



1,5-Benzodiazepine synthesis *via* cyclocondensation of 1,2-diamines with ketones using iron-based metal–organic framework MOF-235 as an efficient heterogeneous catalyst



Thuan D. Le, Khoa D. Nguyen, Vu T. Nguyen, Thanh Truong*, Nam T.S. Phan*

Department of Chemical Engineering, HCMC University of Technology, VNU-HCM, 268 Ly Thuong Kiet, District 10, Ho Chi Minh City, Viet Nam

ARTICLE INFO

Article history:

Received 4 August 2015

Revised 29 October 2015

Accepted 29 October 2015

Available online 6 December 2015

Keywords:

Metal–organic framework

MOF-235

1,5-Benzodiazepine

1,2-Phenylenediamine

Heterogeneous catalyst

ABSTRACT

A crystalline iron-based metal–organic framework MOF-235 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 MOF-235 could be used as a heterogeneous catalyst for the synthesis of 1,5-benzodiazepines by the cyclocondensation of 1,2-diamines with ketones. Excellent conversions to 1,5-benzodiazepines were achieved in the presence of 5 mol% MOF-235 catalyst using molecular oxygen in air as the stoichiometric oxidant. The Fe-MOF exhibited higher catalytic activity for the cyclocondensation reaction than those of other MOFs including MOF-5, Mn(BDC), MOF-199, and Ni₂(BDC)₂(DABCO). The Fe-MOF catalyst could be separated from the reaction mixture by centrifugation, and could be recovered and reused several times without a significant degradation in catalytic activity. To the best of our knowledge, 1,5-benzodiazepines were not previously synthesized using MOFs as heterogeneous catalysts.

© 2015 Elsevier Inc. All rights reserved.

1. Introduction

1,5-Benzodiazepines, an important family of nitrogen-containing heterocycles, have attracted significant attention due to their wide applications as anticonvulsant, analgesic, sedative, anti-depressive, anti-inflammatory, and antibiotic agents [1–6]. The use of these bioactive heterocyclic compounds has been extended to therapeutics for viral infection and cardiovascular disorder [7–9]. Moreover, 1,5-benzodiazepines have been employed as important intermediates for the synthesis of numerous fused ring compounds such as triazolo-, oxazino-, oxadiazolo-, and furano-benzodiazepines [10]. Traditionally, these structures were prepared by the cyclocondensation of 1,2-diamines with ketones in the presence of a homogeneous catalyst, such as sulfanilic acid [11], boric acid [12], ytterbium triflate [13], scandium(III) triflate [14], boron trifluoride [15], and acetic acid [16]. Under the green chemistry point of view, heterogeneous catalysts should be used for the synthesis of 1,5-benzodiazepines, as these protocols would offer advantages in terms of the ease of handling, simple workup, recyclability and reusability [17,18]. Indeed, several heterogeneous catalysts

have been investigated for this transformation, including cage type mesoporous aluminosilicate [19], clay-supported polyoxometalates [20], polymer-supported ferric chloride [21], Preyssler (NaH₁₄P₅W₃₀O₁₁₀) heteropolyacid [22], solid superacid catalyst 'sulfated zirconia' [23], and silica supported polyfluorinated-zinc (II) phthalocyanine complex [24]. However, developing an efficient and recyclable heterogeneous catalyst system for the synthesis of 1,5-benzodiazepines still remains to be explored.

Applications of crystalline porous metal–organic frameworks (MOFs) in several fields have been extensively studied during the last few years, ranging from gas capture and storage to catalysis [25–29]. The combination of organic linkers and metal ions in the structure of MOFs produces many frameworks with special properties, such as high surface areas, tunable pore size, well-defined structures, the possibility to modify the surface hydrophobicity/hydrophilicity, and the opportunity for post-synthesis modification [25,26,30–37]. Although a very large number of MOFs have been produced, most of them have been explored for gas capture and storage, and only a small number of them have been employed as catalysts for organic transformations [38–43]. MOFs as catalysts would offer the advantages of high dispersion and high loading of catalytically active sites, as each organic linker or each metal in the framework could be useful for catalysis [39,44–50]. During the last few years, both carbon–carbon [51–61] and

* Corresponding authors. Fax: +84 (8) 38637504.

E-mail addresses: tvthanh@hcmut.edu.vn (T. Truong), ptsnam@hcmut.edu.vn (N.T.S. Phan).

carbon-heteroatom forming transformations [62–69] using MOF-based catalysts have been mentioned in the literature. Recently, iron-based metal–organic frameworks have been synthesized and used as heterogeneous catalysts for many oxidation reactions [70–74]. In this work, we wish to report the synthesis of 1,5-benzodiazepines by the cyclocondensation of 1,2-diamines with ketones using the iron-based metal–organic framework MOF-235 [$\text{Fe}_3\text{O}(\text{BDC})_3$, H_2BDC = 1,4-benzenedicarboxylic acid] as an efficient heterogeneous catalyst in the presence of molecular oxygen in air as the stoichiometric oxidant. The Fe-MOF catalyst could be recycled and reused several times for the transformation without a significant degradation in catalytic activity.

