Can Tho University Journal of Science
website: sj.ctu.edu.vn

DOI: 10.22144/ctu.jen.2018.042

Benzimidazole synthesis *via* oxidative condensation of 1,2-diaminoarenes with primary amines using MOF-235 as an effective heterogeneous catalyst

Nguyen Thi Ngoc Tran[1], Dang Thi Hang[1], Lieu Ngoc Thien[1], Dang Huynh Giao[1,2] and Phan Thanh Son Nam[1*]

[1]Faculty of Chemical Engineering, Ho Chi Minh City University of Technology, Vietnam National University – Ho Chi Minh City

[2]College of Engineering Technology, Can Tho University

**Correspondence: Phan Thanh Son Nam (email: ptsnam@hcmut.edu.vn)*

Article info.

Received 27 Dec 2017
Revised 09 Mar 2018
Accepted 30 Nov 2018

Keywords

1,2-diaminoarenes, benzimidazoles, condensation, cyclization, MOF-235

ABSTRACT

Iron-organic framework MOF-235 was synthesized from 1,4-benzenedicarboxylic acid and iron(III) chloride by a solvothermal method. Physical characterizations of the solid catalyst were achieved by using a variety of techniques. The Fe-MOF was used as a productive heterogeneous catalyst for the synthesis of benzimidazoles via oxidative condensation of primary amines with 1,2-diaminoarenes. The MOF-235 was found to be more catalytically active for the oxidative condensation of primary amines with 1,2-diaminoarenes than other Metal-organic frameworks (MOFs). Leaching tests verified that the cyclization of 1,2-phenylenediamine with benzylamine to generate 2-phenyl-1H-benzo[d]imidazole was only possible in the presence of the iron-based framework catalyst, thus indicating that the transformation progressed via truly heterogeneous catalysis.

Cited as: Tran, N.T.N., Hang, D.T., Thien, L.N., Giao, D.H. and Nam, P.T.S., 2018. Benzimidazole synthesis via oxidative condensation of 1,2-diaminoarenes with primary amines using MOF-235 as an effective heterogeneous catalyst. Can Tho University Journal of Science. 54(8): 88-95.

1 INTRODUCTION

Benzimidazole derivatives are pervasive structural skeletons recognized in innumerable agrochemicals and pharmaceuticals, and also in wide range of functional polymers and organic materials (Singh *et al*., 2009; Noël *et al.*, 2013). Classically, these nitrogen-containing heterocyclic motifs could be generated by the condensation of aldehydes or carboxylic acids with 1,2-diaminoarenes accompanied by oxidative cyclization utilizing acid catalysts (Chen *et al*., 2008; Mahesh *et al*., 2015). To inaugurate more efficient synthetic strategies for the construction of benzimidazole, transition metal-catalyzed protocols have been investigated. Ma *et al.* (2009) previously reported a CuI-catalyzed coupling of 2-iodoacetanilides with aqueous ammonia at ambient temperature, which experienced *in situ* cyclization to form 1*H*-benzimidazoles (Diao *et al*., 2009). Lv and Bao (2009) employed an effective CuI-catalyzed domino addition/C-N coupling process to produce a broad range of benzimidazoles from *N*- or *O*-nucleophiles and *o*-haloarylcarbodiimides. Punniyamurthy *et al.* (2015) synthesized innumerable benzimidazoles by a CuI-catalyzed cascade reaction between azides, aryl amines, and aldehydes (Mahesh *et al*., 2015). Zhou *et al.* (2013) demonstrated a straightforward protocol for the generation of benzazoles *via* $CuBr_2$-catalyzed oxidative cyclization of benzylamines with hydroxyanilines/mercaptan/*o*-amino

(Xiao *et al.*, 2013). Taddei *et al.* (2012) mentioned the production of benzimidazoles starting from amines and o-phenylenediamines in the existence of palladium on charcoal as catalyst (Pizzetti *et al.*, 2012). Very recently, Gopalaiah and Chandrudu (2015) developed an $FeBr_2$-catalyzed oxidative coupling of 2- amino/mercapto/hydroxyanilines with benzylamines to generate varied 1,3-benzazoles. To acquire more environmentally benevolent synthetic approaches for the production of benzimidazoles, heterogeneous catalysts should be investigated (Leadbeater and Marco, 2002).

