

Accepted Manuscript

Title: Zeolite imidazolate frameworks in catalysis: Synthesis of benzimidazoles via cascade redox condensation using Co-ZIF-67 as an efficient heterogeneous catalyst

Authors: Viet D. Nguyen, Chung K. Nguyen, Kien N. Tran, Thach N. Tu, Tung T. Nguyen, Ha V. Dang, Thanh Truong, Nam T.S. Phan



PII: S0926-860X(18)30065-6
DOI: <https://doi.org/10.1016/j.apcata.2018.02.007>
Reference: APCATA 16547

To appear in: *Applied Catalysis A: General*

Received date: 25-10-2017
Revised date: 2-1-2018
Accepted date: 6-2-2018

Please cite this article as: Nguyen VD, Nguyen CK, Tran KN, Tu TN, Nguyen TT, Dang HV, Truong T, Phan NTS, Zeolite imidazolate frameworks in catalysis: Synthesis of benzimidazoles via cascade redox condensation using Co-ZIF-67 as an efficient heterogeneous catalyst, *Applied Catalysis A, General* (2018), <https://doi.org/10.1016/j.apcata.2018.02.007>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Zeolite imidazolate frameworks in catalysis: Synthesis of benzimidazoles via cascade redox condensation using Co-ZIF-67 as an efficient heterogeneous catalyst

Viet D. Nguyen^a, Chung K. Nguyen^a, Kien N. Tran^a, Thach N. Tu^b, Tung T. Nguyen^a, Ha V.

Dang^a, Thanh Truong^a, Nam T. S. Phan^{a*}

^a Faculty of Chemical Engineering, HCMC University of Technology, VNU-HCM,

268 Ly Thuong Kiet, District 10, Ho Chi Minh City, Viet Nam

^b Center for Innovative Materials and Architectures, VNU-HCM,

Quarter 6, Linh Trung ward, Thu Duc District, Ho Chi Minh City, Viet Nam

*Email: ptsnam@hcmut.edu.vn

Ph: (+84 8) 38647256 ext. 5681

Fx: (+84 8) 38637504

Graphical abstract



Research Highlights

- Co-ZIF-67 was used as catalyst for cascade redox condensation.
- High yields of benzimidazoles were obtained.
- The catalyst could be recovered and reused.

Abstract

Zeolite imidazolate framework Co-ZIF-67 was synthesized and utilized as a recyclable catalyst for the synthesis of benzimidazoles via the cascade redox condensation of 2-nitroanilines with benzylamines without added oxidizing or reducing agents. The Co-ZIF-67 catalyst expressed better performance in the generation of benzimidazoles than many MOFs and many conventional homogeneous catalysts. The transformation progressed via genuinely heterogeneous catalysis, and the formation of benzimidazoles via homogeneous catalysis due to the leaching phenomenon, if any, was not considerable. The cobalt-based framework catalyst could be reutilized many times for the reaction without losing its efficiency. The fact that the cascade redox condensation could proceed readily with a recyclable catalyst while additional reducing or oxidizing agents were not required would outperform previous synthetic protocols. To the best of our knowledge, this is the first heterogeneous catalytic approach to achieve benzimidazoles via the cascade redox condensation of 2-nitroanilines with benzylamines.

Keywords: Zeolite imidazolate; benzimidazoles; Co-ZIF-67; cascade; cobalt.

1. Introduction

Benzimidazoles, immensely distributed in plentiful bioactive compounds, have emerged as momentous structural motifs in a variety of medicinal and agrochemical products, as well as in manifold functional materials [1-4]. These heterocycles have been customarily prepared by the acid-catalyzed oxidative cyclization of 1,2-aryldiamines with carboxylic acids or aldehydes [5,

6]. However, the prerequisite of strong acidic medium at high temperature has restricted the meaning of this protocol, and the development of productive synthetic approaches for the construction of benzimidazoles still continues to be explored [5]. Zhao et al. previously reported a CuBr-catalyzed preparation of benzimidazoles via domino reactions of amidine hydrochlorides with *o*-haloacetanilide derivatives [7]. Buchwald and Brasche demonstrated a Cu(OAc)₂-catalyzed production of benzimidazoles from amidines utilizing HOAc as additive and oxygen as oxidant [8]. Punniyamurthy et al. pointed out that benzimidazoles could be prepared by the CuI-catalyzed cascade reaction between azides, aryl amines, and aldehydes [5]. Fe(NO₃)₃-catalyzed preparation of benzimidazoles by the cyclization of primary amines [9] or imines [10] with 1,2-diaminoarenes was also reported. Chandrudu and Gopalaiah performed the same conversion utilizing FeBr₃ as catalyst and oxygen as oxidant [11]. Chaudhari et al. synthesized benzimidazoles from 1,2-diaminoarenes and alcohol using Pt/TiO₂ catalyst [12]. Recently, Nguyen *et al.* demonstrated the first illustration of CoBr₂-catalyzed synthesis of benzimidazoles via the cascade redox condensation of benzylamines with 2-nitroanilines *without* using any added reducing or oxidizing agent [13]. To attain greener synthetic protocols, reactions utilizing recyclable heterogeneous catalysts must be targeted [14-17].

Metal-organic frameworks (MOFs) have been regarded as a new class of porous materials comprising metal-linking points and multidentate organic ligands [18-23]. Utilizing copious linkers and multifarious metals of miscellaneous oxidation states as well as coordination geometries, innumerable frameworks could be generated [24-26], presenting several benefits over ordinary crystalline materials [27-29]. Although more attempts are yet compulsory for the expansion of the research area, attainable applications of MOFs have been substantially

inspected [30-33]. Zeolite imidazolate frameworks (ZIFs), topologically isomorphic with zeolites, have been classified as a new sub-collection of MOFs [34]. These zeolite-like materials integrate numerous special properties from both zeolites and conventional MOFs [35-38]. Surveys on applications of ZIFs in catalysis are comparatively delaying behind those of conventional frameworks, and indeed, the number of publications on catalytic studies of ZIFs for organic reactions has been *limited* in the literature [39-42]. Co-ZIF-67 with the formula of $\text{Co}(\text{mim})_2$ ($\text{mim} = 2\text{-methylimidazole}$) was generated by bridging cobalt (II) cations with 2-methylimidazolate anions to form a porous three dimensional structure [43, 44]. In this manuscript, we would like to present the synthesis of benzimidazoles via the cascade redox condensation of 2-nitroanilines with benzylamines utilizing Co-ZIF-67 as a productive heterogeneous catalyst, without utilizing any added oxidizing or reducing agents. The zeolite-like catalyst could be reused for the generation of the benzimidazoles via the cascade redox cyclization without a noticeable deterioration in performance. To our best consciousness, this cascade redox cyclization reaction was not previously conducted via heterogeneous catalysis.

