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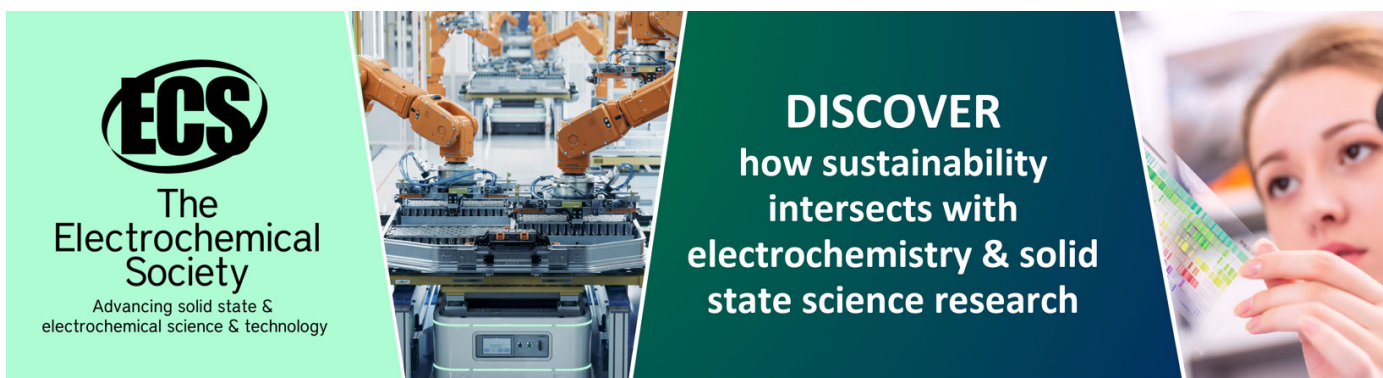
Applications of bimetallic metal-organic frameworks (Ni/Fe-Base) catalyzed for reaction synthesis benzimidazole derivatives

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Applications of bimetallic metal-organic frameworks (Ni/Fe-Base) catalyzed for reaction synthesis benzimidazole derivatives

O T K Nguyen^{1,*}, H T Vu,² Q H Tran³, B T Hoang⁴, H L T Anh⁵, S T Do³

¹Center of Excellence for Green Energy and Environmental Nanomaterials (CE@GrEEN), Nguyen Tat Thanh University, 300A Nguyen Tat Thanh, District 4, Ho Chi Minh City 755414, Vietnam

²Faculty of Hydro-Meteorology, HCMC University of Natural Resources and Environment, Ho Chi Minh City, Viet Nam

³Laboratory of Material and Environment Technology, Institute of Chemistry, Vietnam Academy of Science and Technology, Hanoi City, Viet Nam

⁴Institute of Natural Products Chemistry, Vietnam Academy of Science and Technology, Hanoi, Vietnam

⁵Mientrung Institute for Scientific Research, Vietnam Academy of Science and Technology, Vietnam

*ntkoanh@ntt.edu.vn

Abstract. Ni/Fe-Base, a Bimetallic Metal-Organic Frameworks (BMOFs), was established for the first time to present photocatalytic activity in the decomposition of rhodamine B (RhB) under a compact fluorescent daylight lamp. However, the BMOFs material was not mainly utilized to perform catalytic for organic synthesis reaction. In this study, the biologically active benzimidazole derivatives were synthesized from o-phenylenediamine and carboxylic acid in the chlorobenzene as a solvent with the presence of Ni/Fe-Base for high yields (approx. 84%) using isolated chromatography column. The characteristic of products was analyzed utilizing NMR Spectroscopy and GC-MS. The structure of solid catalyst was analyzed utilizing a diversity of different techniques, including in X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), and nitrogen physisorption measurements (BET). The Ni/Fe-Base catalytic might be easily isolated from the reaction compound, and might be recycled five runs without a considerable reduction in catalyst activity.

1. Introduction

Benzimidazole derivatives are important heterocyclic compounds because of its scope range applications in the pharmaceutical industry. Sometimes, the medicinal chemists have still interested in the heterocyclic samples of benzimidazole, because there are plenty of curative applications and effectively demonstrated druggability [1]. Several benzimidazole derivatives with different pharmacological effects, consisting of antifungal, anti-helminthic, anti-HIV, antihistaminic, antiulcer, cardiostonic, antihypertensive and neuroleptic are in clinical use [2][3]. Moreover, benzimidazoles have important donation to industrial chemistry applications, such as in cases of chemical UVB filters,



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pigments, optical brighteners for coatings, and thermostable membranes for fuel cells [4]. For instance, some of benzimidazole derivatives were utilized in kinds of 1. Dovitinib, 2. Tiabendazole, 3. Pimobendan, and 4. Hoechst stain drugs (Refer figure 1).