Metal-organic frameworks (MOFs) have come up as a new grade of crystalline materials, furnishing interesting applications in diverse disciplines (Chae *et al*., 2004; Tranchemontagne *et al*., 2008; Kuppler *et al.*, 2009). The nature of these frameworks enables the greatest flexibility of structures and properties, and hence offering advantages as correlated to ordinary porous materials (Chae *et al*., 2004; Tranchemontagne *et al*., 2008; Kuppler *et al.*, 2009). Although the prosperity of these sponge-like materials is still challenging, MOFs are an area of intense research around the world throughout the most recent decade (Mason *et al.*, 2014; Jusoh *et al*., 2015). Employing these materials as heterogeneous catalysts has recently attracted notable interests from both industry and academy (Dhakshinamoorthy and Garcia, 2012; Leus *et al.*, 2014; Liu *et al*., 2014). The application of iron-based frameworks in catalysis has been updated in the literature (Cele *et al*., 2014; Wang *et al.*, 2014). In this research, the synthesis of benzimidazoles *via* oxidative condensation of primary amines with 1,2-diaminoarenes utilizing an iron-based framework MOF-235 as a heterogeneous catalyst was described. To our best understanding, the generation of benzimidazoles using iron-based heterogeneous catalysts was not previously disclosed in the literature.

2 MATERIALS AND METHODS

2.1 Materials and instrumentation

All reagents and starting materials were purchased from Sigma-Aldrich and Acros, and used as received without further purification. Gas chromatographic (GC) analyses were performed using a Shimadzu GC 2010-Plus equipped with a flame ionization detector 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 100 °C for 1 min; heated them from 100 to 280 °C at 40 °C/min; held them at 280 °C for 5 mins. Inlet and detector temperatures were set constant at 280 °C. Dodecane 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 5 mins. Inlet temperature was set constant at 280 °C. MS spectra were compared with the spectra gathered in the NIST library. The ^1H NMR and ^{13}C NMR were recorded on Bruker AV 500 spectrometers using residual solvent peak as a reference.

2.2 Catalyst synthesis

The framework MOF-235 was synthesized in a yield of 73% in conformity with a literature procedure (Haque *et al.*, 2011; *Anbia et al*., 2012). A solid mixture of $FeCl_3.6H_2O$ (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 hrs, 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 x 10 mL) for 3 days. Solvent exchange was then performed with ethanol (3 x 10 mL) at room temperature for 3 days. The product was then dried under vacuum at 140 °C for 6 hrs, yielding 0.3 g of MOF-235 in the form of brick red crystals (43 % based on H_2BDC).

2.3 Catalytic studies

In a representative experiment, a solution of 1,2-phenylenediamine (0.108 g, 1 mmol), benzyl amine (0.214 g, 2 mmol) in chlorobenzene (2 mL) was added into a 15 mL vial containing the required catalyst. Diphenyl ether (0.17g, 1 mmol) as an internal standard was then introduced to the vial. The catalyst amount was calculated regarding the iron/1,2-phenylenediamine mole proportion. The reactor was connected with an oxygen balloon through a needle, the reaction mixture was magnetically stirred for 7 hrs at 130 °C. The samples were withdrawn, dissolved in methanol, and analyzed by GC concerning diphenyl ether. The expected product, 2-phenyl-1*H*-benzo[d]imidazole, was isolated using column chromatography. The product specification was verified by GC-MS, ^1H NMR and ^{13}C NMR. For the recyclability experiment, the catalyst was separated, washed many times with ethanol, heated at 150 °C under vacuum in a shlenkline for 6 hrs, and reused for new catalytic run. In the leaching experiment, the reaction was ceased after 2 hrs, and centrifuged to isolate the catalyst. The reaction solution was then heated with magnetic stirring for additional 5 hrs. The formation of 2-phenyl-1*H*-benzo[d]imidazole in the absence of the solid catalyst was then monitored.

3 RESULTS AND DISCUSSION

The Fe-MOF was evaluated for its efficiency in the oxidative condensation of benzylamine with 1,2-phenylenediamine to generate 2-phenyl-1*H*-benzo[d]imidazole as the main product (Fig. 1). The expected product was isolated using column chromatography, and analyzed by GC-MS, ^{1}H NMR and ^{13}C NMR. Opening studies aimed at the impression of temperature on the yield of the expected product. The reaction was executed in chlorobenzene under an oxygen atmosphere for 7 hrs, using 1,2-phenylenediamine:benzylamine mole proportion of 1:2, at 1,2-phenylenediamine concentration of 0.5 M, in the presence of 5 mol% catalyst, at ambient temperature of 60 ºC, 100 ºC, 110 ºC, 120 ºC, and 130 ºC, respectively. It was spotted that only 5% yield of 2-phenyl-1*H*-benzo[d]imidazole was recognized after 7 hrs at ambient temperature. The conversion also carried on with obstacle at 60 ºC, offering only 8% yield after 7 hrs. Boosting the temperature contributed a notable augmentation in the yield of 2-phenyl-1*H*-benzo[d]imidazole, with 26% and 66% yields being recorded after 7 hrs for the reaction conducted at 100 ºC and 110 ºC, respectively. It was possible to improve the yield to 70% after 7 hrs when the reaction temperature was increased to 120 ºC. Experimental data displayed that the cyclization reaction between benzylamine and 1,2-phenylenediamine utilizing the framework catalyst could proceed to 92% yield after 7 hrs at 130 ºC (Fig. 2).

