

Research paper

One-pot synthesis of benzoazoles *via* dehydrogenative coupling of aromatic 1,2-diamines/2-aminothiophenol and alcohols using Pd/Cu-MOF as a recyclable heterogeneous catalyst

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ABSTRACT

In this paper we report an efficient synthetic approach for the preparation of the widespread numbers of benzoazoles *via* dehydrogenative coupling of 1,2-phenylenediamine or 2-aminothiophenol and benzyl alcohols by Pd/Cu₂(BDC)₂(DABCO)-MOF as new heterogeneous catalyst under solvent-free condition. The catalyst recycled and reused for four times without loss of catalytic activity. The structures of benzoazoles were corroborated spectroscopically (¹H- and ¹³C NMR, and elemental analysis) and were confirmed by comparison with reference compounds. A plausible mechanism for this type of reaction is proposed.

1. Introduction

Benzoazoles and their derivatives are important building blocks found in miscellaneous series of biologically active compounds, agricultural chemicals, pharmaceutical chemicals, and organic materials [1–5]. Furthermore, they are the basis of special chemicals for industrial applications such as pigments [6], optical brighteners for coatings [7] and etc.

The classical methods for the synthesis of these skeletons are the reaction between 1,2-phenylenediamines or 2-aminothiophenols and carboxylic acid, formic acid and aldehydes [8–12], hence experiencing disadvantages with regard to green chemistry points of view. Recently, different strategies for these structures have been developed and mentioned in the literature. Among the methods used for the synthesis of benzoazoles, [11–13] dehydrogenative coupling between alcohols and 1,2-phenylenediamine or 2-aminothiophenols are one of the most effective synthetic pathway by using homogeneous and heterogeneous catalyst such as Ir(2.0 wt%)/CeO₂, (PNNH)Co^ICl, Pt/TiO₂, Pt/Al₂O₃, Ru₂Cl₄(CO)₆ and etc. [14] that require stoichiometric amounts of hydrogen acceptors, strong bases, high temperature, unsafe solvent and in the case of homogeneous catalyst, failure to recover the catalyst [14–16]. So, the development of novel heterogeneous catalysts that can realize environmentally-benign synthesis of benzoazoles is an important topic. Application of supported palladium nanoparticles (PdNPs/support) as green and efficient heterogeneous catalysts has

attracted a considerable attention [17–19]. Metal–organic frameworks (MOFs), as a new class of organic inorganic hybrid porous materials, have attracted considerable attention for stabilization and support for the metal nanoparticles due to their high surface areas, tunable pore sizes, and thermal stability [20]. Encapsulation of metal nanoparticles (NPs) in MOF structure generates new collaborative effects, by which the catalytic activity, selectivity and stability of the metal NPs can be enhanced effectively [21]. Recently, the application of MOFs as the supports for Pd nanoparticle has attracted considerable interest [22]. For catalytic applications Pd NPs have been successfully deposited at the outer surface of the MOF supports (Pd/MOFs) [23–28] or loaded inside the cavities of the MOFs (Pd@MOFs) via various methods such as impregnation and chemical vapor deposition [29–35].

We previously uncovered synthesis of Pd-NPs/Cu₂(BDC)₂DABCO-MOF using *via* temperature controlling program and its role as reusable heterogeneous catalyst in Suzuki cross coupling and oxidation of benzyl alcohols [36]. Herein, in continues of our work and importance of the introduction and application of new catalysts in the synthesis of organic compounds and drawback of the reported methods in the literature as mentioned above, we report the development of this heterogeneous catalyst that are effective for the selective synthesis of benzimidazoles and benzothiazoles *via* a dehydrogenative coupling of 1,2-aryldiamines or 2-aminothiophenols with alcohols under mild conditions (Scheme 1).

