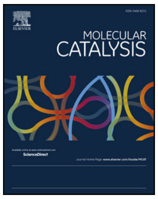
Molecular Catalysis 450 (2018) 104–111

Contents lists available at ScienceDirect

Molecular Catalysis

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



Mild direct amination of benzoxazoles using interpenetrating Cobalt(II)-based metal-organic framework as an efficient heterogeneous catalyst

Sheng-Chun Chen[a], Nan Li[a], Feng Tian[b], Nan-Nan Chai[a], Ming-Yang He[a,b,**], Qun Chen[a,*]

[a] Jiangsu Key Laboratory of Advanced Catalytic Materials and Technology, School of Petrochemical Engineering, Changzhou University, Changzhou 213164, China
[b] School of Chemical Engineering, Nanjing University of Science & Technology, Nanjing 210094, China

ARTICLE INFO

Keywords:
Co(II) MOF
Heterogeneous catalysis
Direct amination
Benzoxazoles

ABSTRACT

Based on the acid-base mixed-ligand assembly strategy, a new acid- and base-stable cobalt(II) metal-organic framework $\{[Co(tcpa)(Fbtx)(H_2O)_2]\cdot 0.5H_2O\}_n$ (denoted as Co-MOF, Fbtx = 1,4-bis(1,2,4-triazole-1-ylmethyl)-2,3,5,6-tetrafluorobenzene, H_2tcpa = 3,4,5,6-tetrachloro-phthalic acid) was synthesized under hydrothermal conditions and characterized by various spectral and analytical techniques. Single-crystal X-ray diffraction analysis revealed that Co-MOF features a rare three-dimensional two-fold interpenetrating **cds**-type framework. The crystalline Co-MOF exhibited excellent activity toward the direct amination of 5-methylbenzoxazoles with TBHP as oxidant and acetic acid as an additive under mild reaction conditions, and various 2-aminobenzoxazoles were synthesized in moderate to good yields under optimized reaction conditions. Furthermore, the Co-MOF catalyst could be easily recovered and reused several times without loss of its crystallinity and activity.

1. Introduction

2-Aminobenzoxazole derivatives not only occur as substructures in a variety of biologically active natural products [1], but also are promising targets for the treatment of schizophrenia [2], insomnia [3], CNS disorders [4], and Alzheimer's disease [5]. Methods for the efficient synthesis of 2-aminobenzoxazoles have thus attracted much attention from synthetic organic chemists in recent years [6–10]. In this field, transition-metal-catalyzed direct oxidative cross-dehydrogenative coupling (CDC) amination of benzoxazoles with unactivated amines represents one of the most efficient routes [11]. To date, a range of homogeneous Cu- [12], Ni- [13], Mn- [14], Co- [15], and Hf-based [16] catalysts in combination with stoichiometric amount of oxidants have been developed for the direct oxidative CDC amination of benzoxazoles. Nevertheless, a major drawback of homogeneous catalytic systems is the difficult recovery of these metal catalysts. From both economical and sustainable point of view, it is especially important to develop heterogeneous catalysts for amination of benzoxazoles, because these protocols would offer several advantages over homogeneous ones, including the ease of handling, recyclability and reusability. For example, Panda and Ghosh with their co-workers reported recyclable γ-MnO_2 as heterogeneous catalyst for oxidative CDC amination of benzoxazoles with molecular oxygen as oxidant [17]. Very recently, Zhao and co-workers developed a heterogeneous catalytic system using manganese octahedral molecular sieve supported copper hydroxide as catalyst for the oxidative synthesis of benzoxazoles at room temperature [18].

Metal-organic frameworks (MOFs) are an emerging class of functional organic-inorganic hybrid materials, providing a highly tunable platform to develop new heterogeneous catalysts for important organic transformations [19–22]. In the past decade, the MOFs-catalyzed heterogeneous C—H activation transformations have been recently reported by several research groups [23–26]. Recently, Phan and co-workers reported that a series of Cu(II) [27], Ni(II) [28], and Hf(IV)-based [29] MOFs could efficiently catalyze the direct heterocycle C—H arylation reactions to synthesize 2-substituted benzoxazoles under heterogeneous conditions. Similarly, Wu and co-workers prepared an anionic zeolite-like Cu(I)-based MOF that also showed catalytic activity for the C—H activation of benzoxazoles [30]. While remarkable progress has been made in the field, many challenging issues still remain unsolved. With the rapid development of heterogeneous catalytic C—H activation, new efficient MOF-based catalysts with well-defined structure are still in high demand. Moreover, some of the MOF catalysts are extremely sensitive to air, moisture and organic solvents. Thus far, these shortcomings have limited the practicality of MOFs in some catalytic transformations.