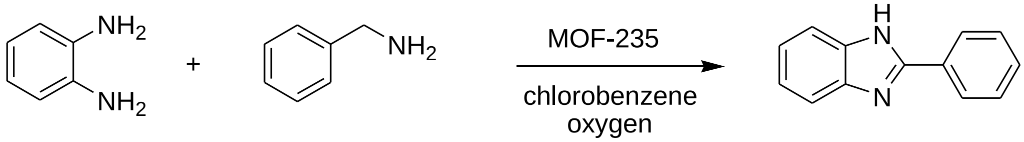


Fig. 1: The oxidative condensation of benzylamine with1,2-phenylenediamine utilizing MOF-235 catalyst

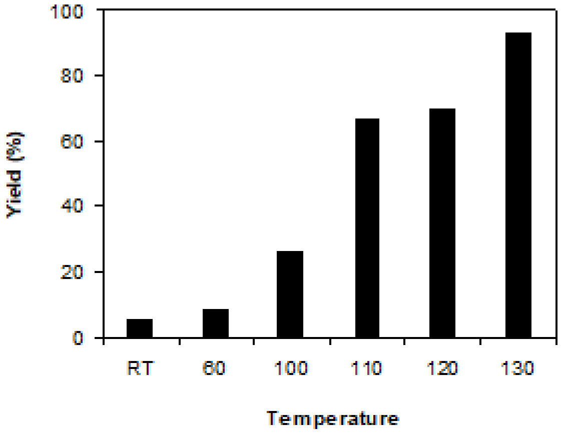


Fig. 2: Yields of 2-phenyl-1H-benzo[d]imidazole vs temperature

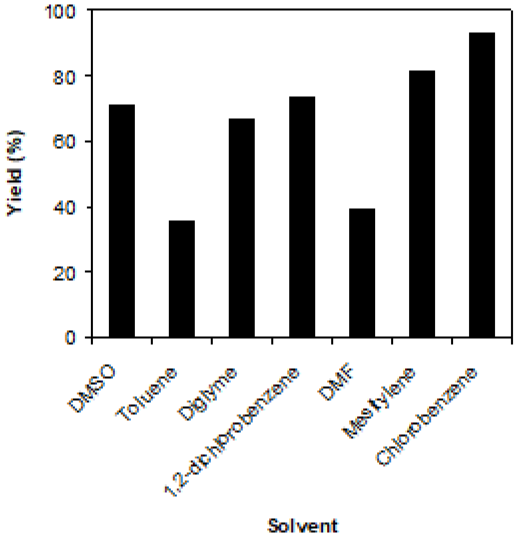


Fig. 3: Yields of 2-phenyl-1H-benzo[d]imidazole vs solvent

For reactions utilizing solid catalysts, the reaction rate might be considerably altered by the solvent. In the previous report of the iron-catalyzed cyclization between 2-amino/mercapto/hydroxyanilines and benzylamines, Gopalaiah and Chandrudu (2015) performed the conversion in different solvents, and pointed out that chlorobenzene should be used. It was consequently determined to inspect the formation of 2-phenyl-1*H*-benzo[d]imidazole in various solvents. The reaction was conducted at 130 ºC under an oxygen atmosphere for 7 hrs, in the presence of 5 mol% catalyst, utilizing 1,2-phenylenediamine:benzylamine mole proportion of 1:2, at 1,2-phenylenediamine concentration of 0.5

M, in DMSO (DMSO = dimethyl sulfoxide), diglyme, 1,2-dichlorobenzene, DMF, mesitylene, and chlorobenzene as solvent, respectively. Compared to other solvents, DMF offered poorest performance, though the conversion could provide 39% yield of 2-phenyl-1*H*-benzo[d]imidazole after 7 h. The reaction continued more effortlessly in diglyme, DMSO, and 1,2-dichlorobenzene, reaching 66%, 71%, and 73% yields, respectively, after 7 hrs. The yield of 2-phenyl-1*H*-benzo[d]imidazole could be upgraded to 81% for the reaction executed in mesitylene. Chlorobenzene emerged as the solvent of choice for the reaction between 1,2-phenylenediamine and benzylamine with 92% yield of the expected product being recorded after 7 h (Fig. 3).