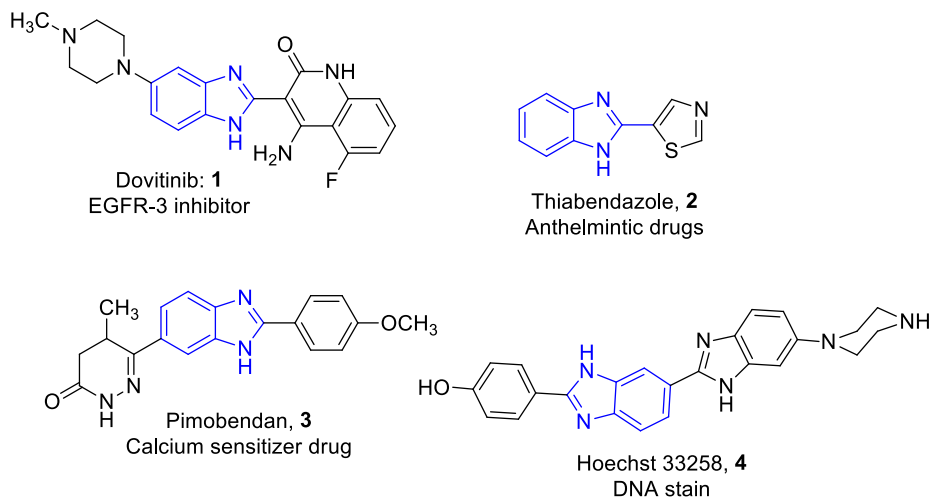


Figure 1. Prototypical examples of benzimidazole concluding crucial molecules [5].

Typically, the traditional method of synthesis benzimidazole is the condensation of 1,2-diaminobenzene with carboxylic acid or carboxylic acid-derivatives. Another broadly utilized strategy includes the condensation o-phenylenediamine with aldehydes or alcohols with the presence of a variety of oxidizing agents [6]. However, most of this approach undergo either from the utility of stoichiometric quantity of oxidizing agents or expensive catalysts or homogeneous catalysts. In 2008, Harjyoti Thakuria *et al.* [7] reported research about synthesis method of benzimidazole derivatives which obtained under solvent-free conditions with high efficiency (80–95%). However, this reaction was carried out at a high temperature of around 140 °C. Similarly, Hossein Naeimi *et al.* [8], in 2017, illustrated that they have successfully synthesized for heterocyclization of 1,2-phenylenediamine and aldehydes utilizing 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (60 mol% DDQ) as oxidizing reagent with the presence of microwave irradiation (approx. 89%). In these conditions, although the reaction achieved high yields and short reaction time, authors have used a big amount of oxidant agent in a reaction which was expensive.

In this study, we demonstrate and discuss results on the synthesis of benzimidazoles directly between 1,2-amino benzene and phenylglyoxylic acid. The reaction was catalyzed by the heterogeneous catalyst of Ni/Fe-BDC with using chlorobenzene as a reaction solvent.

2. Experimental section

2.1. Preparation of Ni/Fe-BDC catalyst

Materials Ni/Fe-BDC were synthesized by hydrothermal method, according to the calibrated process of Vinh Huu Nguyen *et al.* [9]. Accordingly, the mixture of terephthalic acid (H₂BDC, 9 mmol), FeCl₃·6H₂O (4.6 mmol) and 1.4 mmol of Ni(NO₃)₂·6H₂O were dissolved in the solvent of N,N-dimethylformamide (DMF, 60 mL). The act of mixing was then stirred to form a homogeneous mixture, the mixture was added to the autoclave Teflon and heated at 100 °C for 3 days. Finally, the solid material was dried at 60 °C for 24 h, yielding 0.8525 g Ni/Fe-BDC in the form of orange crystals.

2.2. General procedure for the synthesis of 2-phenyl-1H-benzo[d]imidazole

The compound of *o*-phenylenediamine (1 equiv, 0.2 mmol) and phenylglyoxylic acid (1 equiv, 0.2 mmol) were dissolved in a mixture of chlorobenzene (1.5 mL), water (0.5 mL) in a 15 mL reaction flask. Reaction compound was then stirred on a magnetic stirrer and heated at 100 °C in 24 hours with the presence of 10 mol % Ni/Fe-BDC catalytic under air, until the finish consumption of *o*-phenylenediamine as observed by TLC. After the reaction was stopped, the compound was cooled to room temperature, and diluted in ethylacetate and washed with distilled water. The organic component was lost water over anhydrous Natri sulfate, separated and the solvent was evaporated under decrease pressure. The raw material was isolated by silica column chromatography (with the solvent mixture of ethylacetate: hexane = 1: 2) to afford the desired product and analyzed by ¹H-NMR, ¹³C-NMR spectra.