On the basis of the Irving-Williams series [31], late 3d transition

---

[*] Corresponding author.
[**] Corresponding author at: Jiangsu Key Laboratory of Advanced Catalytic Materials and Technology, School of Petrochemical Engineering, Changzhou University, Changzhou 213164, China.

E-mail addresses: hemingyangjpu@yahoo.com (M.-Y. He), chenqunjpu@yahoo.com (Q. Chen).

https://doi.org/10.1016/j.mcat.2018.03.011
Received 2 March 2018; Accepted 10 March 2018

metal ions (soft Lewis acids, such as Co^{II}, Ni^{II}, Cu^{II}, or Zn^{II}), being coordinated with *N*-heterocyclic aromatic ligands (soft Lewis bases, such as pyridine-, imidazole-, or triazole-based ligands), can favor the formation of stable complexes. Recently, Garcia and co-workers have illustrated that acid-base mixed-ligand MOFs possess superior robust and catalytic activity over those with only single ligand [32]. Previously, we synthesized a new stable Cu-MOF based on mixed ligands of Fbtx and phthalic acid and found that this MOF could be used as a highly efficient heterogeneous catalyst for selective aerobic oxidation of alcohols to aldehydes [33]. To further demonstrate the utility of mixed-ligand strategy, herein we wish to report the synthesis and characterization of a new Co(II)-based MOF $\{[Co(tcpa)(Fbtx)(H_2O)_2]\ 0.5H_2O\}_n$, denoted as Co-MOF, constructed from mixed ligands of 1,4-bis(1,2,4-triazole-1-ylmethyl)-2,3,5,6-tetrafluorobenzene (Fbtx) and 3,4,5,6-tetrachlorophthalic acid (H_2tcpa). The crystalline Co-MOF with a rare two-fold interpenetrating **cds**-type framework indicated good chemical stability toward dilute acidic and basic aqueous solutions as well as various boiling solvent systems, and was shown to a highly active, readily recyclable and reusable catalyst for oxidative CDC amination of benzoxazoles through C—H bond activation under mild conditions. The Co-MOF also exhibited higher catalytic activity than that of Co-containing hydrotalcite $CO_3{}^{2}$-Co_4Al-LDH and Co-doped zeolites including Co-Ets-10, Co-ZSM-5 and Co-Beta.

2. Experimental

2.1. Preparation of Co-MOF catalyst

In a typical preparation, a mixture of $Co(OAc)_2{\cdot}4H_2O$ (24.9 mg, 0.1 mmol), H_2tcpa (30.4 mg, 0.1 mmol), Fbtx (31.2 mg, 0.1 mmol) and water (6 mL) was stirred for 60 min at room temperature and then sealed in a 15-mL Teflon-lined stainless steel autoclave, which was heated to 140 °C for 2 days. After it was cooled down to room temperature at a rate of 5 °C h^{-1}, pink block-shaped crystals suitable for X-ray diffraction analysis were obtained in *ca.* 65% yield (46.5 mg, based on H_2tcpa). Anal. calcd for $C_{20}H_{10}Cl_4CoF_4N_6O_{6.5}$: C, 33.59; H, 1.39; N, 11.75%; found: 33.68; H, 1.38; N, 11.72%. IR (cm^{-1}, KBr pellet): 3433 br, 3124 m, 3118 m, 2976 m, 1587 s, 1536 m, 1491 s, 1414 m, 1382 s, 1336 m, 1285 s, 1208 w, 1124 s, 1034 s, 898 m, 854 w, 784 m, 661 s, 610 m.

2.2. Catalytic studies

Co-MOF-catalyzed CDC amination of benzoxazoles: in a typical procedure, 5-methylbenzoxazole (0.5 mmol, 1.0 equiv), morpholine (0.6 mmol, 1.2 equiv), Co-MOF (0.015 mmol, 3 mol%), acetic acid (1 mmol, 2 equiv), TBHP (70% in H_2O) (1 mmol, 2 equiv) and acetonitrile (2 mL) were taken in a 10-mL Schlenk flask. The reaction mixture was stirred for 12 h at room temperature under air atmosphere. The progress of the reaction was monitored via gas chromatography (Shimadzu GC-2010AF) equipped with fused silica capillary HP-5 column (30 m × 0.32 mm) and a flame ionization detector. The products were further confirmed by using GC–MS, ^{1}H NMR and ^{13}C NMR. The concentration of 5-methylbenzoxazole and 5-methyl-2-(4-morpholinyl)benzoxazole was calibrated by external standard method with standard samples. The reaction solution containing Co-MOF catalyst was easily separated by filtration, and the catalyst was washed with DMF and ethanol and dried under vacuum before reutilization.

