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Quinoxaline synthesis via oxidative cyclization reaction using metal–organic framework Cu(BDC) as an efficient heterogeneous catalyst

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ABSTRACT

A metal–organic framework Cu(BDC) was synthesized, and characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), Fourier transform infrared (FT-IR), atomic absorption spectrophotometry (AAS), and nitrogen physisorption measurements. The Cu(BDC) was employed as an efficient heterogeneous catalyst for the oxidative cyclization reaction between α-hydroxyacetophenone and phenylenediamine to form 2-phenylquinoxaline as the principal product. The optimal conditions involved the use of air atmosphere oxidant in toluene solvent at 100 °C in 3 h. In addition, the Cu(BDC) exhibited higher catalytic activity in the quinoxaline synthesis reaction than that of others Cu–MOFs such as MOF-199, MOF-118, and $Cu_2(BDC)_2$(DABCO), and higher than that of Mn(BDC), and $Ni_2(BDC)_2$(DABCO). The Cu(BDC) catalyst could be recovered and reused several times without a significant degradation in catalytic activity.

1. Introduction

Quinoxalines have emerged as important intermediates commonly employed in the synthesis of numerous pharmaceutical candidates and agrochemicals as well as a variety of functional organic materials [1–5]. Traditionally, these structures have been prepared by the acid-catalyzed condensation of 1,2-aryldiamines with 1,2-diketones [6–8]. The synthesis protocol has been improved by using 1,2-diketone alternatives, such as epoxides [9], α-bromoketones [10,11], and α-hydroxyketones [4,12]. Under the green chemistry point of view, organic transformations using heterogeneous catalysts would offer advantages in terms of the ease of handling, simple workup, recyclability and reusability [13,14]. Moreover, the contamination of the desired products with transition metals would be minimized under heterogeneous catalysis conditions [15,16]. The quinoxaline synthesis from 1,2-diketones was previously carried out using several solid catalysts, such as nickel nanoparticles [17], silica-supported antimony(III) chloride [18], Amberlyst-15 [19], silica-supported sulfonic acid [20], and Montmorillonite K-10 [21]. Das and co-wokers reported the quinoxaline synthesis from α-bromoketones using silica-supported perchloric acid catalyst [10]. Lingaiah and co-workers demonstrated an iron-exchanged molybdophosphoric acid as a solid catalyst for the quinoxaline synthesis from α-hydroxyketones [22]. Manganese octahedral molecular sieves [23], ruthenium immobilized on charcoal [24], and $CuCl_2$ combined with molecular sieve 4A [25] were also employed as heterogeneous catalysts for the quinoxaline synthesis from α-hydroxyketones. However, developing an efficient heterogeneous catalyst system for the quinoxaline synthesis still remains to be explored.

Metal–organic frameworks (MOFs) are extended porous materials constructed from metal ions or metallic clusters and polyfunctional organic linkers [26,27]. These structures offer potential applications in many fields, including gas storage media, separations, chemical sensors, thin film devices, optics, drug carriers, biomedical imaging, and catalysis [28–35]. Recently, the use of MOFs with transition metal clusters as catalysts or catalyst supports for organic reactions has increasingly gained attention [36–38]. In particular, numerous conditions for valuable transformations such as carbon-carbon [39–42] and carbon-heteroatom forming reactions [43–50] have been described under MOFs catalysis. Among several kinds of MOFs, it was previously reported that copper-based frameworks exhibited high activity for many organic reactions due to their unsaturated open copper metal sites [45,51–58]. We recently demonstrated that the metal–organic framework Cu(BDC) could catalyze the modified Friedländer transformation between 2-aminobenzyl alcohol and acetophenone to

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form 2-phenylquinoline as the principal product [57]. In this work, we present the quinoxaline synthesis via oxidative cyclization reaction between α-hydroxyketones and 1,2-aryldiamines using Cu(BDC) as an efficient and recyclable heterogeneous catalyst.

2. Experimental

2.1. Materials and instrumentation

All reagents and starting materials were obtained commercially from Sigma-Aldrich and Merck, and were used as received without any further purification unless otherwise noted. Nitrogen physisorption measurements were conducted using a Micromeritics 2020 volumetric adsorption analyzer system. Samples were pretreated by heating under vacuum at 150 °C for 3 h. A TGA Q500 was used for thermogravimetric analysis (TGA) with a heating rate of 10 °C/min under a nitrogen atmosphere. X-ray powder diffraction (XRD) patterns were recorded using a Cu *K*α radiation source on a D8 Advance Bruker powder diffractometer. Scanning electron microscopy studies were conducted on a JSM 5500 scanning electron microscope (SEM). Transmission electron microscopy studies were performed using a JEOL JEM 1010 Transmission electron microscope (TEM) at 80 kV. The Cu(BDC) sample was dispersed on holey carbon grids for TEM observation. Elemental analysis with atomic absorption spectrophotometry (AAS) was performed on an AA-6800 Shimadzu. Fourier transform infrared (FT-IR) spectra were obtained on a Nicolet 6700 instrument, with samples being dispersed on potassium bromide pallets. For hydrogen temperature programmed reduction (H_2-TPR), the sample was outgassed at 100 °C for 30 min with helium, then cooled down to room temperature, and exposed to 50 mL/min of 10% H_2/Ar as the temperature ramped at 2.5 °C/min to 600 °C. The amount of hydrogen consumption was determined from TCD signal intensities, which were calibrated using an Ag_2O reference sample.