Prepared as shown in the general experimental procedure and purified on silica gel (hexane/ethyl acetate = 2:1): light yellow solid, 84% yield. ¹H-NMR (500 MHz, CDCl₃) δ 12.88 (s, 1H), 8.18 – 8.16 (m, 2H), 7.66 (d, *J* = 7.5 Hz, 1H), 7.57 – 7.48 (m, 4H), 7.23 – 7.17 (m, 2H); ¹³C-NMR (125 MHz, CDCl₃) δ 151.16, 143.76, 134.94, 130.12, 129.77, 128.88, 126.37, 122.46, 121.60, 118.82, 111.25.

3. Results and discussion

3.1. Characteristic of catalyst

The physical and chemical characteristic of catalyst was analyzed by XRD, FTIR, Raman, SEM, TGA, and nitrogen physisorption measurements. According to the XRD pattern of the catalyst sample, the crystallinity of Ni/Fe-BDC was sharply confirmed in Figure 1. From figure 2A, we can see six well-defined diffraction peaks at 7.5, 8.0, 13.0, 16.0, 17.0, and 27°, which is in accordance with that of Ni-MOFs in previous report literature [10][11]. Besides, the main diffraction peaks which appear at 9.0, 11.0, 17.5, 18.0, 22.5, and 25.5° are suitable for MIL-53(Fe) in literature [12][13]. To prepare catalyst material, the thermal stability of Ni/Fe-BDC is vital and characterized by TGA in the atmosphere at a heating rate of 1 °C/min. The TGA curve which is in figure 2B, it depicted that has three stages for mass loss of Ni/Fe-BDC sample with rising temperature. The first stage material reduces around 17% weight below 200 °C that can be assigned to the withdrawal of adsorbed water and DMF. The second stage mass loss between 200 and 376 °C is around 20%. This result showed that have a little residue of DMF and decomposed a little of oxygen-containing groups in the framework. With the rising temperature, the weight loss of stage 3 from 370 °C to 540 °C around 31.03% can be attributed to the decomposition of aromatic rings, the confirmation of nickel oxides, iron oxides and the change between metal oxides. The completion of the decomposition process of sample residues around 23.32% weight, which can be metal oxides and carbon composition. TGA analysis results showed that Ni/Fe-BDC materials have high thermal stability and can completely meet the thermal stability requirements in most organic synthesis reactions.

