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Inorganic Chemistry Communications

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

Feature article

Two-dimensional copper-based metal–organic framework as a robust heterogeneous catalyst for the *N*-arylation of imidazole with arylboronic acids

many cycles without loss of catalytic activity.

N-arylation of imidazole was accomplished with a two-dimensional (2D) $[Cu(ima)_2]_n$ metal–organic frame-

work in methanol at room temperature. A variety of N-arylimidazoles were isolated in good yields after a

short reaction time. Moreover, the robust MOF may be readily recovered after the reaction and reused for

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ARTICLE INFO

ABSTRACT

Article history: Received 7 September 2012 Accepted 21 October 2012 Available online 2 November 2012

Keywords: N-arylation Imidazole Arylboronic acids Metal-organic framework

Contents

Acknowledgments 121 References 121

N-arylimidazoles are important organic compounds due to their significant pharmaceutical, biological, and chemical activities [1–5]. During the past few years, homogeneous copper-catalyzed cross-coupling reactions of imidazole and commercially widely-available arylboronic acids are facile methods available for the construction of *N*-arylimidazoles [6–10]. However, homogeneous processes easily suffer from the problems concerning separation and recovery, disposal of spent catalysts, and therefore their uses are greatly limited. In principle, the use of heterogeneous catalysts could overcome some of these drawbacks mentioned above. Thus, the practical applications have greatly driven the need for the development of recyclable and efficient heterogeneous copper catalysts. In this regard, heterogeneous copper catalysts exhibit particularly promising performances for the reaction [11,12].

In recent years, metal–organic frameworks (MOFs) have received a great deal of attention owing to their many potential applications in gas storage, separation, magnetism, luminescence, catalysis, sensor technology and optoelectronics [13–17]. However, the metal ions are integral parts of the framework in many MOF structures, and therefore all of the coordination sites around the metal centers are occupied by organic ligands, leaving no free coordination positions available for substrates in organic reaction. So far, only a few examples of MOFs containing coordinatively unsaturated metal ions for heterogeneous catalysis have been investigated in comparison with a large numbers of being discovered MOFs. Moreover, most works focused on organic transformations such as Knoevenagel condensation, cyanosilylation, oxidation, aldol condensation, Michael condensation, Friedel–Crafts alkylation, and Biginelli reaction [18–29]. Indeed, reports on heterogeneous *N*-arylation of imidazole using Cu-MOF catalysts are very limited in the literature [12].

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It is well known that the main drawbacks of MOFs as heterogeneous catalysts compared to traditional catalysts are their chemical stabilities and lower reaction activities. Therefore, explore stable and efficient heterogeneous catalysts become particularly desirable for the improvement in catalytic performance. As a part of our ongoing research on heterogeneous cross-coupling reactions [30], we report the facile *N*-arylation of imidazole catalyzed by a robust twodimensional (2D) Cu-MOF catalyst (Fig. 1) at room temperature. The catalyst exhibits high catalytic activity in a short reaction time and may be readily recovered after the reaction and reused for many cycles without loss of catalytic activity.



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Fig. 1. Crystal structure of the 2D Cu-MOF exhibiting four-coordinate Cu^{2+} centers.

2D Cu-MOF catalyst was prepared using a modified literature procedure and structural description of the Cu-MOF was outlined elsewhere [31]. In brief, the local coordination environment around the Cu^{2+} ion shows that each four-coordinate Cu^{2+} center is in a square-planar geometry formed by two identical monodentate carboxylate groups and two imidazole nitrogen atoms with axial positions left uncoordinated. Each ima ligand uses both the carboxylate oxygen and imidazole nitrogen atoms to bridge two Cu²⁺ ions, furnishing a (4, 4) 2D wavelike rhombic layer. Adjacent 2D layers are packed according to the ABAB sequence along the b-axis by weak intermolecular C-H-O hydrogen bonding, which caused no open channel or cavity in the 2D Cu-MOF. It should be noted, Cu²⁺ center is in a distorted square-planar geometry and the axial positions are vacant, so the exposed Cu^{2+} centers are chemically accessible. Furthermore, the robust Cu-MOF is air-stable and possesses good thermal stability up to 285 °C [30]. These interesting structural features promoted us to study catalytic activity of the Cu-MOF. In initial study, imidazole and phenylboronic acid were chosen as two model substrates using the Cu-MOF as a catalyst in methanol at room temperature. As shown in Table 1 [32], the 2D Cu-MOF afforded a very good yield (Table 1, entry 1). For comparison, we also made a survey of the effect of different homogeneous copper salts and found Cul, CuBr. CuSO₄ \cdot 5H₂O and Cu(OAc)₂ \cdot 2H₂O gave very low yield under identical conditions (Table 1, entries 2–5). Moreover, the controlled N-arylation reaction conducted under identical conditions devoid of Cu-MOF gave no coupled product despite prolonged reaction time (Table 1, entry 6). In addition, the coupling reactions display substantially reduced reaction times compared with literature reports (5 h in contrast to 12-24 h) [3,12].