Having these data, it is continuously determined to explore the influence of catalyst quantity on the generation of 2-phenyl-1*H*-benzo[d]imidazole. The reaction was performed at 130 °C in chlorobenzene under an oxygen atmosphere for 7 hrs, utilizing 1,2-phenylenediamine:benzylamine molar ratio of 1:2, at 1,2-phenylenediamine concentration of 0.5 M, in the presence of 2.5 mol%, 5 mol%, 7.5 mol%, and 10 mol% catalyst, respectively. As mentioned earlier, the reaction utilizing 5 mol% catalyst could offer 92% yield after 7 hrs. Dropping the catalyst quantity to 2.5 mol% caused a loss in the yield of the predicted product, though 70% yield was yet monitored after 7 hrs. It must be noted that 11% yield of 2-phenyl-1*H*-benzo[d]imidazole was detected after 7 hrs without using the catalyst, hence signifying the demand of the solid catalyst for the conversion. Expanding the catalyst quantity to more than 5 mol% was unreasonable as the yield of the benzimidazole was not intensified tremendously (Fig. 4). Indeed, Gopalaiah and Chandrudu (2015) previously employed 5 mol% $FeBr_2$ as catalyst for the coupling of 2-amino/mercapto/hydroxyanilines with benzylamines to produce substituted 1,3-benzazoles (Gopalaiah *et al.*, 2015). Additionally, it was recognized that the reactant mole proportion displayed a marked influence on the generation of 2-phenyl-1*H*-benzo[d]imidazole. The reaction deploying one equivalent of benzylamine afforded 59% yield after 7 hrs, while 71% yield was recorded for that employing 1.5 equivalents of benzylamine. This number could be upgraded to 92% and 96% when 2 and 2.5 equivalents of benzylamine, respectively, were utilized (Fig. 5).