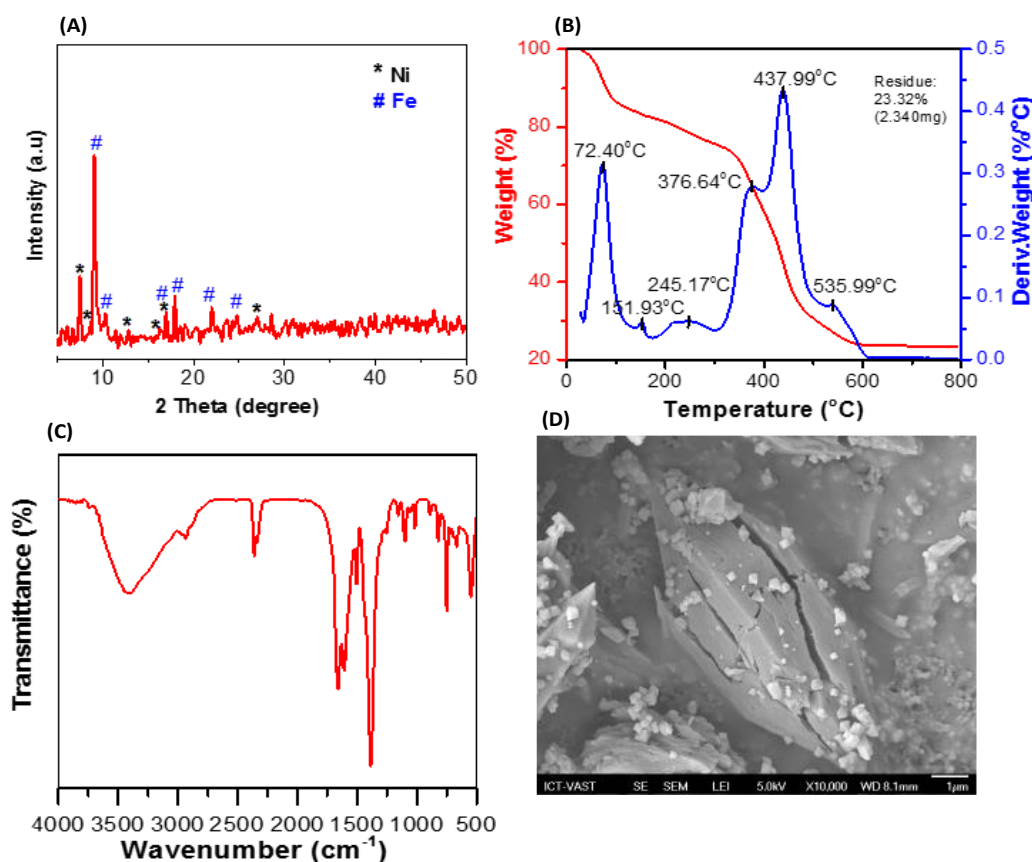


Figure 2. Shown in X-ray powder diffraction (A), TGA curves (B), FTIR spectra (C) and SEM image (D) of Ni/Fe-BDC material.

The FTIR spectra of Ni/Fe-BDC (Refer figure 2C) illustrates adsorption peaks at around 3387 cm^{-1} , 1657 cm^{-1} , 1504 cm^{-1} , 1391 cm^{-1} , and 749 cm^{-1} , which are the features vibrational bands of the framework $\nu(\text{O-H})$, $\nu\text{N}(\text{C=O})$, $\nu(\text{COO})$ and $\delta(\text{C-H})$ groups in the catalyst material. The Ni/Fe-BDC also shows a few of adsorption peaks at around 720 cm^{-1} and 547 cm^{-1} that are the characteristic bond of Fe_2NiO and FeO (or NiO), confirming the successful preparation of Ni/Fe-BDC. SEM image was used to study the surface properties and topography of Ni/Fe-BDC (Refer figure 2D). The SEM result showed that Ni/Fe-BDC crystals had micro-size hexagonal rods and other smaller pseudo-spherical particles.

A typical nitrogen physisorption isotherm at 77 K and the mesopore size dispersion bend of samples counted by Barrett–Joyner–Halenda (BJH) model of Ni/Fe-BDC were shown in figure 3A. The BET result indicated that surface range of Ni/Fe-BDC is around $247\text{ m}^2/\text{g}$, and the pore width is around 13 nm (Refer figure 3B). Basing on these results of XRD, FT-IR, SEM, DSC, TGA, and BET was described above, illustrated that a compound metal Ni/Fe-BDC was successfully synthesized by the solvothermal method.

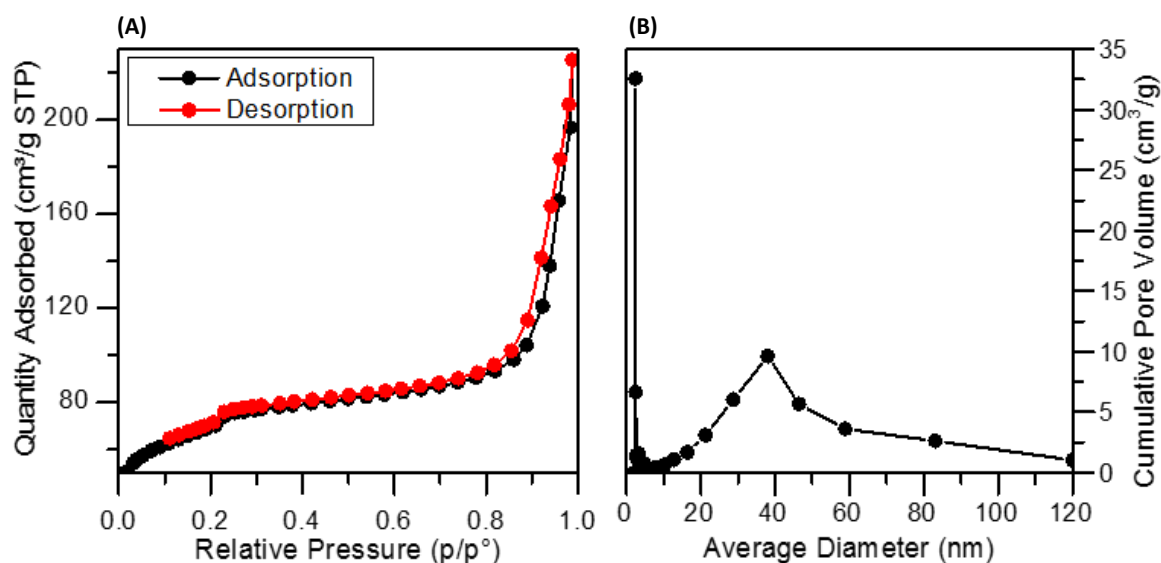


Figure 3. N₂ adsorption-desorption isotherms (A) and pore size distributions (B) of Ni/Fe-BDC samples.

