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A Reusable MOF Supported Single-Site Zinc(II) Catalyst for Efficient Intramolecular Hydroamination of *o*-Alkynylanilines

Beibei Li,^[a,b] Zhanfeng Ju,^[a] Mi Zhou,^[a] Kongzhao Su,^[a,b] and Daqiang Yuan*^[a,b]

Abstract: The exploitation of new and active earth-abundant metal catalysts is critical for sustainable chemical production. Herein, we demonstrate the design of highly efficient, robust, and reusable Zn(II)-bipyridine-based metal-organic framework (MOF) catalysts for the intramolecular hydroamination of *o*-alkynylanilines to indoles. Similar conditions in a homogeneous catalytic system mainly provide hydrolysate. This result can prove that MOFs support unique internal environments that can affect the direction of chemical reactions. The Zn(II)-catalyzed hydroamination reaction can be conducted without additional ligands, base or acid, and is thus a very clean reaction system which is mild with respect to the natural environment.

Metal-organic frameworks (MOFs), a new emerging class of crystalline porous materials, assembled of metal ions or clusters and organic ligands by means of coordination bonds, have attracted increasing interest mainly as a result of their high degree of crystallinity and surface area, well-defined pore structure, and adjustable pore size.^[1] The advantages of low density and a tunable local environment, facilitating massdiffusion^[2] have led MOFs to diverse applications, including catalysis and biomimetics,^[3] gas sorption and separation,^[4] luminescence,^[5] chemical sensors,^[6] and others.^[7] To actually reduce energy emission and consumption, a single-site solid catalyst affords high selectivity and maximum atom efficiency and has been shown to have great potential, as a new member of the catalyst community.^[8] However, isolated metal sites possess the drawbacks of high surface energy, uneven dispersion and poor thermodynamic stability during the construction process, and these are still great challenges. MOFs, with defined crystal structures, uniform pores, high surface area and the periodically dispersed active sites,^[9] are a promising platform of single-site catalysts.

Indole moieties, commonly found in many natural products, play a prominent role in biological and pharmaceutical areas.^[10] The economical and efficient formation of indole skeletons is of great concern in chemical synthesis. The cyclization of *o*-alkynylanilines and their derivatives provides one of the most simple, direct and atom-economical methods with which to assemble indoles.^[11] In the field of both homogeneous and heterogeneous catalysis, chemists have devoted themselves to studying the diverse catalysts which facilitate the assembly of

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indole skeletons.^[11b, 12] Among the various catalytic syntheses, heterocyclization of o-alkynylanilines through heterogeneous metal-based catalysts is considered to be one of the most efficient approaches.^[11a] However, most heterogeneous metalbased catalysts involve noble metals, such as Au,^[13] Ag^[14] or Pt^[15] (Scheme 1a).^[16] Hence, the development of single-site nonnoble metals as the heterogeneous catalysts of heterocyclization is indispensable, because a) use of non-noble metals can lower the cost; b) single-site metals have unsaturated coordinated sites which can access reactions more easily;^[8b] c) heterogeneous single-site catalysts combine the merits of homogeneous and heterogeneous catalysts;^[8a] and d) they can be readily separated, recycled and reused. Inspired by these facts, we have synthesized isolated non-noble metal sites supported on metal-organic frameworks as hydroamination catalysts.

a) Previous methods for the intramolecular hydroamination of o-alkynylanilines





Zn-UiO-67-BP

Scheme 1. a) Previous hydroamination methods and b) the proposed MOF supported single-site zinc catalyst for intramolecular hydroamination of *o*-alkynylanilines.

In this work, a strategy of postsynthetic functionalization (PSF) was used to synthesize MOF supported single-site Zn(II) catalyst. Zirconium-based MOFs (UiO series) with the advantages of porosity, stability, adjustability have been regarded as an excellent niche in heterogeneous catalysis.[17] Initially, UiO-67-BPY was synthesized via the solvothermal reaction of ZrCl₄ and 2,2'-bipyridine-5,5'-dicarboxylic acid $(H_2 \text{BPY})$ in the circumstance of benzoic acid and $\text{DMF},^{[18]}$ then the postsynthetic metalation was carried out by impregnation (Scheme 1b). UiO-67-BPY was treated with 1.0 equiv of Zn(BF₄)₂•xH₂O in DMF to afford Zn-UiO-67-BPY as a white powder. The purity of UiO-67-BPY and the crystallinity of Zn-UiO-67-BPY were proved by their PXRD patterns that match well with simulated patterns^[19] (Figure 1a). Inductively coupled plasma (ICP) and element analyses of the digested Zn-UiO-67-BPY provided that Zn loading of 2.26 wt%, which corresponded

