed on a Vario El III elementar. The Cu content was determined by a Jarrell-Ash 1100 ICP analysis. The elemental concentration distribution on the sample was verified by energy dispersive X-ray analysis (EDX, Horiba 7593H). X-ray powder diffraction patterns were recorded on a Rigaku diffractometer using CuK $\alpha$  ( $\lambda$  = 1.54 Å). Nitrogen adsorption/desorption isotherms were measured on a Micromeritics ASAP 2020 surface analyzer at -196 °C. Thermogravimetric analyses, in a range of 20– 800 °C, were carried out on a TGA (Scinco S-1000) system under a N<sub>2</sub> flow at a heating rate of 10.0 °C/min. Products were purified by flash chromatography on 200-300 mesh silica gel. SiO<sub>2</sub>, IRMOF-3 was prepared using a method previously reported in the literature [15,20]. Details of the synthesis and characterization of the catalyst were provided in the Supporting Information.

#### 3. Results and discussion

The starting material chosen for this investigation was IRMOF-3, which presented the free  $NH_2$  groups allows for easy covalent modification. Since *N*,*O*-bidentate ligand has proved to be a versatile ligand, the use of copper catalysts containing *N*,*O*-ligands is a very interesting strategy [39,40]. Herein glyoxal, a well-known ligand for binding a variety of transition metals in known coordination environment, was chose as ligand. The post-synthetic functionalization route for IRMOF-3 is shown in Scheme 1. IRMOF-3-GI was prepared by



Fig. 1. X-Ray powder patterns of IRMOF-3, IRMOF-3-Gl, and IRMOF-3-Gl-Cu.

dissolving glyoxal in acetonitrile and treating the resulting solution with freshly prepared IRMOF-3 at room temperature for 24 h. The obtained the solid was washed with acetonitrile sufficiently and dried under vacuum to remove the unreacted glyoxal. The functionalized IRMOF-3-Gl was then treated with Cul to generate the corresponding Cu(I)-containing catalyst material, IRMOF-3-Gl-Cu<sup>1</sup> [25,41,42]. The new MOF was full characterized by various techniques including powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA), nitrogen adsorption measurement, IR spectroscopy, and microanalysis (Supplementary Information for details). The PXRD patterns of both IRMOF-3 and modified IRMOF-3 show well-resolved identical peaks (Fig. 1), thus confirming that the original MOF framework structure was maintained with high phase purity even after the functionalization



Fig. 2. N<sub>2</sub> adsorption-desorption isotherm at 77 K.

with imine and ensuing coordination with the Cu(I). The thermal stability of the functionalized IRMOF-3-GI and IRMOF-3-GI-Cu<sup>I</sup> was studied by TGA (Fig. S1 in Supplementary Information). IRMOF-3-GI showed a gradual weight-loss step of 14.0% from room temperature to 165 °C, corresponding to partial loss of guest solvent species, and a second weight loss due to combustion of the organic part of the framework between 270 and 493 °C. IRMOF-3-GI-Cu<sup>I</sup> showed a gradual weight loss from room temperature to 165 °C, corresponding to the release of the guest solvent molecules and a major weight (ca. 47.4 wt.%) loss occurring at 292–477 °C due to the removal of the organic components. An important structural feature of the MOFs is that they possess nanoscale pores. The N<sub>2</sub> adsorption–desorption experiment was recorded in order to evaluate the porosity of the modified MOFs (IRMOF-3-Gl and IRMOF-3-Gl-Cu<sup>1</sup>) (Fig. 2). The experiment results show a decrease in BET surface area and pore volume of IRMOF-3-Gl to 764 m<sup>2</sup>·g<sup>-1</sup> and 0.65 cm<sup>3</sup>·g<sup>-1</sup> after IRMOF-3 was modified with glyoxal. Subsequently the coordination with the Cu(I) made the decrease in BET surface area and pore volume of IRMOF-3-Gl-Cu to  $642 \text{ m}^2 \cdot \text{g}^{-1}$  and 0.57 cm<sup>3</sup>·g<sup>-1</sup>. Similar results have been observed in MOF material after post-modification [37]. FTIR spectra of both IRMOF-3

#### Table 1

A<sup>3</sup>-coupling reaction catalyzed by IRMOF-3-GI-Cu<sup>a</sup>.