2. Experimental

The zeolite imidazolate framework Co-ZIF-67 was synthesized from 2-methylimidazole and cobalt nitrate hexahydrate in line with a literature protocol [45], and was characterized by conventional techniques (see Supporting information). In a typical catalytic experiment, a mixture of 2-nitroaniline (0.2818 g, 2.0 mmol) and benzylamine (0.66 mL, 6.0 mmol) in DMSO (1 ml) was added into an 8 ml vial containing the required quantity of the catalyst. The reaction mixture was magnetically stirred at 140 °C for 24 h under air. Following this period, the mixture was cooled down to ambient temperature, and 4-bromoanisole (0.187 g) as an internal standard

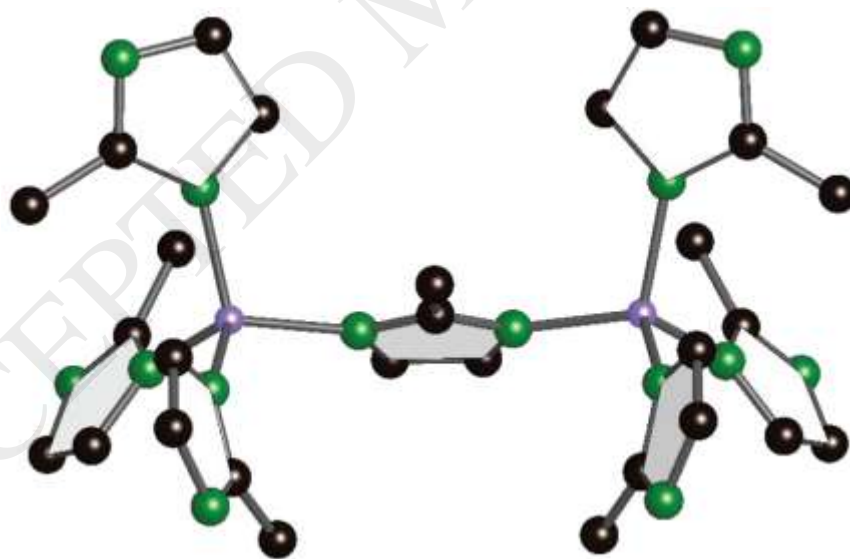
was introduced to the reaction mixture. The organic ingredients were extracted into methanol, shaken vigorously with anhydrous Na_2SO_4 , analyzed by GC regarding 4-brommoanisole. The expected product, 2-phenylbenzimidazole, was isolated utilizing column chromatography. GC-MS, ^1H NMR and ^{13}C NMR analyses were performed to verify the product structure. For the catalyst reusability experiment, the imidazolate framework was collected, washed thoroughly with large amounts of methanol, dried at $100\text{ }^\circ\text{C}$ under vacuum condition on a Shlenk line for 6 h, and reused for further experiment.

3. Results and discussion

3.1. Catalyst characterization

The Co-ZIF-67 was synthesized in a yield of 73% from the reaction between 2-methylimidazole and cobalt nitrate hexahydrate in line with a literature protocol [45]. The cobalt-based framework was subsequently characterized by conventional analysis methods (Fig. S1 – Fig. S7). An immensely sharp peak with 2θ of 7.6 was noticed on the X-ray powder diffractogram, suggesting that a crystalline framework was achieved (Fig. S1). The SEM image demonstrated that cubic crystals with particles sizes of less than $500\text{ }\mu\text{m}$ were produced (Fig. S2). Unfortunately, TEM micrograph did not display a clear pore structure of the Co-ZIF-67 (Fig. S3). Nitrogen physisorption analysis disclosed the pore diameter of less than $20\text{ }\text{\AA}$, pointing out that the framework would be microporous (Fig. S4). Langmuir surface areas of $1809\text{ m}^2/\text{g}$ and BET surface areas of $1309\text{ m}^2/\text{g}$ were recorded for the cobalt-based framework, being appropriate for application in catalysis (Fig. S5). The most notable characteristic in the TGA result was that

small weight loss was recorded in the temperature range of 200 – 400 °C, implying that the Co-ZIF-67 was durable at high temperature (Fig. S6). FT-IR analysis results of the Co-ZIF-67 displayed a considerable difference as compared to those of 2-methylimidazole (Fig. S7). The Co-ZIF-67 structure was further elucidated by Powder XRD analysis, in which, the full profile pattern refinement (Rietveld method) from the structural model of the Co-ZIF-67 was in consistency with experimental pattern respecting both factors, the peak positions and intensity as the refinement converging with satisfactory residual values ($R_{wp}= 1.90\%$, $R_p = 1.20\%$) (Fig. S8). This yielded the final unit cell parameters ($a = 16.9525 \text{ \AA}$) with $I-43m$ space group and the fractional atomic coordinates. The Co-ZIF-67 structure was identified the same with ZIF-67 structure [44], in which, the cobalt SBU was coordinated by four 2-methylimidazole molecules and each 2-methylimidazole molecule coordinated to two adjacent cobalt SBU in order to form a porous three dimensional structure, highlighted by 12 Å cage diameter (Fig. 1).