2.3. Single crystal X-ray diffraction

The crystal data of Co-MOF were collected on a Bruker Apex II CCD diffractometer at 293 K with Mo Kα radiation (λ = 0.71073 Å). A semiempirical absorption correction was applied using SADABS [34], and the program SAINT was used for integration of the diffraction profiles [35]. The structure was solved by the direct methods using SHELXS program of SHELXTL packages and refined anisotropically for all non-hydrogen atoms by full-matrix least squares on F^2 with SHELXL [36]. C-bound hydrogen atoms were placed in geometrically calculated positions by using a riding model. O-bound hydrogen atoms were firstly localized by difference Fourier maps and then fixed geometrically with isotropic temperature factors. Further crystal data and structural refinement parameters are summarized in Table S1.

CCDC-1814834 (Co-MOF) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.can.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Centre, 12 Union Road, Cambridge CB21EZ, UK; Fax: +44 1223–336033; or deposit@ccdc.cam.ac.uk).

2.4. Characterization of Co-MOF catalyst

Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku D/max-2000 diffractometer at 40 kV and 100 mA for a Cu-target tube (λ = 1.5418 Å), and the calculated PXRD patterns were obtained from the single-crystal diffraction data using the PLATON software [37]. Thermogravimetric analysis (TGA) experiment was carried out in the temperature range of 25–800 °C on a Dupont thermal analyzer under N_2 atmosphere at a heating rate of 10 °C min^{-1}. BET surface area analysis was performed by nitrogen sorption isotherms in a Micromeritics ASAP2460 surface area analyzer at 77 K. Scanning electron microscopy (SEM) images were obtained on a field scanning emission Gemini Zeiss SUPRA55 at an accelerating voltage of 5 kev. X-ray photoelectron spectroscopy (XPS) measurements were performed on a PHI 5000 Versa Probe II XPS system with a monochromatic Al Kα X-ray source ($h\nu$ = 1486.7 eV) and a charger neutralizer. The Fourier transform (FT) IR spectra (KBr pellet) were taken on a Nicolet ESP 460 FT-IR spectrometer in the range of 4000–400 cm^{-1}. Elemental analyses were performed on a PE–2400II (Perkin-Elmer) analyzer. Gas chromatographic analyses were carried out using an Agilent 7890 B GC system equipped with fused silica capillary HP-5 column (30 m × 0.32 mm) and a flame ionization detector (FID).

3. Results and discussion

3.1. Synthesis and characterization of catalyst

During the acid-base mixed-ligand self-assembly process, the nature of organic ligands plays a crucial role in determining the final MOF structures and properties [38]. Recently, our group has utilized a series of halogen-substituted dicarboxylate acids and *N*-heterocyclic bridging ligands as the functional and structural units to develop families of halogen-modified metal-organic hybrid materials [39–45]. Meanwhile, a new stable copper(II) MOF based on the mixed ligands of Fbtx and phthalic acid has been reported by us [33]. Considering the unique coordination geometry of cobalt(II) ion and its potential catalytic properties, we hoped to build more robust cobalt(II) complexes based on mixed halogen-substituted ligands of acid- and base-type. Although many attempts have been devoted to the combination of Fbtx with several analogues dicarboxylate ligands, such as phthalic acid, 3,4,5,6-tetrafluoro-phthalic acid, 3,4,5,6-tetrabromo-phthalic acid, it was a pity that pink precipitates but not crystals which are unsuitable for X-ray single-crystal analyses were always obtained. Therefore, it should be pointed out that the choice of carboxylate ligands plays an important role in the self-assembly. In addition, when cobalt(II) sources including $Co(NO_3)_2$ and $CoCl_2$ were used, only amorphous powders were obtained under the similar reaction conditions. Moreover, the introduction of NaOH, KOH or Et_3N to adjust the pH value was also examined, where such bases were ineffective during the assembly processes.

As shown in Fig. 1a, photo of single crystals of Co-MOF shows high quantity. Single-crystal X-ray diffraction analysis reveals that Co-MOF crystallizes in the monoclinic system with the *C*2/*c* space group, and shows a three-dimensional two-fold interpenetrating framework with