R <sup>1</sup> -=== + R <sup>2</sup> CHO	+ R <sub>3</sub> N <sub>R3</sub> IRMOF-3-GI-Cu CHCl <sub>3</sub>	$\begin{array}{c} R_1 & \longrightarrow \\ & & \\ &$			
Entry	Alkyne	Aldehyde	Amine	Yield <sup>b</sup> (%)	TON <sup>c</sup>
1	—=	(CH <sub>2</sub> 0) <sub>n</sub>		91	282
2		(CH <sub>2</sub> O) <sub>n</sub>	HNO	90	273
3		(CH <sub>2</sub> O) <sub>n</sub>	HN_N-	90	273
4	—=	(CH <sub>2</sub> O) <sub>n</sub>	HN	91	282
5	—=	(CH <sub>2</sub> O) <sub>n</sub>		88	267
6	—=	(CH <sub>2</sub> O) <sub>n</sub>		87	264
7	—=	СНО	HN	90	273
8 <sup>d</sup>		СНО	HN	74	224
9 <sup>d</sup>	—=	СНО	HN	76	230
10 <sup>d</sup>		С—сно	HN	80	242
11		СНО	HNO	82	248
12	 	СНО		84	255
13		(CH <sub>2</sub> O) <sub>n</sub>		87	264
14	Ph-	(CH <sub>2</sub> O) <sub>n</sub>	HN	85	258
15	ci–	(CH <sub>2</sub> O) <sub>n</sub>	HN	84	255
16	>=	(CH <sub>2</sub> O) <sub>n</sub>	HN	82	248

<sup>a</sup> Reaction conditions: aldehyde (1.0 mmol), amine (1.1 mmol), alkyne (1.2 mmol), IRMOF-3-Gl-Cu (20 mg, 0.0033 mmol) at 40 °C for 6 h.

<sup>b</sup> Isolated yields.

<sup>c</sup> Mol of aldehyde converted/mol of catalyst.

 $^{\rm d}\,$  At 40 °C for 12 h.

and post-modified MOFs exhibited intense bands at 1570 cm<sup>-1</sup>, due to the presence of the original amino group in the pores. The spectra of the functionalized MOFs exhibited a new band at 1625 cm<sup>-1</sup>, which may be attributed to vibration of the generated imine bond (Fig. S2 in Supplementary Information). The exact composition of IRMOF-3-Gl-Cu was determined by combined elemental analysis, TGA, EDX and ICP analyses. The crystallized particles of IRMOF-3-Gl-Cu revealed by EDX mainly consist of Zn, along with a small amount of Cu and the Zn:Cu ratio appears to be 20:1 (Fig. S3 in Supplementary Information). ICP analysis indicated that the coordination with Cul led to a weight loading of 1.05 wt.% (0.16 mmol·g<sup>-1</sup>) Cu in IRMOF-3-Gl-Cu<sup>1</sup>, corresponding to 4.7% of the  $- NH_2$  groups has been functionalized. Elemental analysis of the modified MOFs revealed that about 4.3% of the  $- NH_2$  groups has been functionalized.

The new class of heterogeneous IRMOF-3-Gl-Cu catalyst should then be of catalytic interest due to the presence of well-defined Cu(I) stable active site. Three-component coupling reaction of aldehyde, alkyne, and amine (A<sup>3</sup>-coupling) is one of the most useful reactions in organic synthesis [43,44], various highly efficient A<sup>3</sup>-couplings catalyzed by transition catalysts under homogeneous and heterogeneous reaction conditions have been reported [45–48]. More recently, Corma's group has reported Cu-MOFs as solid catalysts for three-component coupling reaction [49]. Herein, the A<sup>3</sup>-coupling reaction was investigated in presence of IRMOF-3-Gl-Cu<sup>1</sup> catalyst. The MOF catalyst was first employed in the A<sup>3</sup>-coupling of *para*-formaldehyde, phenylacetylene, and piperidine as standard substrates to optimize the reaction conditions. Among the solvents tested, CH<sub>3</sub>CN, CHCl<sub>3</sub>, and CH<sub>2</sub>Cl<sub>2</sub> were the most suitable reaction media for the reaction. The reaction of phenylacetylene with para-formaldehyde and piperidine in chloroform afforded the product in 91% yield (Table 1, entry 1). The effects of reaction temperature and time were also investigated and it was found that most of the reaction was accomplished at 40 °C for 6 h. To examine the scope of the reaction, the combinations of various aldehydes, alkynes, and amines were studied. At the beginning of the search for amine substrate scope, paraformaldehyde and phenylacetylene were used as the model substrates and various amines were examined. The results indicated that secondary aliphatic amines gave high yields of the desired products (Table 1, entries 1-6). To the aldehyde substrates, aliphatic aldehydes, including cyclic and acyclic ones, displayed good reactivity. Although the reactivity is a little lower when changing *para*-formaldehyde to butyraldehyde, iso-pentaldehyde or cyclohexanecarbaldehyde, good yields can still be obtained through prolonging the reaction time (Table 1, entries 7–10). In addition, the combination of phenylacetylene and iso-butylaldehyde with various amines also gave good yields (Table 1, entries 11 and 12). Subsequently, the aromatic alkynes substrates were examined. Aromatic alkynes, including those bearing functional groups, such as methyl, phenyl, and chloro were able to undergo the coupling reaction smoothly and generate the corresponding products in excellent yields (Table 1, entries 13–15). Furthermore, the reactions involving heterocyclic alkyne also gave higher yield (Table 1, entry 16).