(a)

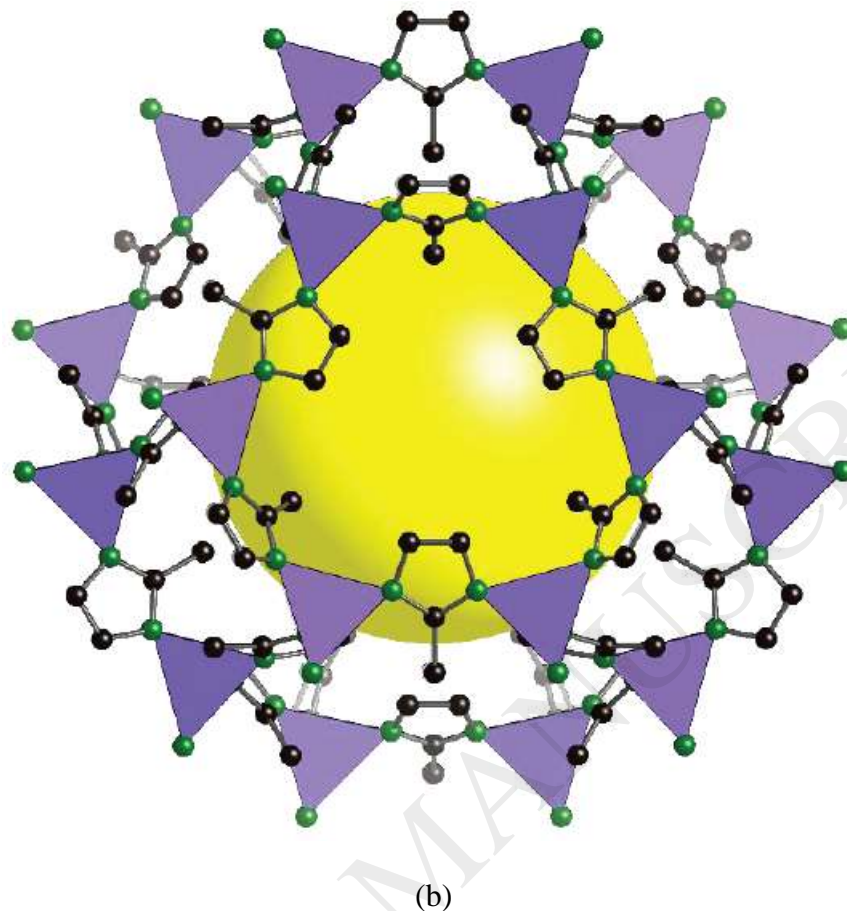
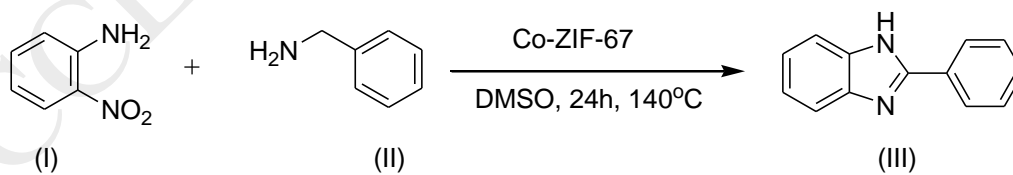


Fig. 1. Co-ZIF-67 structure zoomed in coordinated geometry of cobalt metal (a) and the porous cage (b).

3.2. Catalytic studies



Scheme 1. The reaction of benzylamine with 2-nitroaniline utilizing Co-ZIF-67 catalyst.

The Co-ZIF-67 was then used as catalyst for the cascade redox condensation of 2-nitroaniline (reactant I) with benzylamine (reactant II) to produce 2-phenylbenzimidazole (product III) as the

major product (Scheme 1). Using this protocol, the benzimidazole skeleton could be produced via 4 reaction sequences including benzylamine oxidation, nitro reduction, condensation, and aromatization, without any additional oxidizing or reducing reagents [13]. Initial studies considered the optimization of reaction conditions (Table 1). It was noticed that the yield of 2-phenylbenzimidazole was remarkably affected by temperature (Entries 1-7), and 97% yield was achieved for the reaction conducted at 140 °C (Entry 5). Boosting the temperature to more than 140 °C was not necessary for the transformation (Entries 6-7). One more aspect that must be explored for the reaction is the catalyst amount (Entries 8-14). No product was detected in the absence of the catalyst, verifying the role of the Co-ZIF-67 (Entry 8). Expanding the catalyst amount to more than 5 mol% was pointless as the yield was not intensified considerably (Entries 13-14). The amount of benzylamine also exhibited an impressive influence on the reaction (Entries 15-18), and best yield was achieved when 3 equivalents of benzylamine were employed (Entry 17). The reaction was found to be notably regulated by changing the solvent (Entries 19-24), and DMSO emerged as the solvent of choice (Entry 19). Moreover, the reactant concentration expressed a noticeable impact on the generation of the expected product (Entries 25-31). Best yield was recorded for the transformation utilizing 2-nitroaniline concentration of 2 M (Entry 29).

Table 1. Screening the reaction conditions in the presence of Co-ZIF-67 catalyst.

Entry	Temperature (°C)	Catalyst amount (mol%)	(I):(II) (mol: mol)	Solvent	(I) concentration (M)	Yield (%)

1	80	5	1:3	DMSO	2	0
2	100	5	1:3	DMSO	2	0
3	120	5	1:3	DMSO	2	39
4	130	5	1:3	DMSO	2	56
5	140	5	1:3	DMSO	2	97
6	150	5	1:3	DMSO	2	89
7	160	5	1:3	DMSO	2	87
8	140	0	1:3	DMSO	2	0
9	140	0.5	1:3	DMSO	2	66
10	140	1	1:3	DMSO	2	74
11	140	3	1:3	DMSO	2	89
12	140	5	1:3	DMSO	2	97
13	140	7	1:3	DMSO	2	95
14	140	10	1:3	DMSO	2	97
15	140	5	1:1	DMSO	2	44
16	140	5	1:2	DMSO	2	87
17	140	5	1:3	DMSO	2	97
18	140	5	1:4	DMSO	2	83
19	140	5	1:3	DMSO	2	97
20	140	5	1:3	DMF	2	60

21	140	5	1:3	DMA	2	34
22	140	5	1:3	p-xylene	2	6
23	140	5	1:3	diglyme	2	3
24	140	5	1:3	dichlorobenzene	2	4
25	140	5	1:3	DMSO	0.4	5
26	140	5	1:3	DMSO	0.6	52
27	140	5	1:3	DMSO	1	62
28	140	5	1:3	DMSO	1.3	77
29	140	5	1:3	DMSO	2	97
30	140	5	1:3	DMSO	3	91
31	140	5	1:3	DMSO	4	89

The performance of the cobalt-based zeolite imidazolate framework as catalyst in the reaction between 2-nitroaniline and benzylamine to generate 2-phenylbenzimidazole was next compared with that of other homogeneous catalysts, including CoCl_2 , $\text{Co}(\text{NO}_3)_2$, $\text{Co}(\text{OAc})_2$, FeCl_3 , and 2-methylimidazole (Table 2). It was noted that cobalt salts expressed high activity in the production of 2-phenylbenzimidazole. The $\text{Co}(\text{NO}_3)_2$ -catalyzed transformation could proceed to 86% yield (Entry 2). Both CoCl_2 and $\text{Co}(\text{OAc})_2$ were recognized to be able to catalyze the reaction effectively, with 91% (Entry 1) and 93% (Entry 3) yields of 2-phenylbenzimidazole being obtained. FeCl_3 was noted to be less active for the transformation than cobalt salts, though the reaction could progress to 51% yield (Entry 4). 2-Methylimidazole, a precursor of the

imidazolate framework, was entirely inactive, and no evidence of 2-phenylbenzimidazole was recorded (Entry 5).