3.2. Catalytic studies

The catalytic activity of Ni/Fe-BDC was studied for the condensation reaction of 2-phenyl-1*H*-benzo[*d*]imidazole from *o*-phenylenediamine with phenylglyoxylic acid as shown in figure 4. Effects of several factors on the reaction were investigated, including temperatures, catalysts loading, reagent ratios, kinds of solvent and various substrates on conversions.

As is known, the temperature is a factor that influences the speed and selectivity of the product. This reaction has been conducted at many different temperatures depending on the catalyst nature, a ligand as well as the used substance and the reaction temperature. The lower the reaction temperature, the longer reaction time is required even up to 24 hours [14]. In this study, the reaction was performed in chlorobenzene as a solvent (2 mL) with a molar ratio of *o*-phenylenediamine : phenylglyoxylic acid is 1:1, using 15 mol% catalyst is Ni/Fe-BDC at temperatures of room temperature, 60 °C, 80 °C, 100 °C and 120 °C for 16 hours. The research results in figure 5A illustrates that the efficiency of the reaction depends significantly on the reaction temperature. The reaction did not seemingly occur at room temperature, at 60 °C only 21% and 80 °C only 45%. Typically, temperature plays a vital role in promoting a rapid response to equilibrium, but this is probably only appropriate when temperatures increase to 100 °C. Experiments show that when the temperature enhances from 100 to 120 °C, the reaction efficiency rises insignificant from 84% to 88%.

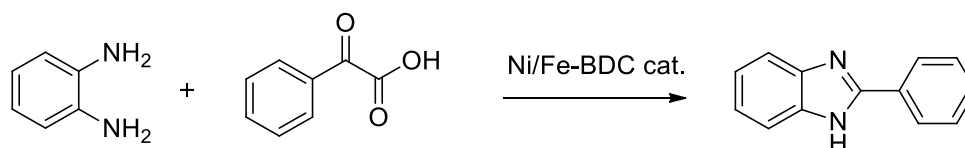


Figure 4. The reaction of *o*-phenylenediamine with phenylglyoxylic acid.

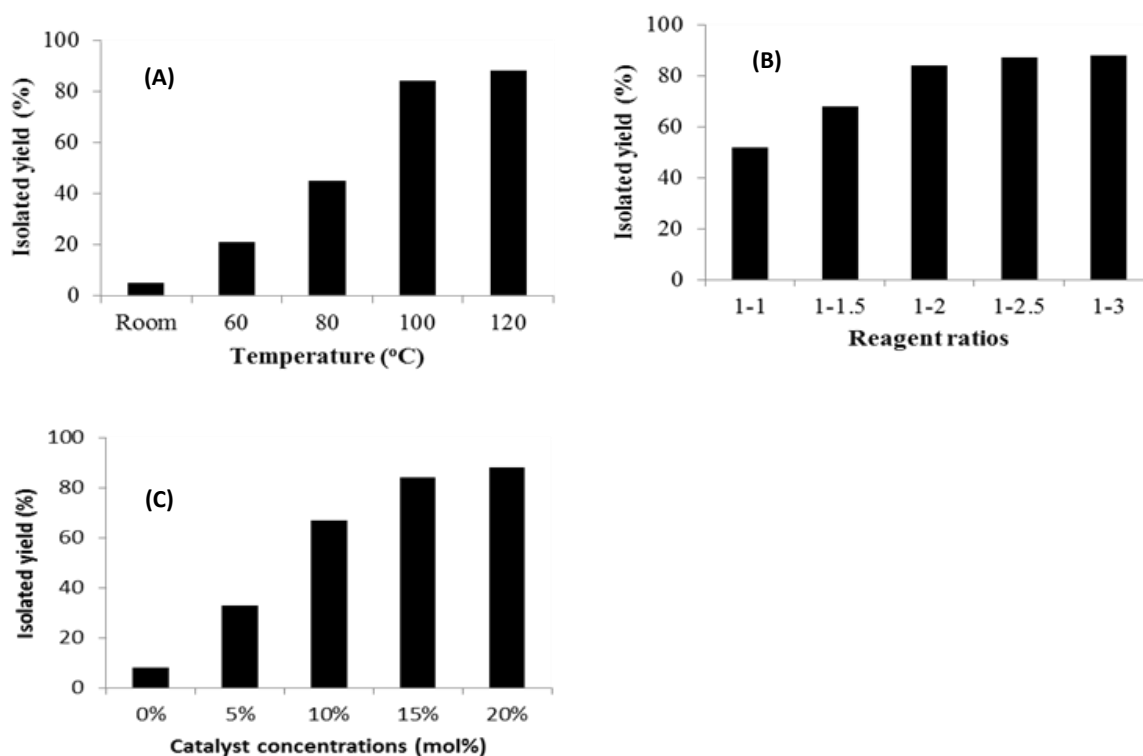


Figure 5. Effects of temperatures (A), reagent ratios (B) and catalyst concentrations (C) on conversion of reaction.