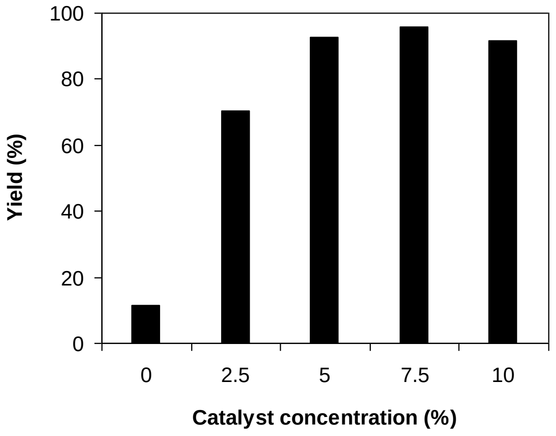


Fig. 4: Yields of 2-phenyl-1*H*-benzo[d]imidazole vs catalyst concentration

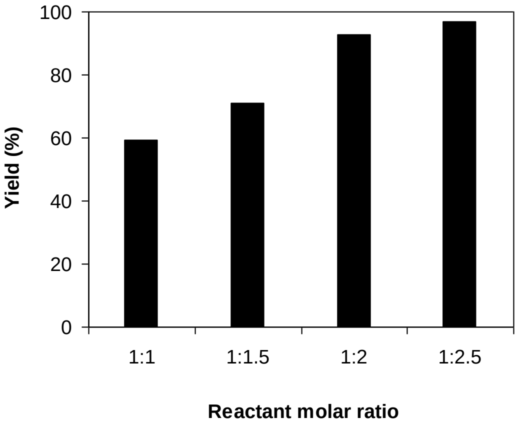


Fig. 5: Yields of 2-phenyl-1*H*-benzo[d]imidazole vs reactant mole proportion

As the reaction between 1,2-phenylenediamine and benzylamine to generate 2-phenyl-1*H*-benzo[d]imidazole using the framework catalyst was executed in liquid phase, the likelihood of leaching must be studied. In a number of circumstances, as a result of the leaching phenomenon, homogeneous catalysis donated dramatically to the transformation. In order to verify that 2-phenyl-1*H*-benzo[d]imidazole was generated via heterogeneous catalysis, the leaching experiment was conducted. The reaction was executed at 130 °C in chlorobenzene under an oxygen atmosphere for 7 hrs, in the presence of 5 mol% catalyst, utilizing 1,2-phenylenediamine:benzylamine mole proportion of 1:2, at 1,2-phenylenediamine concentration of 0.5 M. The solid catalyst was isolated after 2-hour reaction time by centrifugation. The solution phase was then transported to a new flask, and heated at 130 °C with magnetic stirring for extra 5 hrs under argon. It was noticed that no more 2-phenyl-1*H*-benzo[d]imidazole was generated from the reaction between 1,2-phenylenediamine and benzylamine in the absence of the solid catalyst

(Fig. 6). These data would denote that the cyclization of 1,2-phenylenediamine with benzylamine to generate 2-phenyl-1*H*-benzo[d]imidazole was only possible in the attendance of the framework catalyst, and hence verifying that the reaction progressed via truly heterogeneous catalysis.

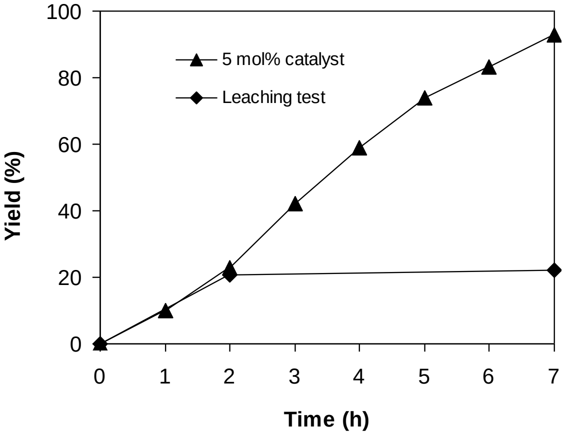


Fig. 6: Leaching test indicated no contribution from homogeneous catalysis of active species leaching into reaction solution

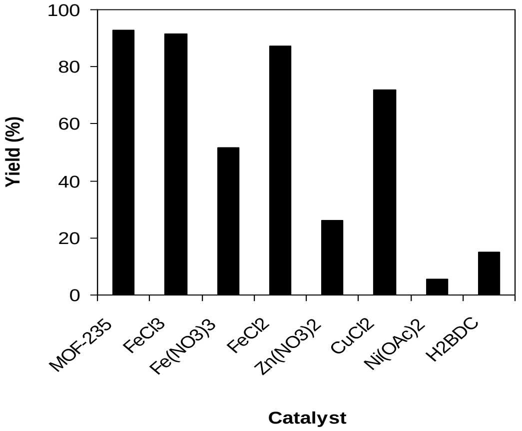


Fig. 7: Yields of 2-phenyl-1*H*-benzo[d]imidazole with various homogeneous catalysts

The catalytic performance of MOF-235 in the reaction between 1,2-phenylenediamine and benzylamine to generate 2-phenyl-1*H*-benzo[d]imidazole was correlated with a number of homogeneous catalysts. The reaction was conducted at 130 ºC in chlorobenzene under an oxygen atmosphere for 7 hrs, in the presence of 5 mol% catalyst, utilizing 1,2-phenylenediamine:benzylamine mole proportion of 1:2, at 1,2-phenylenediamine concentration of 0.5 M. $FeCl_3$ expressed similar catalytic activity to the framework in the synthesis of 2-phenyl-1*H*-benzo[d]imidazole, with 91% yield being noticed after 7 hrs. $FeCl_2$ was less catalytically active than $FeCl_3$, though 87% yield was yet achieved after 7 hrs. However, the $Fe(NO_3)_3$-catalyzed cyclization reaction carried on with dilemma, reaching only 51% yield of the benzimidazole after 7 hrs. $CuCl_2$ displayed reasonable efficiency for the reaction, and 71% yield of the expected product was detected after 7 hrs. $Ni(OAc)_2$ and $Zn(NO_3)_2$ should not be used as catalyst for this transformation. 1,4-Benzenedicarboxylic acid, the organic linker used to prepare the framework, disclosed low activity (Fig. 7). To underscore the impressive aspect of MOF-235 in the reaction between 1,2-phenylenediamine and benzylamine to generate 2-phenyl-1*H*-benzo[d]imidazole, its catalytic activity was then differentiated with other MOFs. Among these heterogeneous catalysts, MOF-235 displayed the best presentation, with 92% yield of the expected product being realized after 7 hrs (Fig. 8).