To emphasize the critical attribute of employing the zeolite imidazolate framework as catalyst for this reaction, the performance of Co-ZIF-67 was compared with that of other MOFs under identical reaction conditions. $\text{Co}_2(\text{BDC})_2(\text{DABCO})$ and Co-MOF-74 expressed low activity for the reaction, affording only 8% (Entry 6) and 22% (Entry 7) yields, respectively. These results were rationalized by the negative effect of carboxylate cobalt complexes toward the redox cyclization as compared to electron-poor imidazolate cobalt complexes. Fe-MOFs such as $\text{Fe}_3\text{O}(\text{BDC})_3$ and $\text{Fe}_3\text{O}(\text{BPDC})_3$ afforded < 20 % yield though FeCl_3 was reported to be efficient [13]. It was presumed due to the limited accessibility of metal site which was generally observed within Fe-MOFs [46]. Reactions under Cu-MOF-74 (Entry 8), Zn-MOF-74 (Entry 9) catalysis generated insufficient amount of desired products indicating the necessity of cobalt metal active site in reaction pathway. The reaction using Co-ZIF-4 as catalyst could proceed to 75% yield (Entry 12). Co-ZIF-9, a cobalt-based zeolite imidazolate framework from benzimidazole, displayed reasonable activity for the transformation, providing the expected product in 82% yield (Entry 13). Superior activity of Co-ZIF-67 was proposed as the result of possessing larger pore size than Co-ZIF-4 and Co-ZIF-9 [47]. In addition, mimicking the previous study using cobalt salts, neat reactions was carried out under tested homogeneous catalysts (Entries 1-3) and Co-ZIF-67 (Entry 14). The results revealed that heterogeneous Co-ZIF-67 provided similar activity as compared to bare cobalt salts. It is worth mentioning that the use of homogeneous catalysts in industry, especially in pharmaceutical applications, often represent a major problem in removal of contaminated metals in final products.

Table 2. The cascade redox condensation utilizing different homogeneous and heterogeneous catalysts.

Entry	Homogeneous catalysts	Heterogeneous catalysts	Yield (%)
1	CoCl ₂		91 (84 ^a)
2	Co(NO ₃) ₂		86 (88 ^a)
3	Co(OAc) ₂		93 (87 ^a)
4	FeCl ₃		51
5	2-methylimidazole		0
6		Co ₂ (BDC) ₂ (DABCO)	8
7		Co-MOF-74	22
8		Cu-MOF-74	12
9		Zn-MOF-74	14
10		Fe ₃ O(BDC) ₃	16
11		Fe ₃ O(BPDC) ₃	19
12		Co-ZIF-4	75
13		Co-ZIF-9	82
14		Co-ZIF-67	97 (89 ^a)

^aReaction yields under solvent-free conditions

As the cascade redox condensation of 2-nitroanilines with benzylamines was conducted in solution phase, the potentiality that 2-phenylbenzimidazole might be generated via homogeneous catalysis should be explored. In some cases, active sites on solid catalysts could dissolve into liquid phase throughout the sequence of the transformation, and these leached species contributed enormously to the production of the expected product. In order to inspect if active cobalt species traveled from the cobalt-organic framework were essential to the generation of 2-phenylbenzimidazole during the transformation, a control experiment was conducted. The framework catalyst was isolated from the reaction mixture after 8 h by centrifugation. The liquid phase was subsequently transported to a new reactor, and stirred for an extra 16 h at 140 °C. The formation of 2-phenylbenzimidazole during the experiment, if any, was analyzed by GC. Experimental results demonstrated that no further product was generated in the reaction mixture after the framework catalyst was removed (Fig. 2). Moreover, ICP analysis was performed, showing that only approximately 0.1 mol% of cobalt as compared to limiting reagent or 2 mol% of cobalt as compared to the total amount of cobalt was dissolved into the liquid phase during the course of experiments. It was consequently proposed that the cascade redox condensation of 2-nitroanilines with benzylamines to produce 2-phenylbenzimidazole should progress via genuinely heterogeneous catalysis, and the generation of this product via homogeneous catalysis due to the leaching phenomenon, if any, was not considerable.