to 0.35 mmol/g, while the contents of Zr and N were 17.41 wt% and 6.06 wt%, respectively. Hence, the molar ratio of Zr/N/Zn was 5.6:12.3:1, which is in approximate accord with $Zr_6O_4(OH)_4(BPY)_5[BPYZn(BF_4)_2]$, the presumed formulation. Nitrogen adsorption measurements revealed that Zn-UiO-67-BPY has a reduced adsorbed quantity (443 cm³/g), a BET surface area (1482 m²/g) and pore sizes (Figure 1b and inset plot). The decrease of pore volumes, surface area, and pore sizes was consistent with Zn(II) cations and associated counterions in MOF linkers.



Figure 1. (a) PXRD patterns of simulated UiO-67-BPY (black), pristine UiO-67-BPY (red), fresh Zn-UiO-67-BPY (blue), Zn-UiO-67-BPY recovered from hydroamination after one cycle (purple) and five cycles (green). (b) N₂ sorption isotherms for UiO-67-BPY (red) and Zn-UiO-67-BPY (blue) at 77 K. Inset: Pore size distribution of UiO-67-BPY (red) and Zn-UiO-67-BPY (blue). (c) XPS spectrum of the Zn 2p region for Zn-UiO-67-BPY. (d) XPS spectra of the N 1s region for UiO-67-BPY and Zn-UiO-67-BPY, respectively.

The X-ray photoelectron spectroscopy (XPS) characterizations were conducted to verify the invariable valence state of Zn(II) and coordination between Zn(II) and UiO-67-BPY. As displayed in the Supplementary Information (SI) Figure S2, the XPS survey spectra of UiO-67-BPY before and after impregnation of Zn(BF₄)₂·xH₂O solution revealed the existence of Zn and F, which signified the successful insertion into the UiO-67-BPY framework of Zn and the BF4⁻ anions as counter ions. The XPS spectrum of Zn 2p for Zn-UiO-67-BPY is shown in Figure 1c. Two main peaks of binding energies located at 1021.6 and 1044.7 eV correspond to Zn $2p_{3/2}$ and Zn $2p_{1/2}$ of Zn-UiO-67-BPY, respectively, demonstrating that the valence state of Zn element in Zn-UiO-67-BPY could be divalent Zn(II),[20] which was further verified by X-ray absorption near-edge structure (XANES) spectra (Figure 2c). As shown in Figure 1d, the binding energy of N 1s in UiO-67-BPY is 398.3 eV, which was attributed to the nitrogen in BPY.^[21] In Zn-UiO-67-BPY there were two N 1s peaks of binding energies at 398.3 and 399.3 eV, implying that nitrogen atoms presented two types of coordination environments. One peak was analogous to that of BPY, while another shifted to a higher value, which could signify the coordination between Zn(II) and some of the uncoordinated BPY units in UiO-67-BPY framework.



Figure 2. (a) The SEM image (scale bar: 3 µm) of Zn-UiO-67-BPY. (b) The aberration-corrected HAADF-STEM (scale bar: 2 nm) image of Zn-UiO-67-BPY. (c) Zn K-edge XANES spectra. (d) κ^2 -weighted Fourier transform of Zn K-edge EXAFS spectra, and the corresponding EXAFS fitting curve for Zn-UiO-67-BPY (black circles).