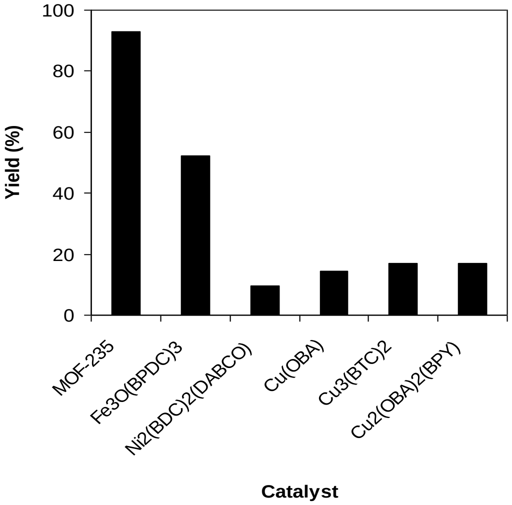
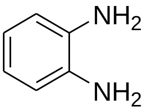
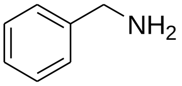
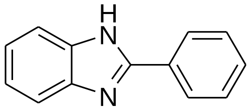
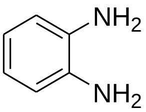
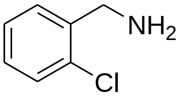
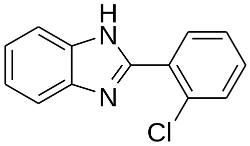
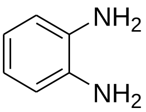
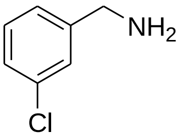
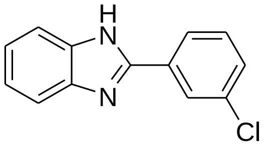
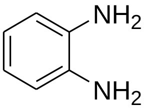
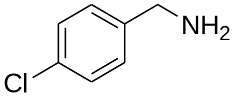
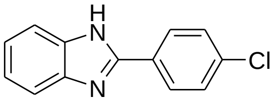
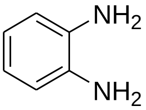
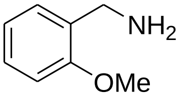
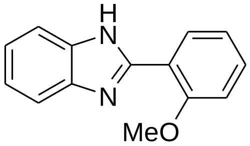
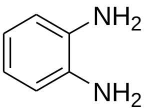
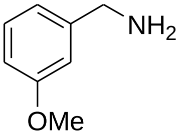
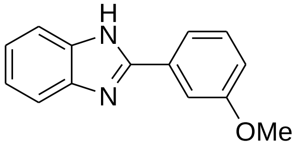
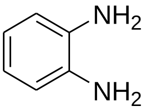
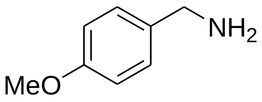
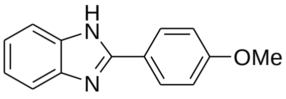
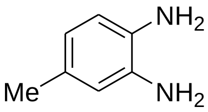
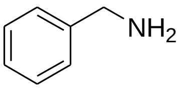
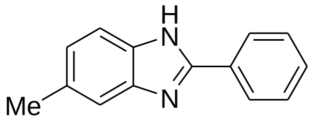
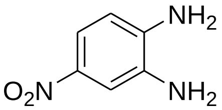
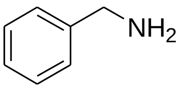
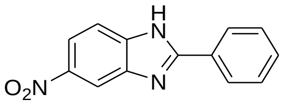
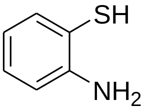
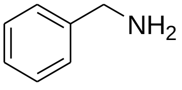
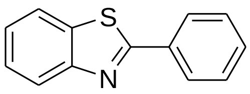


Fig. 8: Yields of 2-phenyl-1*H*-benzo[d]imidazole with numerous MOF-based catalysts

Table 1: The reaction of 1,2-phenylenediamines with benzylamines utilizing the framework catalyst

Entry	1,2-Phenylenediamines	Benzylamines	Products	Isolated yields (%)
1				92
2				79
3				90
4				74
5				74
6				79
7				66
8				75
9				96
10				87