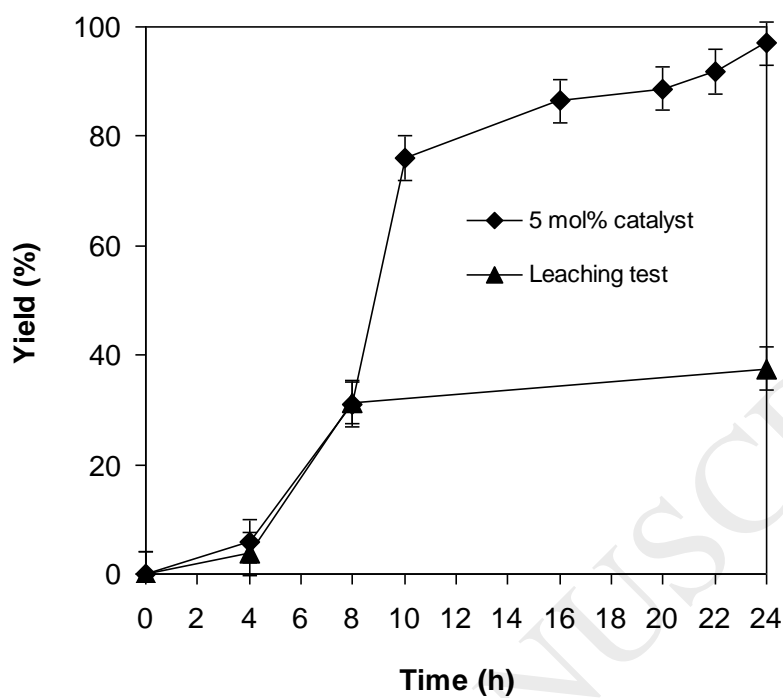
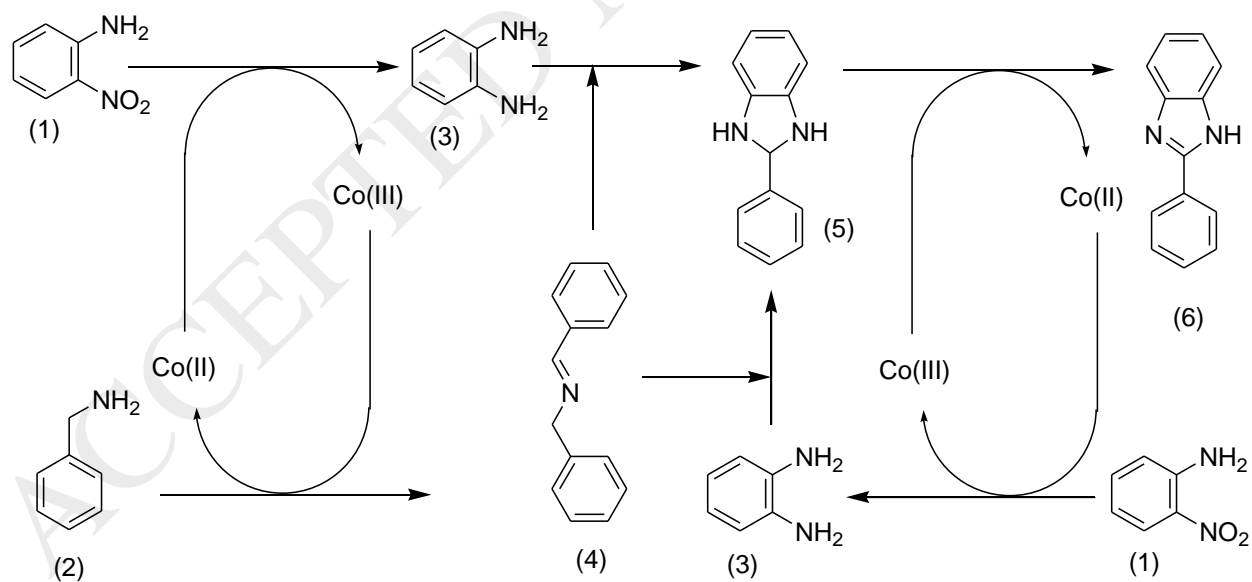


Fig. 2. Leaching test confirmed that 2-phenylbenzimidazole was not produced in the absence of Co-ZIF-67 catalyst.



Scheme 2. Proposed reaction mechanism.

Based on previous reports [13, 48], a plausible pathway for the reaction between 2-nitroaniline and benzylamine to generate 2-phenylbenzimidazole was proposed (Scheme 2). Initially, 2-nitroaniline (1) was reduced to benzene-1,2-diamine (3), while Co(II) species on the Co-ZIF-67 were oxidized to Co(III) oxidation state. Indeed, it was previously reported that cobalt species in Co-ZIF-67 were Co(II) [43, 44]. Trace amount of (3) was detected in the reaction mixture by GC-MS. Next, benzylamine (2) was oxidized to (*E*)-*N*-benzylidene(phenyl)methanamine (4), reducing Co(III) species back to Co(II) state. The oxidation of benzylamine to phenylmethanimine, and subsequently converted to (4) was previously reported [49-51]. Certainly, GC-MS analysis of the reaction mixture after 5 h reaction time revealed the presence of (4). Subsequently, the reaction between (3) and (4) led to the generation of 2-phenyl-2,3-dihydro-1*H*-benzo[d]imidazole (5). GC-MS analysis also indicated the presence of (5) in the reaction mixture. This intermediate product (5) was then oxidized to 2-phenylbenzimidazole (6), while Co(III) species was reduced back to Co(II) state. Indeed, the condensation of (3) and (4) to produce (6) via the formation of (5) was also known in the literature, however an oxidant was required for the transformation [48]. Unfortunately, partially reduced or oxidized intermediates were not detected by GC-MS. Indeed, Nguyen *et al.* previously explored the mechanism of this transformation, and was also not able to observe the formation of these partially reduced intermediates in the crude reaction mixture [13].

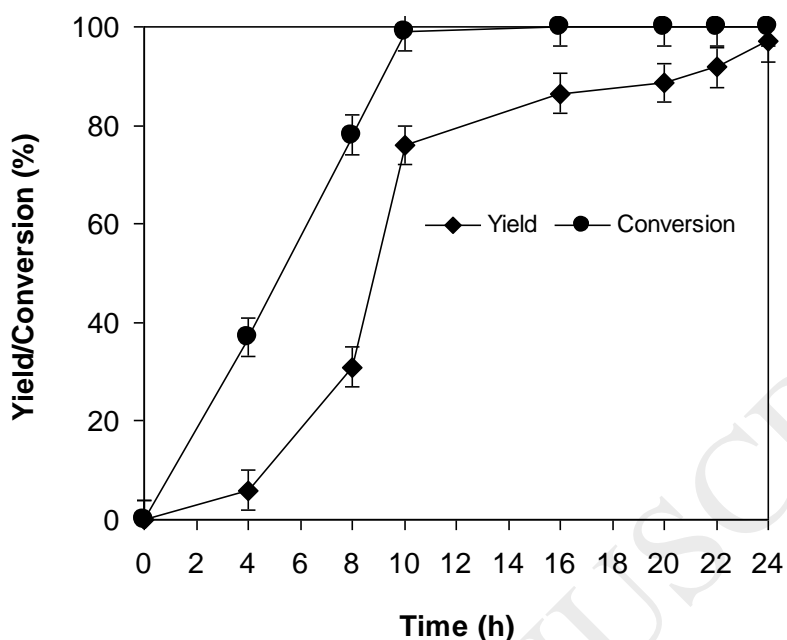


Fig. 3. Yield of 2-phenylbenzimidazole vs conversion of 2-nitroaniline during the course of the reaction.