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 Netzsch Thermoanalyzer STA 409 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 $\text{Cu K}\alpha$ radiation source on a D8 Advance Bruker powder diffractometer. Scanning electron microscopy studies were conducted on a JSM S4800 Scanning Electron Microscope (SEM). Transmission electron microscopy studies were performed using a JEOL JEM 1010 Transmission Electron Microscope (TEM) at 80 kV. The MOF-235 sample was dispersed on holey carbon grids for TEM observation. Elemental analysis with inductively coupled plasma optical emission spectrometry (ICP-OES) was performed on an ICPE-9000 Shimadzu. Fourier transform infrared (FT-IR) spectra were obtained on a Nicolet 6700 instrument, with samples being dispersed on potassium bromide pallets. The particle size distribution of the MOF-235 was determined by dynamic laser light scattering (DLS) method using a Horiba LA 950.

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 held samples at 120 °C for 1 min, heated them from 120 °C to 180 °C at 40 °C/min and held them at 180 °C for 1 min; then heated from 180 °C to 280 °C at 50 °C/min and held them at 280 °C for 1.5 min. Inlet and detector temperatures were set constant at 280 °C. 4-Bromoanisole 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 ^1H 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 MOF-235

In a typical preparation, a solid mixture of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.541 g, 2.0 mmol) and H_2BDC (H_2BDC = 1,4-benzenedicarboxylic acid; 0.332 g, 2.0 mmol) was dissolved in a mixture of DMF (DMF = N, N'-dimethylformamide; 40 mL) and ethanol (40 mL). The resulting solution was distributed to eight 20-mL vials. The vials were

tightly capped and then heated at 85 °C in an isothermal oven for 48 h, yielding light orange crystals. After cooling the vial to room temperature, the solid product was obtained by decanting with mother liquor and washed with DMF (3×10 mL) for 3 days. Solvent exchange was then performed with ethanol (3×10 mL) at room temperature for 3 days. The product was then dried under vacuum at 140 °C for 6 h, yielding 0.285 g of MOF-235 [$\text{Fe}_3\text{O}(\text{BDC})_3$] in the form of brick red crystals (42% based on H_2BDC).

2.3. Catalytic studies

In a typical experiment, a mixture of 1,2-phenylenediamine (0.108 g, 1.0 mmol), 4-bromoanisole (0.1 mL) as internal standard, and acetone (0.222 mL, 3 mmol) in 4 mL ethanol was added into a round-bottom flask containing the pre-determining amount of MOF-235 catalyst. The catalyst amount was calculated with respect to the iron/1,2-phenylenediamine molar ratio. The reaction mixture was stirred at 50 °C for 180 min. Reaction conversion was monitored by withdrawing aliquots from the reaction mixture at different time intervals. The organic components were then extracted into diethyl ether (3 mL), filtered over a small silica column to remove insoluble solids, dried over anhydrous Na_2SO_4 , and analyzed by GC with reference to 4-bromoanisole. The product identity was further confirmed by GC–MS, ^1H NMR, and ^{13}C NMR. To investigate the recyclability of the MOF-235, the catalyst was separated from the reaction mixture by simple centrifugation, washed with copious amounts of acetone and ethanol, activated under vacuum at 140 °C for 6 h, and reused if necessary. For the leaching test, a catalytic reaction was stopped after 30 min, analyzed by GC, and centrifuged 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 iron-based metal–organic framework MOF-235 was synthesized according to a slightly modified literature procedure [75,76], and was characterized by several techniques, including XRD, SEM, TEM, TGA, FT-IR, AAS, and nitrogen physisorption measurements (Figs. S1–S7). It is reported that iron atom in MOF-235 is trivalent. MOF-235 possesses high symmetric *acs* topology and is built-up from octahedral iron trimers which are connected through linear terephthalic acid linkers [76,77]. The analysis results are in good agreement with previous reports [76,77]. In brief, powder XRD patterns showed the typical reflections of MOF-235 phase. The basically type-1 adsorption/desorption isotherm indicated the permanent micro-porosity with Brunauer–Emmett–Teller specific surface area of 540 m^2/g , a pore volume of 0.13 cm^3/g and an average pore diameter of about 7 Å. Scanning electron microscopy analysis revealed homogeneity with respect to octahedral crystals. TGA result of activated MOF-235 shows high thermal stability (>360 °C) and the measured mass percent of presumably residue FeO is in satisfactory agreement with the elemental analysis data. AAS provided 25.0% iron content which is in line calculated value of 24.9%. Finally, FT-IR spectra indicated the presence of bonded carboxylate organic linkers.

For catalytic studies, hypotheses about the use of MOF-235 catalyst for this sequential reaction are based on following considerations: (1) iron has been reported to be efficient Lewis acid for this transformation while other transition metal catalysts such as copper favored the formation of 2H-benzo[d]imidazole [78]; (2) within MOFs synthesis viewpoint, BDC (1,4-benzenedicarboxylic acid) linker is the simplest and easily accessible as compared to other dicarboxylic linkers; (3) metal active sites in catalyst will act as Lewis acid, and requirements for other organometallic

Download English Version:

<https://daneshyari.com/en/article/60659>

Download Persian Version:

<https://daneshyari.com/article/60659>

[Daneshyari.com](https://daneshyari.com)