With these promising results, we subjected other substrates to the reaction system in order to study the scope of the reaction (Table 2). Similar results were obtained when different substituted phenylboronic acids were used as arylating agent. It should be noted that electron-poor to electron-rich arylboronic acids were tolerated, with the more

Table 1

Different copper catalysts catalyzed N-arylation of imidazole and phenylboronic acid.^a



| Entry | Catalyst | Time (h) | Yield (%) ^b |
|-------|--------------------------------------|----------|------------------------|
| 1 | 2D Cu-MOF | 5 | 86 |
| 2 | CuI | 5 | 25 |
| 3 | CuBr | 5 | 27 |
| 4 | CuSO ₄ ·5H ₂ O | 5 | 14 |
| 5 | $Cu(OAc)_2 \cdot 2H_2O$ | 5 | 17 |
| 6 | None | 12 | 0 |

^a Reaction conditions: phenylboronic acid (1.0 mmol), imidazole (1.2 mmol), methanol (3 mL), and catalyst (5 mol%), under air.

^b Isolated yields.

electron-rich substrates demonstrating higher isolated yields (Table 2, entries 2 and 3). Slightly lower but acceptable yields were achieved with ortho-substituted and electron-poor arylboronic acids (Table 2, entries 4–6).

For practical application in the reaction, the lifetime of the MOF-Cu catalyst and its reusability are very important factors. This catalyst is not soluble in the reaction mixture and the reaction system is heterogeneous unlike other homogeneous processes. After the reaction, the Cu-MOF catalyst was easily recovered quantitatively from the catalytic solution by simple filtration and reused several times with consistent activity even after the fourth cycle (Table 2). The liquid phase of the reaction mixture was collected by hot-filtration and analyzed by ICP-AES. The absence of copper in the filtrate was confirmed (0.05 ppm), indicating no leaching of copper during the reaction. Moreover, a filtration experiment was also run to investigate whether the reaction proceeded in a heterogeneous or homogeneous fashion. After 30 min of the N-arylation between imidazole and phenylboronic acid, the solid catalyst was separated by filtration and the filtrate was further performed for another 5 h and no further conversion of the reactants into products was thus observed. These results suggested that the reaction may take place on the catalyst surface in a heterogeneous fashion.

To better verify the stability of the Cu-MOF catalyst, the powder X-ray diffraction (PXRD) pattern of the recovered Cu-MOF catalyst after the fifth recycling experiment was obtained. The pattern indicated that the framework was very robust and exhibited a very similar diffraction pattern of the fresh catalyst (Fig. 2). In addition, we employed the as-prepared Cu-MOF as a catalyst without any prior treatment and the catalyst is quite stable in the solid state in air for a prolonged period of time.

In summary, we have developed a simple and efficient heterogeneous 2D Cu-MOF catalyst system for the *N*-arylation of imidazole under mild conditions, in which unsaturatedly coordinated Cu ions

Table 2

Recyclable N-arylation of imidazole with arylboronic acids.^a



| Entry | R | (Cycle) Yield (%) ^b | |
|-------|--------------------|--------------------------------|--------|
| 1 | Н | (1) 90 | (5) 89 |
| 2 | 4-CH ₃ | (1) 92 | (2) 89 |
| 3 | 4-OCH ₃ | (1) 90 | (2) 91 |
| 4 | 4-F | (1) 76 | (2) 71 |
| 5 | 4-CF ₃ | (1) 88 | (2) 85 |
| 6 | 2-CH ₃ | (1) 78 | (2) 67 |

 $^{\rm a}\,$ Reaction conditions: arylboronic acids (1.0 mmol), imidazole (1.2 mmol), and methanol (3 mL), 5 h, under air.

^b Isolated yields.



Fig. 2. PXRD patterns for the simulation from X-ray crystallography (a), as-prepared Cu-MOF catalyst (b), and the retrieved Cu-MOF after fifth recycling experiment of *N*-arylation between imidazole and phenylboronic acid (c).

serve as catalytic centers. The readily available catalyst has high stability and may be easily reused without loss of reactivity.

Acknowledgments

We thank the Natural Science Foundation of China (no. 21172105), and the Foundation of the Education Department of Henan Province (no. 2011A150021) for the financial support. Great thanks to Prof. W.-P. Su and Dr. J. Kan in FJIRSM for earnestly helping.

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 - (b) Synthetic procedure and characterization data for Cu-MOF catalyst. A mixture of Sm_2O_3 (0.088 g, 0.25 mmol), $CuSO_4$ ·5H₂O (0.1248 g, 0.5 mmol), and Hima (0.1250 g, 1 mmol) were added to deionized water (8.0 mL). The mixture was added to a 23 mL Teflon-lined autoclave and kept under autogenous pressure at 443 K for five days and then cooling to room temperature at a rate of 5 Kh⁻¹. Purple block-like crystals could be isolated in ca. 82% yield (based on Cu). Anal. calcd for C₁₀H₁₀CuN₄O₄· C, 38.3; H, 3.2; N, 17.8. Found: C, 39.0; H, 3.4; N, 18.6. IR data (KBr, cm⁻¹): 3159vs, 3132vs, 2985m, 2948m, 1634vs, 1532m, 1358m, 1309vs, 1239m, 1218m, 1096vs, 1046m, 989m, 962m, 932m, 868m, 793m, 749vs, 701vs, 658m, 624m, 599m, 537m.
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