We also carried out the reaction under air, oxygen, and argon, respectively. It was noticed that similar yields of 2-phenylbenzimidazole were obtained. These data would verify that the reaction between 2-nitroaniline and benzylamine to generate 2-phenylbenzimidazole was not affected by an external oxidant or reductant, and the Co-ZIF-67 was crucial for the transformation. The fact that the cascade redox condensation between 2-nitroaniline and benzylamine could proceed readily without using any added reducing or oxidizing agents would outperform previous synthetic protocols. Furthermore, conversions of 2-nitroaniline were higher than yields of 2-phenylbenzimidazole during the course of the reaction (Fig. 3), indicating that the transformation proceeded via several steps. However, after 24 h reaction time, 97% yield was observed, indicating that almost 2-nitroaniline was successfully converted to 2-phenylbenzimidazole. As up to 3 equivalents of benzylamine were employed, from experimental point of view, it must be

noted that excess benzylamine and its oxidized products were present in the product mixture. GC-MS analysis indicated the presence of (*E*)-*N*-benzylidene(phenyl)methanamine, one oxidized product of benzylamine, in the product mixture. Moreover, trace amounts of benzaldehyde and benzonitrile were also detected as by-products due to the oxidation of benzylamine. Indeed, the formation of these by-products was previously mentioned in the literature [52-54].

Regardless of the fact that many cobalt salts expressed high productivity in the cascade redox condensation of 2-nitroanilines with benzylamines to generate 2-phenylbenzimidazole, it would be impossible to recover and reuse these homogeneous catalysts without a troublesome experimental procedure. To highlight the benefit of Co-ZIF-67, the readiness of reusing the solid catalyst in this transformation was then explored. It would be expected that the cobalt-based framework could be collected after each catalytic run, and could be reused many times without a substantial deterioration in activity. After 24 h reaction time, the cobalt-organic framework was isolated, washed intensively with large amounts of methanol, dried at 100 °C under vacuum condition on a Shlenk line for 6 h. The recovered framework was subsequently reused in further catalytic reaction under analogous conditions to those of the first run. Experimental data recognized that it should be feasible to reuse the catalyst in the reaction of 2-nitroanilines with benzylamines to generate 2-phenylbenzimidazole. Undoubtedly, 89% yield of the expected product was still obtained in the 7th run (Fig. 4). In addition, the structure and properties of the recovered Co-ZIF-67 were explored by a variety of analysis techniques. XRD (Fig. S9), FT-IR (Fig. S10), and TEM (Fig. S11) results of the reused catalyst were noticed to be similar with those of fresh Co-ZIF-67. Surface areas of the catalyst were slightly decreased after 7th run, though Langmuir surface areas of 1579 m²/g and BET surface areas of 1119 m²/g were still

observed (Fig. S12). ICP analysis of the catalyst after 7th run indicated a cobalt loading of 24.5% (wt/wt), being consistent with the fact that a cobalt loading of 26.3% (wt/wt) was observed for the fresh Co-ZIF-67 and a minimal amount of cobalt was dissolved into the liquid phase.

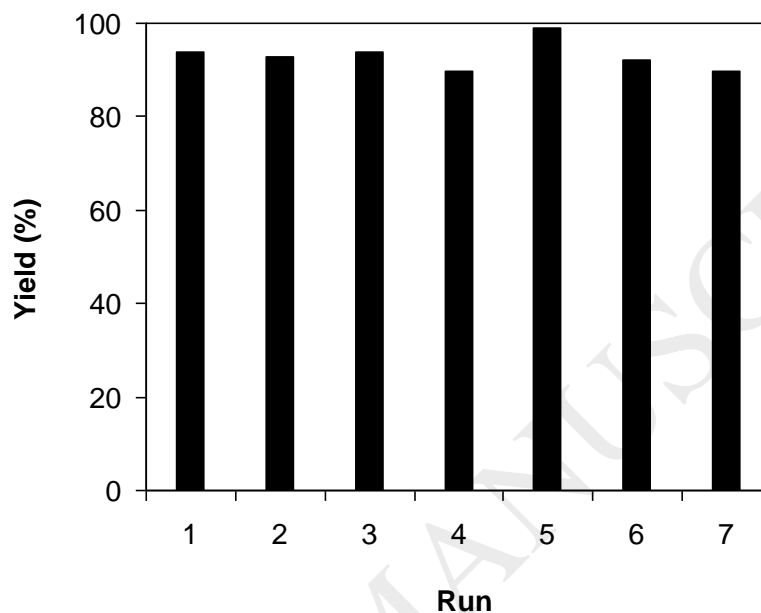
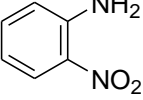
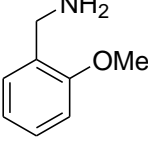
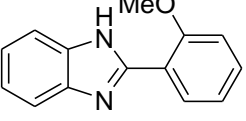
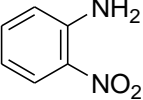
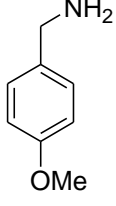
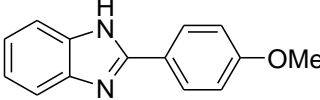
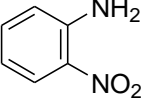
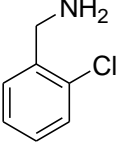
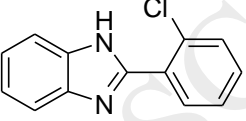
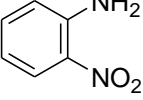
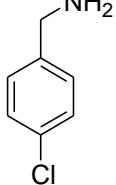
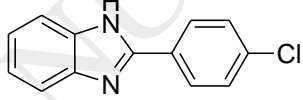
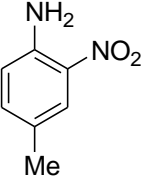
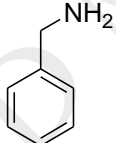
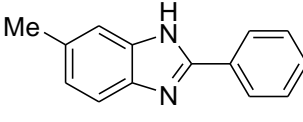
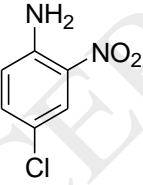
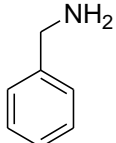
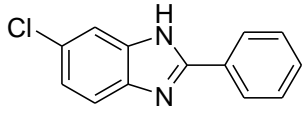
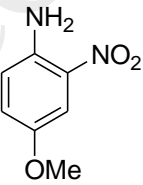
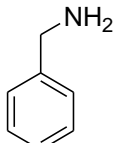
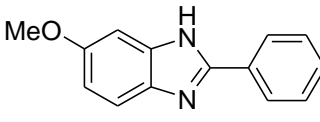
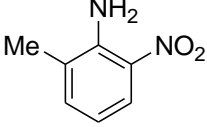
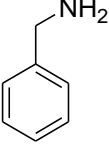
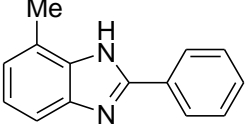


Fig. 4. Catalyst recycling studies.