In order to investigate the heterogeneity of the IRMOF-3-Gl-Cu<sup>I</sup> catalyst, the hot filtration experiment was performed. The organic phase was separated from the solid catalyst after 1 h reaction time by filtration. The reaction solution was then transferred to a new reactor vessel and stirred for an additional 5 h at 40 °C. However, no further reaction was observed in the absence of solid, proving that there was no contribution from leached active species and that conversion was only being possible in the presence of the solid catalyst (Fig. S4 in Supplementary Information). Furthermore, to confirm the coordination of the IRMOF-3-Gl with Cu(I) and not just the adsorbate interaction, the control reaction between the unmodified IRMOF-3 with Cu(I) was also performed [25]. The CuI and IRMOF-3 were immersed in CH<sub>3</sub>CN for 3 h, and then the solid was collected by filtration, washed with CH<sub>3</sub>CN sufficiently, and dried in vacuum. However, under the same reaction conditions, the accepted material showed low catalytic activity for the A<sup>3</sup>-coupling reaction with about 21% conversion. On the other hand, copper leaching in IRMOF-3-Gl-Cu catalyst was determined. ICP analysis of the clear filtrates obtained by filtration after the reaction indicated that Cu content is less than 0.5 ppm. Hence it can be concluded that the process is truly heterogeneous.

Another point of great concern for solid catalysts is the reusability. IRMOF-3-Gl-Cu<sup>1</sup> was therefore investigated for recoverability and reusability for A<sup>3</sup>-coupling reaction of *para*-formaldehyde, phenylacetylene, and piperidine. After carrying out the reaction, the catalyst was separated by centrifugalization and washed with CHCl<sub>3</sub> (2 mL×2) to remove any physic-sorbed reagents. After air-dried, the recovered IRMOF-3-Gl-Cu could be reused directly in further reaction. The temporal evolution of the conversion at different time intervals was analyzed by GC. It was found that the IRMOF-3-Gl-Cu<sup>1</sup> could be recovered and reused over 4 consecutive cycles. It was observed that more than 82% conversion was still achieved at the fourth run (Fig. 3). Furthermore, the PXRD showed that the original MOF framework structure was mainly maintained after the consecutive uses (Fig. S5 in Supplementary Information).

#### 4. Conclusions

In conclusion, an efficient heterogeneous MOF-supported Cu(1) catalyst based on post-synthesis strategy has been prepared and applied



Fig. 3. Catalyst recycling studies.

for the A<sup>3</sup>-coupling reaction. Good yields were achieved under mild conditions. It is apparent that the use of MOFs as catalyst supports might bring new opportunities in the development of highly active heterogeneous catalysts.

#### Acknowledgements

We gratefully acknowledge financial support by the National Natural Science Foundation of China (No. 20972057), the Natural Science Foundation of Anhui Province (No. 090416223).

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at http:// dx.doi.org/10.1016/j.catcom.2012.06.023.

#### References

- [1] M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, O.M. Yaghi, Science 295 (2002) 469.
- S. Kitagawa, R. Kitaura, S. Noro, Angewandte Chemie International Edition 43 (2004) 2334
- [3] O.M. Yaghi, M. O'Keeffe, N.W. Ockwig, H.K. Chae, M. Eddaoudi, J. Kim, Nature 423 (2003) 705.
- [4] O.R. Evans, W. Lin, Accounts of Chemical Research 35 (2002) 511.
- [5] J.L.C. Rowsell, A.R. Millward, K.S. Park, O.M. Yaghi, Journal of the American Chemical Society 126 (2004) 5666.
- [6] J.L.C. Rowsell, O.M. Yaghi, Angewandte Chemie International Edition 44 (2005) 4670
- [7] A.G. Wong-Foy, A.J. Matzger, O.M. Yaghi, Journal of the American Chemical Society 128 (2006) 3494.
- B.L. Chen, L.B. Wang, F. Zapata, G.D. Qian, E.B. Lobkovsky, Journal of the American [8] Chemical Society 130 (2008) 6718.
- A. Corma, H. García, F.X. Llabrés i Xamena, Chemical Reviews 110 (2010) 4606.
- [10] A. Dhakshinamoorthy, M. Alvaro, H. Garcia, ACS Catalysis 1 (2011) 48.
- [11] U.P.N. Tran, K.K.A. Le, N.T.S. Phan, ACS Catal. 1 (2011) 120.
- [12] D. Farrusseng, S. Aguado, C. Pinel, Angewandte Chemie International Edition 48 (2009) 2.
- [13] J. Lee, O.K. Farha, J. Roberts, K.A. Scheidt, S.T. Nguyen, J.T. Hupp, Chemical Society Reviews 38 (2009) 1450.
- L. Ma, C. Abney, W. Lin, Chemical Society Reviews 38 (2009) 1248. [14]
- [15] J.L.C. Rowsell, O.M. Yaghi, Journal of the American Chemical Society 128 (2006) 1304.
- [16] K.K. Tanabe, S.M. Cohen, Chemical Society Reviews 40 (2011) 498.