The research was then continued to the oxidative condensation of 1,2-phenylenediamine with different benzylamines, including 2-chlorobenzylamine, 3-chlorobenzylamine, 4-chlorobenzylamine, 2-methoxybenzylamine, 3-methoxybenzylamine, and 4-methoxybenzylamine, respectively. The reaction was executed at 130 ºC in chlorobenzene under an oxygen atmosphere for 7 hrs, in the presence of 5 mol% catalyst, utilizing 1,2-phenylenediamine:benzylamine molar ratio of 1:2, at 1,2-phenylenediamine concentration of 0.5 M. The reaction between 1,2-phenylenediamine with benzylamine produced 2-phenyl-1*H*-benzo[d]imidazole in 92% isolated yield. The reaction of 1,2-phenylenediamine with 2-chlorobenzylamine afforded 79% yield of 2-(2-chlorophenyl)-1*H*-benzo[d]imidazole, while 90% yield of 2-(3-chlorophenyl)-1*H*-benzo[d]imidazole was recorded for the case of 3-chlorobenzylamine. 4-Chlorobenzylamine was less reactive towards the reaction with 1,2-phenylenediamine than 2-chlorobenzylamine and 3-chlorobenzylamine, though 74% yield of 2-(4-chlorophenyl)-1*H*-benzo[d]imidazole was still obtained. The existence of an electron-donating substituent in benzylamine structure caused a decline in the yield of expected product. Indeed, 74% yield of 2-(2-methoxyphenyl)-1*H*-benzo[d]imidazole, 79% yield of 2-(3-methoxyphenyl)-1*H*-benzo[d]imidazole, and 66% yield of 2-(4-methoxyphenyl)-1*H*-benzo[d]imidazole were obtained for the reaction of 1,2-phenylenediamine with 2-methoxybenzylamine, 3-methoxybenzylamine, and 4-methoxybenzylamine, respectively. In a second experiment series, the reaction between benzylamine and 4-methyl-1,2-phenylenediamine, 4-nitro-1,2-phenylenediamine, and 2-aminobenzenethiol, respectively, was also investigated, and reasonable isolated yields were achieved (Table 1).

4 CONCLUSIONS

Iron-organic framework MOF-235 was synthesized, and subsequently used as a productive heterogeneous catalyst for the synthesis of benzimidazoles *via* oxidative condensation of primary amines with 1,2-diaminoarenes. The nature of solvent exhibited a significant impact on the formation of benzimidazoles, and chlorobenzene emerged as the most suitable solvent for the reaction. The MOF-235 was found to be more catalytically active for the oxidative condensation of primary amines with 1,2-diaminoarenes than other MOFs including $Fe_3O(BPDC)_3$, $Ni_2(BDC)_2(DABCO)$, Cu(OBA), $Cu_3(BTC)_2$, and $Cu_2(OBA)_2(BPY)$. Leaching tests verified that the cyclization of 1,2-phenylenediamine with benzylamine to generate 2-phenyl-1*H*-benzo[d]imidazole was only possible in the presence of the iron-based framework catalyst, thus indicating that the transformation progressed via truly heterogeneous catalysis. The feature that numerous benzimidazoles could be achieved using the MOF-based catalyst would be profitable to the pharmaceutical and chemical industry.

ACKNOWLEDGMENTS

We would like to thank the Vietnam National University – Ho Chi Minh City (VNU-HCM) for financial support under Project No. B2017-20-08.

REFERENCES

Anbia, M., Hoseini, V., and Sheykhi, S., 2012. Sorption of methane, hydrogen and carbon dioxide on metal-organic framework, iron terephthalate (MOF-235). Journal of Industrial and Engineering Chemistry, 18(3): 1149-1152.

Cele, M.N., Friedrich, H.B, and Bala, M.D., 2014. Liquid phase oxidation of *n*-octane to C8 oxygenates over modified Fe-MOF-5 catalysts. Catalysis Communications, 57: 99-102.

Chae, H.K., Siberio-Perez, D.Y., Kim, J., *et al.*, 2004. A route to high surface area, porosity and inclusion of large molecules in crystals. Nature, 427(6974): 523-527.

Chen, Y.-X., Qian, L.-F., Zhang, W. and Han, B., 2008. Efficient Aerobic Oxidative Synthesis of 2-Substituted Benzoxazoles, Benzothiazoles, and Benzimidazoles Catalyzed by 4-Methoxy-TEMPO. Angewandte Chemie International Edition, 47(48): 9330-9333.

Dhakshinamoorthy, A., and Garcia, H., 2012. Catalysis by metal nanoparticles embedded on metal–organic frameworks. Chemical Society Reviews, 41(15): 5262-5284.