Table 3. Synthesis of different 2-phenylbenzimidazoles utilizing Co-ZIF-67 catalyst.

Entry	Reactant 1	Reactant 2	Product	Isolated yields (%)
1				90

2				64
3				87
4				63
5				73
6				68
7				72
8				56

9				86
---	---	---	--	----

The scope of the catalytic transformation was subsequently distended to the condensation of different reactants. In the first reaction series, we conducted the reactions between 2-nitroaniline with various benzylamines containing different substituents, including benzylamine, (2-methoxyphenyl)methanamine, (4-methoxyphenyl)methanamine, (2-chlorophenyl)methanamine, and (4-chlorophenyl)methanamine, respectively (Table 3 and Table S2). After the experiment, the product was isolated by column chromatography on silica gel. Under these conditions, 2-phenylbenzimidazole was obtained in 90% isolated yield (Entry 1). The condensation with benzylamines containing methoxy group on benzene ring also afforded reasonable yields. Certainly, 2-(2-methoxyphenyl)-1*H*-benzo[*d*]imidazole (Entry 2), and 2-(4-methoxyphenyl)-1*H*-benzo[*d*]imidazole (Entry 3) were generated in 64%, and 87% yields in the presence of the cobalt-organic framework catalyst. Similarly, utilizing this protocol, 2-(2-chlorophenyl)-1*H*-benzo[*d*]imidazole (Entry 4), and 2-(4-chlorophenyl)-1*H*-benzo[*d*]imidazole (Entry 5) were isolated in 63%, and 73% yields. In the next series, the reactions between benzylamine and several 2-nitroanilines possessing different substituents were conducted. Under these conditions, 6-methyl-2-phenyl-1*H*-benzo[*d*]imidazole (Entry 6), 6-chloro-2-phenyl-1*H*-benzo[*d*]imidazole (Entry 7), 6-methoxy-2-phenyl-1*H*-benzo[*d*]imidazole (Entry 8), and 7-methyl-2-phenyl-1*H*-benzo[*d*]imidazole (Entry 9) could be produced in 68%, 72%, 56%, and 86% yields, respectively.

4. Conclusions

In summary, zeolite imidazolate framework Co-ZIF-67 was synthesized from 2-methylimidazole and cobalt nitrate hexahydrate, and was characterized by conventional analysis methods. The cobalt-based framework was utilized as a recyclable catalyst for the synthesis of benzimidazoles via the cascade redox condensation of 2-nitroanilines with benzylamines without utilizing any added oxidizing or reducing agents. Although several reports on the synthesis of benzimidazoles from 1,2-diaminoarenes have been mentioned in the literature, the fact that 2-nitroanilines are generally less expensive would make this transformation a promising alternative to conventional protocols. The solvent expressed a noteworthy influence on the reaction, and dimethyl sulfoxide emerged as the best option. The Co-ZIF-67 catalyst outperformed many MOFs in the generation of benzimidazoles. The transformation utilizing the cobalt-based framework catalyst progressed via genuinely heterogeneous catalysis, and the formation of benzimidazoles via homogeneous catalysis due to the leaching phenomenon, if any, was not considerable. The framework catalyst could be reutilized many times for the reaction without losing its efficiency. To the best of our knowledge, this transformation was not previously conducted via heterogeneous catalysis conditions. The fact that the cascade redox condensation could proceed readily with a recyclable catalyst while additional reducing or oxidizing agents were not required would outperform previous synthetic protocols, and would be captivated to the chemical industry.

Acknowledgements

The Vietnam National University – Ho Chi Minh City (VNU-HCM) is acknowledged for financial support via Project No. B2017-20-08.

References

1. S. Singh, N. Bharti, P.P. Mohapatra, *Chem. Rev.* 109 (2009) 1900-1947.
2. P. Ghosh, R. Subba, *Tetrahedron Lett.* 56 (2015) 2691–2694.
3. A. Mieczkowski, V. Roy, L.A. Agrofoglio, *Chem. Rev.* 110 (2010) 1828-1856.
4. D.A. Horton, G.T. Bourne, M.L. Smythe, *Chem. Rev.* 103 (2003) 893-930.
5. D. Mahesh, P. Sadhu, T. Punniyamurthy, *J. Org. Chem.* 80 (2015) 1644-1650.
6. L.C.R. Carvalho, E. Fernandes, M.M.B. Marques, *Chem. Eur. J.* 17 (2011) 12544–12555.
7. D. Yang, H. Fu, L. Hu, Y. Jiang, Y. Zhao, *J. Org. Chem.* 73 (2008) 7841-7844.
8. G. Brasche, S.L. Buchwald, *Angew. Chem. Int. Ed.* 120 (2008) 1958-1960.
9. J. Yu, Y. Xia, M. Lu, *Synth. Commun.* 44 (2014) 3019-3026.
10. J. Yu, M. Lu, *Synth. Commun.* 45 (2015) 2148-2157.
11. M. Casiello, F. Iannone, P. Cotugno, A. Monopoli, N. Cioffi, F. Ciminale, A.M. Trzeciak, A. Nacci, *J. Mol. Catal. A. Chem.* 407 (2015) 8-14.
12. C. Chaudhari, S.M.A.H. Siddiki, K.-i. Shimizu, *Tetrahedron Lett.* 56 (2015) 4885-4888.
13. T.B. Nguyen, J.L. Bescont, L. Ermolenko, A. Al-Mourabit, *Org. Lett.* 15 (2013) 6218-6221.
14. M.L. Kantam, S. Laha, J. Yadav, S. Jha, *Tetrahedron Lett.* 50 (2009) 4467-4469.
15. B.C. Ranu, S. Banerjee, *Tetrahedron Lett.* 48 (2007) 141-143.
16. K. Mantri, K. Komura, Y. Kubota, Y. Sugi, *J. Mol. Catal. A* 236 (2005) 168-175.
17. N.E. Leadbeater, M. Marco, *Chem. Rev.* 102 (2002) 3217-3274.