- [17] Z. Wang, S.M. Cohen, Chemical Society Reviews 38 (2009) 1315.
- [18] S.M. Cohen, Chemical Science 1 (2010) 32. [19] S.M. Cohen, Chemical Reviews 112 (2012) 970.
- [20] K.K. Tanabe, Z. Wang, S.M. Cohen, Journal of the American Chemical Society 130 (2008) 8508 [21] Z. Wang, S.M. Cohen, Journal of the American Chemical Society 129 (2007) 12368.
- [22] E. Dugan, Z. Wang, M. Okamura, A. Medina, S.M. Cohen, Chemical Communications (2008) 3366.
- [23] Z. Wang, K.K. Tanabe, S.M. Cohen, Inorganic Chemistry 48 (2009) 296
- [24] Z. Wang, S.M. Cohen, Angewandte Chemie International Edition 47 (2008) 4699.
- [25] K.K. Tanabe, S.M. Cohen, Inorganic Chemistry 49 (2010) 6766.
- [26] Z. Wang, S.M. Cohen, Journal of the American Chemical Society 131 (2009) 16675.
- [27] S.J. Garibay, S.M. Cohen, Chemical Communications 46 (2010) 7700.
- [28] S.J. Garibay, Z. Wang, S.M. Cohen, Inorganic Chemistry 49 (2010) 8086.
- [29] K.M.L. Taylor-Pashow, J.D. Rocca, Z. Xie, S. Tran, W. Lin, Journal of the American Chemical Society 131 (2009) 14261.
- [30] R. Vaidhyanathan, D. Bradshaw, J.N. Rebilly, J.P. Barrio, J.A. Gould, N.G. Berry, M.I. Rosseinsky, Angewandte Chemie International Edition 45 (2006) 6495.
- [31] M.J. Ingleson, J.P. Barrio, J. Bacsa, C. Dickinson, H. Park, M.J. Rosseinsky, Chemical Communications (2008) 1287.
- X. Zhang, F.X. Llabrés i Xamena, A. Corma, Journal of Catalysis 265 (2009) 155. [32]
- [33] S. Bhattacharjee, D.-A. Yang, W.-S. Ahn, Chemical Communications 47 (2011)
- 3637 [34] M. Savonnet, E. Kockrick, A. Camarata, D. Bazer-Bachi, N. Bats, V. Lecocq, C. Pinel, D. Farrusseng, New Journal of Chemistry 35 (2011) 1892.
- [35] D.J. Lun, G.I.N. Waterhouse, S.G. Telfer, Journal of the American Chemical Society 133 (2011) 5806.
- [36] M.J. Ingleson, J.P. Barrio, J.B. Guilbaud, Y.Z. Khimyak, M.J. Rosseinsky, Chemical Communications 44 (2008) 2680.
- [37] M. Savonnet, S. Aguado, U. Ravon, D. Bazer-Bachi, V. Lecocq, N. Bats, C. Pinel, D. Farrusseng, Green Chemistry 11 (2009) 1729.
- [38] C.D. Wu, A. Hu, L. Zhang, W. Lin, Journal of the American Chemical Society 127 (2005) 8940.
- [39] Y.-J. Jin, D.-H. Lee, Angewandte Chemie International Edition 49 (2010) 1119.
- [40] W. Yang, C. Liu, J. Qiu, Chemical Communications 46 (2010) 2659.
- [41] K.K. Tanabe, S.M. Cohen, Angewandte Chemie International Edition 48 (2009) 7424
- [42] C.J. Doonan, W. Morris, H. Furukawa, O.M. Yaghi, Journal of the American Chemical Society 131 (2009) 9492.
- [43] C.-J. Li, Accounts of Chemical Research 35 (2002) 533.
- C. Wei, J.T. Mague, C.J. Li, Proceedings of the National Academy of Sciences 101 [44] (2004) 5749.
- [45] P. Li, Y. Zhang, L. Wang, Chemistry A European Journal 15 (2009) 2045.
- Y. Zhang, P. Li, M. Wang, L. Wang, Journal of Organic Chemistry 74 (2009) 4364. [46]
- [47] P. Li, L. Wang, Tetrahedron 63 (2009) 5455.
- [48] M. Wang, P. Li, L. Wang, European Journal of Organic Chemistry 13 (2008) 2255.
- [49] I. Luz, F.X.L. Xamena, A. Corma, Journal of Catalysis 285 (2012) 285.