



# Metal–organic framework MOF-199 as an efficient heterogeneous catalyst for the aza-Michael reaction

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## ARTICLE INFO

### Article history:

Received 12 December 2011

Received in revised form 20 February 2012

Accepted 25 February 2012

Available online 3 March 2012

### Keywords:

Metal–organic framework

MOF-199

aza-Michael reaction

Heterogeneous catalyst

Recyclable

## ABSTRACT

A highly porous metal–organic framework (MOF-199) was synthesized from the reaction of copper nitrate trihydrate and 1,3,5-benzenetricarboxylic acid by solvothermal method, and used as a recyclable acid catalyst for the aza-Michael reaction. Physical characterizations of the solid catalyst were achieved by using a variety of different techniques, including X-ray powder diffraction (XRD), scanning electron microscope (SEM), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), Fourier transform infrared (FT-IR), dynamic laser light scattering (DLS), atomic absorption spectrophotometry (AAS), and nitrogen physisorption measurements. Excellent conversions were achieved under mild conditions in the presence of 5 mol% catalyst. The MOF-199 catalyst could be reused several times without a significant degradation in catalytic activity. No contribution from homogeneous catalysis of active species leaching into the liquid phase was detected.

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## 1. Introduction

The aza-Michael reaction of amines and  $\alpha$ ,  $\beta$ -unsaturated carbonyl compounds has attracted significant attention as one of the most effective methods to prepare  $\beta$ -amino carbonyl compounds and their derivatives [1]. These structures serve as essential intermediates in the synthesis of a variety of biologically important natural products, antibiotics, peptide analogues, chiral auxiliaries, and other nitrogen-containing compounds [2]. Traditionally, stoichiometric or catalytic amounts of several Lewis acids have been employed for the process, including  $\text{AlCl}_3$ ,  $\text{HgCl}_2$ ,  $\text{TiCl}_4$  [3],  $\text{Bi}(\text{NO}_3)_3$  [4],  $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ –NaI [5],  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  [6],  $\text{LiClO}_4$  [7],  $\text{Na}_2\text{SnO}_3$  [8],  $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  [9],  $\text{Cu}(\text{OTf})_2$  [10], and boric acid [11]. Employing these Lewis acids required aqueous workup for the catalyst separation, generating of a large amount of waste, and also suffering from difficult product purification [12]. From green chemistry point of view, more environmentally benign protocols should be targeted to improve the green credentials of the reaction [13]. For the development of greener processes, reactions using heterogeneous catalysts would be favored in terms of the ease of handling, simple workup, recyclability and reusability [14]. At the same time, the catalyst recovery also decreases contamination of the desired products with hazardous or harmful metals [15,16]. Indeed, several solid catalysts have been investigated for the aza-Michael reaction, including glutathione supported on magnetic nanoparticles [17],

graphene oxide [18], modified IRMOF-3 [19], Amberlyst-15 [20,21],  $\text{Co}(\text{II})$  complex supported on mesoporous SBA-15 [22], AISBA-15 [23], nanocrystalline copper(II) oxide [14], copper nanoparticles [24], polyaniline supported  $\text{CuI}$  [25], azaphosphatane nitrate salt immobilized on Merrifield resin [26],  $\text{Cu}$ – $\text{Al}$  hydrotalcite [27], silica gel [28],  $\text{KF}/\text{Al}_2\text{O}_3$  [29], and  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  immobilized on montmorillonite K10 [30]. Although interesting results have been achieved for the aza-Michael reaction, the development of simple and environmentally benign approaches for the reaction is still the target of further research in the near future.

Metal–organic frameworks (MOFs) have attracted significant attention during the past decade as promising materials for their potential applications in gas separation and storage, sensors and luminescence, drug storage and delivery, templated low-dimensional material preparation, and catalysis [31–36]. Taking some special properties of both organic and inorganic porous materials, MOF-based structures exhibit several advantages such as high surface areas, tunable pore sizes, and the ease of processability, flexibility, and structural diversity [37–39]. In the field of catalysis, MOFs have been employed as solid catalysts or catalyst supports for a variety of organic transformations [40], including Friedel–Crafts alkylation and acylation [41–43], oxidation [44–49], alkene epoxidation [50–52], cycloaddition of  $\text{CO}_2$  with epoxides [53], cyanosilylation [54,55], hydrogenation [56], Suzuki cross-coupling [57,58], Sonogashira reaction [59], transesterification reaction [60], Knoevenagel condensation [61–63], aldol condensation [64,65], aza-Michael condensation [19], 1,3-dipolar cycloaddition reactions [66],  $N$ -methylation of aromatic primary amines [67], epoxide ring-opening reaction [68–70], hydrolysis

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