Another important parameter that is often of interest when conducting the kinetic survey of a reaction is the proportion of reagent used. Therefore, we decided to conduct reactions at 100 °C, in chlorobenzene solvents in the presence of 15 mol% catalysts, using molar proportions of *o*-phenylenediamine: phenylglyoxylic acid is 1:1, 1:1.5, 1:2, 1:2.5, and 1: 3. Observing the results of the transformation in figure 5B, we can see that with a ratio of 1: 1, the reaction rate is more or less restricted than when using higher ratios. With the conversion after 16 hours reached nearly 52%. When the ratio is increased to 1:1.5, 1: 2, after 16 hours, the conversion rate is 68% and 84%, and when it increases to 1:2.5, and 1: 3 ratios, the conversion rate increases insignificant around 87%, and 88%. So, the ratio of 1:2 was used for the next experiment. The catalyst concentrations, concerning the Ni/Fe content in the Ni/Fe-BDC, were studied in the range of 0 - 20 mol % corresponding to 2-phenyl-1*H*-benzo[*d*]imidazole. The reaction was carried out with a reagent molar ratio of 1:2 in 1 mL chlorobenzene solvent at 100 °C for 16 hours. The results shown in figure 5C indicated that the higher catalyst concentrations, the higher reaction conversion was observed. The highest conversion (84%) was achieved at the catalyst concentration of 15%. As expected, reducing the catalyst concentration effected in a considerable drop in the reaction rate, with the efficiency of 67%, 33% to correspond with catalyst concentrations of 10%, 5%, and only 8% with non-catalyst.

In organic synthesis reactions, solvents are one of the important factors to react; in addition to dissolving the substances as well as products, the solvent also works to stabilize intermediate products. In some cases, the solvent may increase or decrease product metabolism depending on the nature of the solid catalyst [15][16]. Generally, the reaction occurred weakly in the toluene and dimethylformamide (DMF) solvents with 35%, 39%, respectively. When using DMSO or 1,4-dioxane solvents, the efficiency is around 70%. The efficiency reaction increases to 73% if acetonitrile is used as a solvent. The reaction obtained the highest efficiency of 84% when using chlorobenzene as a solvent (Refer figure 6A). The reaction was conducted with the presence of iron (III) chloride hexahydrate, iron (III) nitrate nonahydrate, iron (II) chloride tetrahydrate and nickel (II) nitrate hexahydrate as homogeneous catalysts for the reaction to compare catalytic activity with Ni/Fe-BDC

(Refer figure 6B). This studied result indicated that using iron (III) chloride hexahydrate and Ni/Fe-BDC offered the highest conversion of 89% and 84%. When using iron (III) nitrate nonahydrate, iron (II) chloride tetrahydrate and nickel (II) nitrate hexahydrate, the lower conversion were obtained with a conversion of 54%, 35%, and 55%, respectively. However, heterogeneous catalysts have an outstanding advantage over homogeneous catalysts for recovery and reuse after the reaction. So, Ni/Fe-BDC catalyst was used to comply with green chemistry criteria.