18. H. Xu, C.-S. Cao, X.-M. Kang, B. Zhao, Dalton Trans. 45 (2016) 18003-18017.
19. L.R. Mingabudinova, V.V. Vinogradov, V.A. Milichko, E. Hey-Hawkins, A.V. Vinogradov, Chem. Soc. Rev. 45 (2016) 5408-5431.
20. S.E. Moradi, A.M.H. Shabani, S. Dadfarnia, S. Emami, Anal. Methods 8 (2016) 6337-6346.
21. M. Qamar, A. Adam, B. Merzougui, A. Helal, O. Abdulhamid, M.N. Siddiqui, J. Mater. Chem. A 4 (2016) 16225-16232.
22. N. Li, J. Xu, R. Feng, T.-L. Hu, X.-H. Bu, Chem. Commun. 52 (2016) 8501-8513.
23. C. Chakravarty, B. Mandal, P. Sarkar, Phys. Chem. Chem. Phys. 18 (2016) 25277-25283.
24. J.Z. Huo, X.M. Su, X.X. Wu, Y.Y. Liu, B. Ding, CrystEngComm 18 (2016) 6640-6652.
25. B. Bhattacharya, A. Halder, D.K. Maity, D. Ghoshal, CrystEngComm 18 (2016) 4074-4083.
26. P. Schmieder, D. Denysenko, M. Grzywa, O. Magdysyuk, D. Volkmer, Dalton Trans. 45 (2016) 13853-13862
27. T. Runčevski, M.T. Kapelewski, R.M. Torres-Gavosto, J.D. Tarver, C.M. Brown, J.R. Long, Chem. Commun. 52 (2016) 8251-8254.
28. P.-Y. Du, W. Gu, X. Liu, New J. Chem. 40 (2016) 9017-9020.
29. D. Wang, L. Sun, C. Hao, Y. Yan, Z. Liang, RSC Adv. 6 (2016) 57828-57834
30. W.-J. Li, M. Tu, R. Cao, R.A. Fischer, J. Mater. Chem. A 4 (2016) 12356-12369
31. C. Jiao, X. Jiang, H. Chu, H. Jiang, L. Sun, CrystEngComm 8 (2016) 8683-8687.
32. J. Liu, G. Liu, C. Gu, W. Liu, J. Xu, B. Li, W. Wang, J. Mater. Chem. A 4 (2016) 11630-11634.
33. G.H. Dang, T.T. Dang, D.T. Le, T. Truong, N.T.S. Phan, J. Catal. 319 (2014) 258-264.

34. F. Cacho-Bailo, I. Matito-Martos, J. Perez-Carbajo, M. Etxeberría-Benavides, O. Karvan, V. Sebastián, S. Calero, C. Téllez, J. Coronas, Chem. Sci. DOI: 10.1039/C6SC02411D (2017) In press.
35. I.H. Lim, W. Schrader, F. Schüth, Chem. Mater. 27 (2015) 3088-3095.
36. D.-L. Chen, N. Wang, F.-F. Wang, J. Xie, Y. Zhong, W. Zhu, J.K. Johnson, R. Krishna, J. Phys. Chem. C. 118 (2014) 17831-17837.
37. Y.-Y. Wu, C.-X. Yang, X.-P. Yan, Analyst 140 (2015) 3107-3112.
38. N. Wang, Y. Liu, Z. Qiao, L. Diestel, J. Zhou, A. Huang, J. Caro, J. Mater. Chem. A 3 (2015) 4722-4728.
39. T. Truong, T.M. Hoang, C.K. Nguyen, Q.T.N. Huynh, N.T.S. Phan, RSC Adv. 5 (2015) 24769-24776.
40. T.T. Dang, Y. Zhu, J.S.Y. Ngiam, S.C. Ghosh, A. Chen, A.M. Seayad, ACS Catal. 3 (2013) 1406-1410.
41. L. Lin, T. Zhang, X. Zhang, H. Liu, K.L. Yeung, J. Qiu, Ind. Eng. Chem. Res. 53 (2014) 10916-10913.
42. W. Zhang, Y. Wang, Y. Leng, P. Zhang, J. Zhang, P. Jiang, Catal. Sci. Technol. 6 (2016) 5848-5855.
43. R. Banerjee, A. Phan, B. Wang, C. Knobler, H. Furukawa, M. O'Keeffe, O.M. Yaghi, Science 319 (2008) 939-943.
44. H.T. Kwon, H.-K. Jeong, A.S. Lee, H.S. An, J.S. Lee, J. Am. Chem. Soc. 137 (2015) 12304-12311.
45. W. Xia, J. Zhu, W. Guo, L. An, D. Xia, R. Zou, J. Mater. Chem. A 2 (2014) 11606-11613.

46. J. Park, H. Kim, S.S. Han, Y. Jung, *J. Phys. Chem. Lett.* 3 (2012) 826-829.
47. K.S. Park, Z. Ni, A.P. Côté, J.Y. Choi, R. Huang, F.J. Uribe-Romo, H.K. Chae, M. O'Keeffe, O.M. Yaghi, *Proc. Natl. Acad. Sci. U. S. A.* 103 (2006) 10186-10191.
48. K. Gopalaiah, S.N. Chandrudu, *RSC Adv.* 5 (2015) 5015-5023.
49. S.S. Kim, S.S. Thakur, J.Y. Song, K.-H. Lee, *Bull. Korean Chem. Soc.* 26 (2005) 499-500.
50. J. Zhang, Z. Wang, Y. Wang, C. Wan, X. Zheng, Z. Wang, *Green Chem.* 11 (2009) 1973-1978.
51. R.J. Angelici, *Catal. Sci. Technol.* 3 (2013) 279-296.
52. K.T.V. Rao, B. Haribabu, P.S.S. Prasad, N. Lingaiah, *Green Chem.* 15 (2013) 837-846.
53. A. Kumar, P. Kumar, C. Joshi, S. Ponnada, A.K. Pathak, A. Ali, B. Sreedhar, S.L. Jain, *Green Chem.* 18 (2016) 2514-2521.
54. A. Primo, M. Puche, O.D. Pavel, B. Cojocar, A. Tirsoaga, V. Parvulescu, H. García, *Chem. Commun.* 52 (2016) 1839-1842.