Gas chromatographic (GC) analyses were performed using a Shimadzu GC 2010-Plus equipped with a flame ionization detector (FID) and an SPB-5 column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.25 μm). The temperature program for GC analysis heated samples from 120 °C to 180 °C at 40 °C/min and held them at 180 °C for 0.5 min; then heated from 180 °C to 280 °C at 50 °C/min and held them at 280 °C for 2 min. Inlet and detector temperatures were set constant at 280 °C. Diphenyl ether was used as an internal standard to calculate reaction conversions. GC–MS analyses were performed using a Hewlett Packard GC–MS 5972 with a RTX-5MS column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.5 μm). The temperature program for GC–MS analysis heated samples from 60 to 280 °C at 10 °C/min and held them at 280 °C for 2 min. Inlet temperature was set constant at 280 °C. MS spectra were compared with the spectra gathered in the NIST library. The ^{1}H and ^{13}C NMR were recorded on Bruker AV 500 spectrometers using residual solvent peak as a reference.

2.2. Synthesis of the metal–organic framework Cu(BDC)

The Cu(BDC) was prepared according to a slightly modified literature procedure [59]. In a typical preparation, a solid mixture of H_2BDC (H_2BDC = 1,4-benzenedicarboxylic acid; 0.332 g, 2.0 mmol) and $Cu(NO_3)_2 \cdot 3H_2O$ (0.484 g, 2.0 mmol) was dissolved in DMF (DMF = *N*,*N*′-dimethylformamide; 40 mL), and the resulting solution was distributed to six 10 mL vials. The vial was then heated at 130 °C in an isothermal oven for 48 h. After cooling the vial to room temperature, the solid product was removed by decanting with mother liquor and washed in DMF (3 × 10 mL) for 3 days. Solvent exchange was then carried out with dichloromethane (DCM) (3 × 10 mL) at room temperature for 3 days. The material was then evacuated under vacuum at 160 °C for 6 h and stored in a desicator, yielding 0.3 g of Cu(BDC) in the form of blue crystals (66% based on 1,4-benzenedicarboxylic acid).

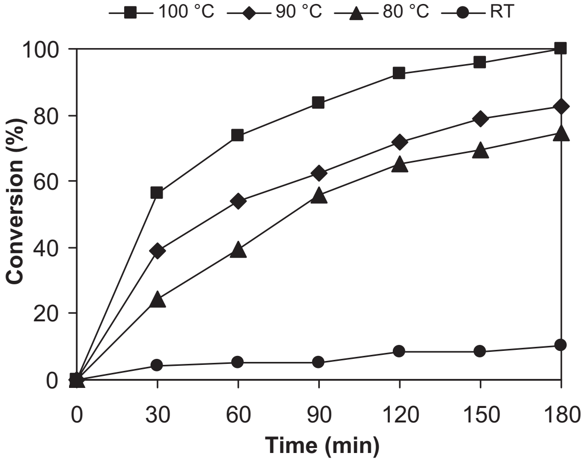

Fig. 1. Effect of temperature on the reaction conversion.

2.3. Catalytic studies

In a typical experiment, a pre-determined amount of Cu(BDC) was added to the flask containing a mixture of α-hydroxyacetophenone (0.136 g, 1.0 mmol), phenylenediamine (0.119 g, 1.1 mmol), and diphenylether (0.05 mL) as internal standard in toluene (4.0 mL). The catalyst loading was calculated based on the molar ratio of copper/α-hydroxyacetophenone. The reaction mixture was stirred at 100 °C for 180 min. Reaction conversion was monitored by withdrawing aliquots from the reaction mixture at different time intervals, quenching with ethylacetate (3 mL), drying over anhydrous Na_2SO_4, and analyzing by GC with reference to diphenylether. The product identity was further confirmed by GC–MS, ^{1}H NMR, and ^{13}C NMR. To investigate the recyclability of Cu(BDC), the catalyst was separated from the reaction mixture by simple filtration, washed with copious amounts of DMF, soaked in DMF, dried under vacuum at 140 °C for 2 h. For the leaching test, a catalytic reaction was stopped after 30 min, analyzed by GC, and hot filtered to remove the solid catalyst. The reaction solution was then stirred for a further 150 min. Reaction progress, if any, was monitored by GC as previously described.

3. Results and discussion

The metal–organic framework Cu(BDC) was synthesized according to a literature procedure [59], and was characterized by several techniques, including XRD, SEM, TEM, TGA, FT-IR, AAS, H_2TPR and nitrogen physisorption measurements (Figs. S11–18). Particle size of about 125 μm was obtained (see Fig. S12). The Cu(BDC) was assessed for its catalytic activity in the oxidative cyclization reaction between α-hydroxyacetophenone and phenylenediamine to form 2-phenylquinoxaline as the principal product (Scheme 1). Initial studies addressed the effect of temperature on the conversion of α-hydroxyacetophenone to 2-phenylquinoxaline. The quinoxaline synthesis reaction was carried out at 5 mol% Cu(BDC) catalyst in toluene for 180 min, using 1.1 equivalent of phenylenediamine (Fig. 1). In details, the reaction could not proceed at room temperature, with less than 10% conversion being detected after 180 min. The reaction carried out at 80 °C afforded 74% conversion, while up to 82% conversion was obtained at 90 °C. Interestingly, it was found that almost quantitative