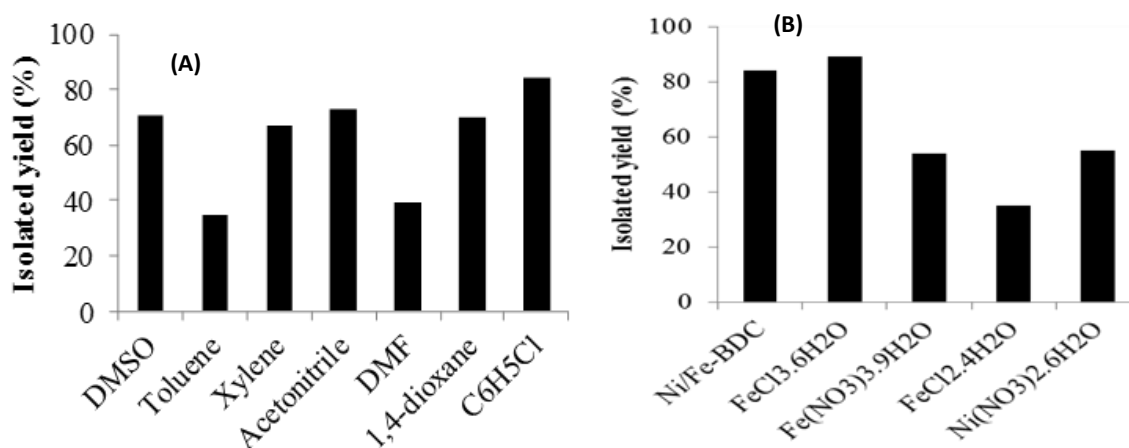


Figure 6. Effects of solvents (A) and homogeneous catalysts (B) on conversion reaction.

In order to eliminate the possibility that some active metal centers can be removed from the solid phase during the reaction, the result is that the reaction does not entirely occur under heterogeneous catalytic conditions. A controlled experiment called “leaching test” was performed on a synthesis of 2-phenyl-1*H*-benzo[*d*]imidazole. The reaction was carried out with the above optimal condition; the reaction temperature was 100 °C with using chlorobenzene as the reaction solvent, and the concentration of *o*-phenylenediamine was 0.13 M, using 15 mol % Ni/Fe-BDC as a catalyst. The reaction was stopped after 4 hours of reaction, analyzed the GC result at this time and centrifuged to remove solid catalysts. The solution after completely removing the catalyst was stirred for another 12 hours under the initial reaction conditions. The sample is further taken after each hour and analyzed for GC to monitor the change in performance when no solid catalyst is present. The results of the test of heterogeneity of catalysts are shown in figure 7A.

According to the principles of green chemistry, problems that should be deliberated when utilizing solid catalysts for organic transformations are the recoverability and the reusability of the catalyst. Therefore, Ni/Fe-BDC was separated from the mixture, washed with solvent and reused. The reaction was conducted at 100 °C using 15 mol % catalysts, reagent molar ratio of 1:2 in 16 hours. After finishing each reaction, the catalytic was recovered by centrifugation and washed thoroughly with DMF, and then exchanged with ethanol. The recovered catalyst was reactivated under vacuum at 60 °C for 6 hours. The recovered catalyst was then being run under the same condition as the initial reaction. The procedure was studied over five runs. According to the experimental result, the conversion was decreased slightly after fourth and fifth runs with a conversion of 80 % and 77 % respectively. It demonstrated that the Ni/Fe-BDC could be reutilized some times without a considerable reducing in catalytic activity (Refer figure 7B).

The Ni/Fe-MOF structure after the reaction was checked by the FTIR spectrum (Refer figure 7C), XRD pattern (Refer figure 7D) and compared with the fresh catalyst. The FTIR spectra and XRD result of the reused Ni/Fe-BDC showed that the structure of Ni/Fe-BDC was maintained after reaction in chlorobenzene solvent, at high temperature.