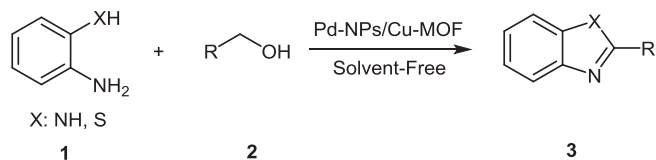
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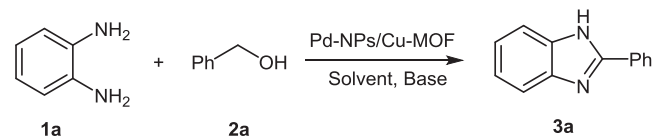
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Scheme 1. Synthesis of benzoazoles catalyzed by Pd/Cu-MOF.

Table 1

Optimization of reaction conditions.^a

Entry	Catalyst (mg)	Solvent	Base (20 mol%)	T (°C)	Yield (%) ^b
1	10	CH ₃ CN	Na ₂ CO ₃	80	20
2	20	CH ₃ CN	Na ₂ CO ₃	80	30
3	20	Toluene	Na ₂ CO ₃	110	60
4	20	DMF	Na ₂ CO ₃	120	65
5	20	–	Na ₂ CO ₃	120	88
6	30	–	Na ₂ CO ₃	120	86
7	40	–	Na ₂ CO ₃	120	84
8	–	–	Na ₂ CO ₃	120	0
9	20	–	–	120	25
10	20	–	Et ₃ N	120	82
11	Cu-MOF	–	Na ₂ CO ₃	120	25

^a Isolated yields.^b Reaction Conditions: benzene-1,2-diamine (1.3 mmol), benzyl alcohol (1.0 mmol), catalyst (20 mg), base (1.0 mmol).

2. Experimental section

2.1. Materials and instruments

All reagents including organic linker H₂BDC, metal salt Cu(OAc)₂·H₂O, 1,4-benzenedicarboxylate (BDC, 99%), 1,4-diazabicyclo[2.2.2]octane (DABCO), Palladium (II) chloride (PdCl₂), 1,2-phenylenediamines, 2-aminothiophenol, benzyl alcohols, sodium carbonate (Na₂CO₃) and ethyl acetate were obtained from commercially available sources such as Sigma–Aldrich and Merck without any purification. X-ray powder diffraction (XRD) measurements were performed using an X'pert MPD. Philips diffractometer with Cu radiation source ($\lambda = 1.54050 \text{ \AA}$) at 40 Kv voltage and 40 mA current. Transmission electron microscopy (TEM) was carried out using an EM10C-100 kV series microscope from the Zeiss Company, Germany and the actual loading of palladium was determined by Inductively Coupled Plasma (ICP) analysis on sequential plasma spectrometer, Shimadzu (ICPS-7000 ver. 2). BET (Brunauer-Emmett-Teller) surface area of the samples was determined from N₂ adsorption–desorption isotherms using a micromeritics ASAP 2020 analyzer. ¹H NMR and ¹³C NMR spectra were measured (CDCl₃) with a Bruker DRX-500 AVANCE spectrometer at 500.13 and 125 MHz. Melting points were measured on an Electrothermal 9100 apparatus.

2.2. Supporting of palladium nanoparticle in MOF (Pd-NPs/Cu₂(BDC)₂(DABCO))

Pd/Cu₂(BDC)₂(DABCO) was synthesized and characterized in the manner previously reported in our previous work [36]. A mixture of Cu(OAc)₂·H₂O (0.6 mmol), H₂BDC (0.6 mmol) and DABCO (0.3 mmol) with molar ratio of 2:2:1 were ball-milled at 28 Hz at room temperature for 2 h. The obtained green powder was washed with DMF (3 × 10 mL), and then with methanol (3 × 10 mL). Resulting green powder dried

under vacuum at 130 °C for 12 h to yield 1.6 g of Cu₂(BDC)₂(DABCO) (94%).

200 mg of the synthesized Cu₂(BDC)₂(DABCO) was dissolved in 2 cc of DMF and then 5 mg of PdCl₂ with purity of 99.9% were added to the mixture. The solution was sonicated for 20 min, stirred at 80 °C for 20 h and finally stirred at 130 °C with the purpose of reduction of Pd(II) to Pd (0). The product (Pd-NPs/Cu₂(BDC)₂(DABCO)) was centrifuged, washed with DMF and methanol and dried in vacuum at 120 °C for 12 h.