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images showed that Zn-UiO-67-BPY maintained octahedral morphology, in keeping with that of UiO-67,^[22] and approximately homogeneous size (Figure 2a, S4a). Elemental mapping spectra (Figure S5) illustrated the homogeneous distribution of C, N, O, F, Zr, and Zn over the entire framework, proving that the existence of Zn(II) ions was uniform in the MOFs and their counter ions might be BF4⁻ anions. More importantly, TEM images at different magnifications (Figure S4) demonstrated that no detectable Zn or Zr nanoparticles could be observed. Bright spots displayed through aberration-corrected HAADF-STEM image (Figure 2b, S7) with red circles were on behalf of isolated atoms, which indicated that the agglomeration of Zn(II) or Zr(IV) ions might not be caused in the process of impregnation. To testify the coordination environment of Zn(II) species in the MOF, the extended X-ray adsorption fine structure (EXAFS) spectra were measured. As shown in Figure 2d, the peak at 1.6 Å revealed the formation of Zn-N coordination mode.^[23] Moreover, the best fitting result of obtained EXAFS data reveals that the coordination number of Zn is about 5 (2 Zn-N and 2.7 Zn-O) (Figure 2d and Table S2). And the peak in ~2.4 Å can be attributed to the Metal...C single scattering path, which can be observed in the similar Metal-BPY system.^[24] These results confirm that the Zn(II) sites are isolated inside the MOFs.

A highly stable, porous and crystalline MOF with uniformly distributed isolated reactive Zn(II) sites had therefore been achieved in Zn-UiO-67-BPY. To explore its catalytic ability, the intramolecular hydroamination of 2-(phenylethynyl)aniline to indole was selected as a catalytic model reaction. Cycloisomerization of 2-(phenylethynyl)aniline proceeded smoothly in toluene or methanol at 100 °C, giving the desired indole (**2a**) in an excellent yield (Table 1, entries 10-11). The quantities of solvent and Zn-UiO-67-BPY in this reaction were investigated (Table 1 and S1). An appropriate type and amount of solvents were required to achieve the effective catalysis. The

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reaction could take place both in toluene and methanol (entries, 1-3). Consequently, it was found that higher and lower amounts of toluene both had a deleterious effect (entries 4-5,10), which might be due to the fact that the solvent impacted the diffusion and concentration of both substrate and product. Unsurprisingly, with lower levers of Zn-UiO-67-BPY, the yield declined (entries 6-10). To further understand the detailed procedure of the cycloisomerization reaction, control experiments were implemented (Table S1). However, the reaction had difficulty proceeding in the presence of only UiO-67-BPY (entries 11-18), neglecting the effect of UiO-67-BPY itself. Meanwhile only Zn(BF₄)₂•xH₂O itself as catalyst was also hard to catalyze the reaction (entries 27-28). This phenomenon could indirectly show that the cycloisomerization reaction was catalyzed by unsaturated Lewis acidic Zn(II) sites inside the MOFs. Reaction conditions similar as to those of Zn-UiO-67-BPY were established in a homogeneous catalytic system (Table S1, entries 19-26) and unexpectedly, the main product was 1-(2aminophenyl)-2-phenylethanone (3a) in 73%-86% yield (Table S1, entries 19, 23), which pertained to hydration of alkynes to construct a carbonyl motif.^[25] Furthermore, the structures of compounds 2a and 3a were unambiguously confirmed by X-ray crystallographic analysis (Figure S10). The totally different reaction routes of 2-(phenylethynyl)aniline proceeded in homogeneous and heterogeneous catalytic systems, resulting from the discrepant micro-environments caused by internal pore structure of MOF and the different states of Zn(II) ions.

To increase the general applicability of the intramolecular hydroamination reaction catalyzed by Zn-UiO-67-BPY with isolated Zn(II) sites, several representative substrates were selected, and the results are summarized in Table 2. Referred to the optimized conditions described above, methanol was initially chosen as solvent, however the selected substrates produced low yields. Nevertheless, toluene replaced of methanol as solvent, and good yields were obtained. Initially, the substitution effect at the aromatic nucleus including electron-rich aryl and electron-deficient aryl groups was examined. Electron-donating and electron-deficient substituents para to the alkyne (R2) were well tolerated, with yields over 92% (entries 2b-2d, 2f). An electron-withdrawing substituent para to the amino group (R1) also led to a high yield (98%, entry 2g). Subsequently, we also tested the terminal alkyne without any substitute, with 1,2dichloroethane as solvent (entry 2e). Although the isolated yield in this case was only 50%, the result proved that the intramolecular hydroamination could be catalyzed by isolated Zn-UiO-67-BPY under the condition of the unsubstituted terminal alkynes, which enlarges the catalytic substrate scope of Zn-UiO-67-BPY catalyst.