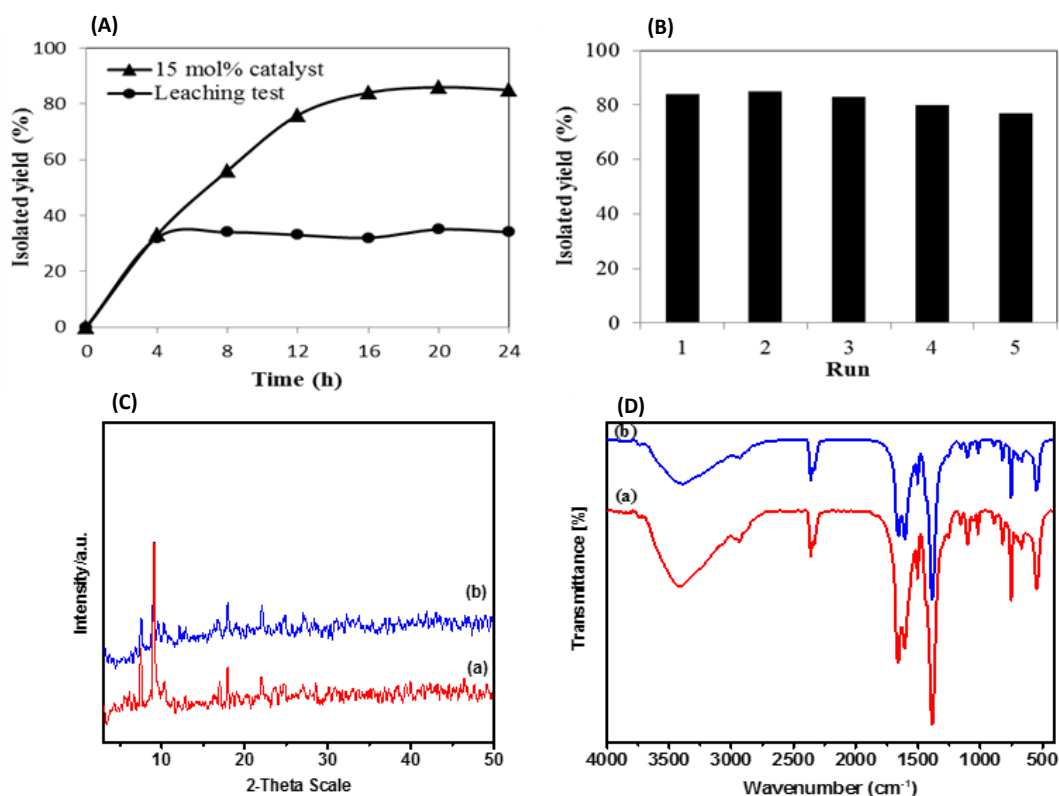


Figure 7. Test results of heterogeneity (A), reuse ability (B), XRD pattern (C) and FTIR spectra (D) of Ni/Fe-BDC (a) before and (b) after reused.

4. Conclusion

A highly porous material, Ni/Fe-BDC, was synthesized from iron (III) chloride hexahydrate, nickel (II) nitrate hexahydrate and terephthalic acid by a solvothermal approach in DMF solvent. Ni/Fe-BDC was analyzed by a diversity of modern techniques, consist of FT-IR, SEM, XRD, TGA, and nitrogen physisorption mensuration. These results revealed that Ni/Fe-BDC in this work has successfully synthesized and it is in comparison to previously reported studies. Moreover, the Ni/Fe-BDC showed that the effectively catalytic activity for reaction synthesis of 2-phenyl-1*H*-benzo[*d*]imidazole (approx. 84% yield) from *o*-phenylenediamine and phenylglyoxylic acid. Furthermore, the catalytic could be recycled five times without a considerable decrease of activities. The condensation reaction could merely progress with the presence of the solid Ni/Fe-BDC catalyst, and there was no donation from leached active species present in the liquid phase. These results indicated that Ni/Fe-BDC was a green heterogeneous catalyst.

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References

- [1] Ajani O O, Tolu-Bolaji O O, Olorunshola S J, Zhao Y and Aderohunmu D V. 2017 *J. Adv. Res.* **8** 703–12
- [2] Chawla A, Kaur R and Goyal A 2011 *J. Chem. Pharm. Res.* **3** 925–44
- [3] Chandrika N T, Shrestha S K, Ngo H X and Garneau-tsodikova S 2016 *s Bioorg. Med. Chem.* **24** 3680–6
- [4] Daw P, Ben-david Y and Milstein D 2017 *ACS Catal.* **2017**, **7** 7456–60

- [5] Jeshma Kovvuri, Burri Nagaraju, Ahmed Kamal and A K S 2016 *ACS Comb. Sci.* **18** 644–650
- [6] Das K, Mondal A and Srimani D 2018 *J. Org. Chem.* **83** 9553–60
- [7] Thakuria H and Das G 2008 *Arkivoc* **2008** 321–8
- [8] Naeimi H and Babaei Z 2017 *Green Chem. Lett. Rev.* **10** 129–33
- [9] Nguyen V, Nguyen T, Bach L, Hoang T, Bui Q, Tran L, Nguyen C, Vo D-V and Do S 2018 *Catalysts* **8** 487
- [10] Wang L, Wu Y, Cao R, Ren L, Chen M, Feng X, Zhou J and Wang B 2016 *ACS Appl. Mater. Interfaces* **8** 16736–43
- [11] Sun Q, Liu M, Li K, Han Y, Zuo Y, Chai F, Song C, Zhang G and Guo X 2017 *Synthesis of Fe/M (M = Mn, Co, Ni) bimetallic metal organic frameworks and their catalytic activity for phenol degradation under mild conditions* vol 4
- [12] Dong W, Liu X, Shi W and Huang Y 2015 *RSC Adv.* **5** 17451–7
- [13] Dong W, Yang L and Huang Y 2017 *Talanta* **167** 359–66
- [14] Gopalaiah K and Chandrudu S N 2015 *RSC Adv.* **5** 5015–23
- [15] Langhendries G, Vos D E De, Baron G V and Jacobs P A 1999 *J. Catal.* **463** 453–63
- [16] Phan N T S and Jones C W 2006 *J. Mol. Catal. A Chem.* **253** 123–31