2.3. Catalyst usage for the dehydrogenative coupling

Typically, *o*-phenylenediamine (1.3 mmol) or 2-aminothiophenol (1 mmol), benzyl alcohols (1 mmol), Na₂CO₃ (20 mol%), and Pd-NPs/Cu₂(BDC)₂(DABCO) (20 mg, 0.01 mol%) were added to a round-bottom flask. The reaction mixture was heated to 120 °C and stirred at for the appropriate time in air (TLC monitoring). Ethyl acetate was added to the reaction mixture and catalyst was filtered. For the purification of impure products, chromatography on silica gel was performed (EtOAc:Hep. (1:6)). The entire products characterized by melting point, CHN, ¹H NMR and ¹³C-NMR spectroscopy.

3. Selected spectral data

3.1. 2-Phenyl-1H-benzo[d]imidazole (3a)

White crystals. mp 294–295 °C, ¹H NMR (500 MHz, DMSO-*d*₆, ppm): δ 12.91 (s, NH), 8.17 (d, 2H, ³J = 7.6 Hz, 2CH of Ar), 7.66 (bs, 2CH of Ar), 7.47–7.56 (m, 4CH of Ar), 7.20 (bs, 2CH of Ar). ¹³C NMR (125 MHz, DMSO-*d*₆, ppm): δ 151.2, 143.8, 134.9, 130.15, 129.8, 128.9, 126.4, 122.5, 121.6, 118.8, 111.3. Anal. Calcd. for C₁₃H₁₀N₂ (194.24): C, 80.39; H, 5.19; N, 14.42. Found: C, 80.35; H, 5.16; N, 14.38.

3.2. 2-Phenylbenzo[d]thiazole (3g)

White solid. m.p. = 113–114 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.07–8.12 (m, 3CH of Ar), 7.91 (d, ³J = 8.0 Hz, CH of Ar), 7.48–7.52 (m, 4CH of Ar), 7.26–7.42 (m, CH of Ar); ¹³C NMR (125 MHz, CDCl₃) δ 167.9, 154.0, 134.9, 133.5, 130.8, 128.9, 127.4, 126.2, 125.0, 123.1, 121.5. Anal. Calcd. for C₁₃H₁₀N₂ (211.28): C, 73.90; H, 4.29; N, 6.63. Found: C, 73.86; H, 4.28; N, 6.61.

4. Result and discussion

Pd/Cu₂(BDC)₂(DABCO) was synthesized and characterized in the manner previously reported in our previous work [36]. The XRD pattern of Pd@Cu₂(BDC)₂(DABCO) shows that the crystalline structure of Cu₂(BDC)₂(DABCO) is maintained after deposition of Pd NPs. The absence of a Pd diffraction pattern relates to the low Pd contents in the materials [36] (Fig. S1). Nitrogen adsorption-desorption and surface areas of Pd-NPs@Cu₂(BDC)₂(DABCO) samples were noticeably reduced compared to Cu₂(BDC)₂(DABCO), indicating that the cavities of Cu₂(BDC)₂(DABCO) may be occupied by highly dispersed Pd nanoparticles (Fig. S2). TEM micrograph (Fig. 2), confirmed that a crystalline and nano-scaled material was produced. It is also to emphasize that Pd nanoparticle has resulted in producing uniformly distributed nano-scale and with a mean particle diameter of 6.5 ± 0.2 nm as estimated from particle size distribution (Fig. 2). The actual loading of Pd (0) was characterized by ICP analysis and found to be 0.9%.

After full characterization of the synthetic PdNPs/Cu₂(BDC)₂(DABCO), it was employed as a heterogeneous catalyst in the dehydrogenative coupling of 1,2-phenylenediamine and benzyl alcohols as model reaction. For this purpose, 1,2-phenylenediamine (1.0 equiv), benzyl alcohol (1.0 equiv), Na₂CO₃ (20 mol%) and catalyst (20 mg, 0.01 mol %) in CH₃CN under open air atmosphere were used as starting parameters. A yield of 30% within 24 h at a temperature of

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