Diao, X., Wang, Y., Jiang, Y., and Ma, D., 2009. Assembly of Substituted 1*H*-Benzimidazoles and 1,3-Dihydrobenzimidazol-2-ones via CuI/L-Proline Catalyzed Coupling of Aqueous Ammonia with 2-Iodoacetanilides and 2-Iodophenylcarbamates. Journal of Organic Chemistry, 74(20): 7974-7977.

Gopalaiah, K., and Chandrudu, S. N., 2015. Iron(II) bromide-catalyzed oxidative coupling of benzylamines with *ortho*-substituted anilines: synthesis of 1,3-benzazoles. RSC Advances, 5(7): 5015-5023.

Haque, E., Jun, J.W., and Jhung, S.H., 2011. Adsorptive removal of methyl orange and methylene blue from aqueous solution with a metal-organic framework material, iron terephthalate (MOF-235). Journal of Hazardous Materials, 185(1): 507-511.

Jusoh, N.W.C., Jalil, A.A., Triwahyono, S., and Mamat, C.R., 2015. Tailoring the metal introduction sequence onto mesostructured silica nanoparticles framework: Effect on physicochemical properties and photoactivity. Applied Catalysis A: General, 492: 169-176.

Kuppler, R.J., Timmons, D.J., Fang, Q.-R., Li, J.-R., Makal, T.A., Young, M.D., Yuan, D., Zhao, D. Zhuang, W., and Zhou, H.-C., 2009. Potential applications of metal-organic frameworks. Coordination Chemistry Reviews, 253(23-24): 3042-3066.

Leadbeater, N.E., and Marco, M., 2002. Preparation of Polymer-Supported Ligands and Metal Complexes for Use in Catalysis. Chemical Reviews, 102(10): 3217-3274.

Leus, K., Liu, Y.-Y., Meledina, M., Turner, S., Tendeloo, G.V., and Voort, P.V.D., 2014. A Mo^{VI} grafted Metal Organic Framework: Synthesis, characterization and catalytic investigations. Journal of Catalysis, 316: 201-209.

Liu, J., Chen, L., Cui, H., Zhang, J., Zhang, L., and Su, C.-Y., 2014. Applications of metal–organic frameworks in heterogeneous supramolecular catalysis. Chemical Society Reviews, 43(16): 6011-6061.

Lv, X., and Bao, W., 2009. Copper-Catalyzed Cascade Addition/Cyclization: An Efficient and Versatile

Synthesis of N-Substituted 2-Heterobenzimidazoles. Journal of Organic Chemistry, 74(15): 5618-5621.

Mahesh, D., Sadhu, P., and Punniyamurthy, T., 2015. Copper(I)-Catalyzed Regioselective Amination of *N*-Aryl Imines Using $TMSN_3$ and TBHP: A Route to Substituted Benzimidazoles. Journal of Organic Chemistry, 80(3): 1644-1650.

Mason, *J.A.,* Veenstra, *M., and* Long, *J.R.,* 2014. Evaluating metal–organic frameworks for natural gas storage. Chemical Science, 5(1): 32-51.

Noël, S., Cadet, S., Gras, E., and Hureau, C., 2013. The benzazole scaffold: a SWAT to combat Alzheimer's disease. Chemical Society Reviews, 42(19): 7747-7762.

Pizzetti, M., Luca, E.D., Petricci, E., Porcheddu, A., and Taddei, M. 2012. A General Approach to Substituted Benzimidazoles and Benzoxazoles *via* Heterogeneous Palladium-Catalyzed Hydrogen-Transfer with Primary Amines. Advanced Synthesis & Catalysis, 354(13): 2453-2464.

Singh, S., Bharti, N., and Mohapatra, P., 2009. Chemistry and natuarally occurring antiamoebic agents. Chemical Reviews, 109(5): 1900-1947.

Tranchemontagne, D.J., Ni, M.O.k. Z., and Yaghi, O.M., 2008. Reticular Chemistry of Metal–Organic Polyhedra. Angewandte Chemie International Edition, 47(28): 5136-5147.

Wang, K., Feng, D., Liu, T.-F., Su, J., Yuan, S., Chen, Y.-P., Bosch, M., Zou, X., and Zhou, H.-C., 2014. A Series of Highly Stable Mesoporous Metalloporphyrin Fe-MOFs. Journal of the American Chemical Society, 136(40): 13983-13986.

Xiao, T., Xiong, S., Xie, Y., Dong, X., and Zhou, L., 2013. Copper-catalyzed synthesis of benzazoles *via* aerobic oxidative condensation of *o*-amino/mercaptan/hydroxyanilines with benzylamines. RSC Advances, 3(36): 15592-15595.