Table 2. Substrate scope for Zn-UiO-67-BPY catalyzed cycloisomerization of o-alkynylanilines.^[a]







The Zn-UiO-67-BPY catalyst could be easily recovered by centrifugation, and was subsequently applied to successive cycles with slight loss of catalytic efficiency (Figure 3), which is in accordance with the minuscule leaching of Zn(II) into the solution of the reaction analyzed by ICP. PXRD patterns and morphology of recyclable catalyst were mostly maintained after one and even five cycles (Figure 1a, S8), which suggests that the stability and structural integrity of the Zn-UiO-67-BPY catalyst could stand the test, thus providing potential to practical

Table 1. Optimization of the Reaction Conditions.^[a]

		Zn-UiO-67-BPY toluene or CH ₃ OH 100 °C, 24 h		
Entry	Solvent / mL	Zn-UiO-67-BPY / mg	T/°C	Yield / % ^[b]
1	DMF 1	15	100	NR
2	CH ₃ OH 0.5	15	100	36
3	Toluene 5	15	100	48
4	Toluene 0.3	25	100	97
5	Toluene 0.1	25	100	90
6	Toluene 0.2	5	100	Trace
7	Toluene 0.2	10	100	10
8	Toluene 0.2	15	100	47
9	Toluene 0.2	20	100	97
10	Toluene 0.2	25	100	100
11	CH ₃ OH 0.2	25	100	100(96)
12	CH ₃ OH 0.2	25	90	94

[a] Reaction conditions: 1a (0.05 mmol), the content of Zn in Zn-UiO-67-BPY was 0.35mmol/g, 24 h under an Ar atmosphere. [b] Yields were determined by GC.

2e^[c], 50%

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application. XPS spectra of the used catalyst (Figure S2, S3) and recycling studies proved that Zn(II) sites still existed and remained active for catalyzing intramolecular hydroamination reaction after multiple cycles. To investigate the homogeneous or heterogeneous nature of the catalyst, a hot filtration experiment was conducted. The reaction in the presence of Zn-UiO-67-BPY was performed for 11 h and the yield reached 23%. At this point, the solid was quickly removed and the reaction was continued with the filtrate for a further 13 h at 100 $^{\circ}$ C, but the yield monitored by GC failed to increase, confirming that the catalyst was Zn-UiO-67-BPY and the reaction was carried out inside the framework.



Figure 3. Plot of yield (%) of 2a at various runs in the recycle and reuse of Zn-UiO-67-BPY.



Scheme 2. Proposed mechanism of intramolecular hydroamination of alkynes catalyzed by an isolated Zn(II) site in the Zn-UiO-67-BPY framework..

Combining these results with previous reports,^[26] a plausible reaction mechanism of intramolecular hydroamination of alkynes was proposed, and is detailed in Scheme 2. Isolated Zn(II) sites in MOFs act as Lewis acidic catalysts, and tend to bond with electron-donating groups. Therefore, the substrate might be activated as an N- and π -coordinated complex **A**, which

rearranged to π -adduct **B**. Based on the Zn(II)-catalyzed homogeneous and heterogeneous hydroamination reactions,^[16d, 27] the reaction process could be as follows: *o*-alkynylanilines are activated by isolated Zn(II) sites, forming a metastable π -adduct **B**. The π -adduct **B** undergoes cyclization to form the σ -complex **C**, which went through protodemetallation to afford the indole (2) and the isolated Zn(II) catalyst (Scheme 2).

In summary, through the incorporation of inorganic zinc salts into the framework of a UiO-67 derivative, we have developed a highly efficient, robust, single-site base-metal catalyst for the hydroamination of alkynes with excellent reusability and recycling performance. Compared with the similar homogeneous catalytic conditions, MOFs create a particular internal environment, resulting in different main products from the reaction of alkynes. The existence of isolated Zn(II) sites and the conducting of control tests make the action sites distinct, which is more beneficial for the exploration of the reaction mechanism. This work thus demonstrates that MOFs can provide a specific environment to change the main direction of a chemical reaction under similar homogeneous catalytic conditions.

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Keywords: metal-organic framework • single Zinc(II) site • hydroamination • indole • heterogeneous catalyst

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A noble-metal-free, reusable and robust single-site Zn(II) catalyst supported on metal-organic framework has been synthesized through postsynthetic functionalization. Due to the high activity of open single Zn(II) site, the Zn(II)-catalyst exhibits outstanding catalytic activity for the intramolecular hydroamination of *o*-alkynylanilines.



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