Received: 2 September 2019 | Revised: 30 November 2019 | Accepted: 4 December 2019
DOI: 10.1002/aoc.5522

FULL PAPER

Applied Organometallic Chemistry WILEY

Co/Cu bimetallic ZIF as New heterogeneous catalyst for reduction of nitroarenes and dyes

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Funding information
University of Alicante; Generalitat Valenciana; Fondo Europeo de Desarrollo Regional (FEDER, EU); Agencia Estatal de Investigación (AEI); Spanish Ministerio de Economía, Industria y Competitividad; Spanish Ministerio de Economía y Competitividad (MINECO); Iran National Science Foundation, Grant/Award Number: 97021804; Institute for Advanced Studies in Basic Sciences (IASBS) Research Council

Nowadays one of the great challenges is to design new bimetallic catalysts with enhanced catalytic activity, selectivity and recycling properties. In this work, the preparation of new Co/Cu bimetallic Zeolitic Imidazolate Framework (Co-Cu/ZIF) as an efficient catalyst for the reduction of nitro compounds and organic dyes is described. Co-Cu/ZIF was characterized with different techniques such as SEM, TEM, XRD, XPS, TGA, FT-IR and UV–vis absorption indicating formation of entirely uniform cubic particles. Using this catalyst, structurally different aromatic nitro compounds were reduced efficiently to corresponding amines in excellent yields. Kinetic studies revealed that the reduction rates of nitrophenol isomers follow 3-NP > 4-NP > 2-NP order. The catalytic activity of Co-Cu/ZIF was further investigated in the reduction of organic dyes such as methyl orange (MO) and rhodamine B (RhB). This catalyst was recycled for at least ten runs in the reduction of 4-nitrophenol without a noticeable decrease in activity and reused catalyst was characterized.

KEYWORDS
catalyst, nitro compounds, organic dyes, zeolite imidazolate framework (ZIF)

1 | INTRODUCTION

Metal–organic frameworks (MOFs) have recently received great attention in different industries such as gas storage, fuel cells, supercapacitors and electrode materials for batteries.[1–5] Among them, zeolitic imidazolate frameworks (ZIFs) which are comprised of metal nodes such as Co^{2+}, Zn^{2+} and imidazole bridging in a 3D tetrahedral framework have demonstrated high surface area, thermal and chemical stability.[6,7] However, despite various applications of ZIFs in gas adsorption/storage, separation, and chemical sensors less attention has been paid for using them in design of heterogeneous catalysts.[8–10] Recently, few attempts have been made to use ZIFs as catalyst or catalyst support in organic transformations.[11–13] For instance, ZIF-8, ZIF-9 and ZIF nanosphere were applied as catalyst in the Knoevenagel and phospha-Michael addition cycloaddition reactions, respectively.[14–16] Also, AgPd and AgAu nanoparticles supported on ZIF employed as catalysts in formic acid dehydrogenation and oxidation of benzyl alcohol, respectively.[17,18]

Nowadays environmental problems as well as green chemistry objectives encourage chemists to design new pathways to eliminate or reduce pollutants or use wastes as staring materials for preparation of useful chemicals. Nitro compounds derived from industrial and agricultural wastewater are classified as toxic and environmental pollutants.[19,20] Among them, nitrophenols have high solubility and stability in water, which lead to health hazards in human and animals.[21–23] One way to solve this problem is the catalytic reduction of nitro compounds to the corresponding amines which are valuable chemicals in synthetic organic chemistry.[24–26] For instance, obtained aminophenols from reduction of nitrophenols are non-toxic and used in the synthesis of drugs, rubber materials, photographic resources and industrial dyes.[27,28] Other type of pollutants which usually found in groundwater and causes allergic dramatic, skin irradiation and cancer in human, are dyes.[29,30] Toxic and extremely colored sewerages of dyeing industries which penetrated in groundwater are a serious threat to both human health and the environment. Therefore, it is still great challenges to develop new efficient and eco-friendly methods and catalysts for the reduction of pollutants such as nitro compounds and dyes. Herein, we report synthesis and characterization of new Co-Cu/ZIF and investigate its catalytic performance in the reduction of nitro compounds and organic dyes.

The synthetic strategy for the Co-Cu/ZIF is shown in scheme 1.

2 | EXPERIMENTAL SECTION

2.1 | Materials and methods

Cobalt acetate tetrahydrate ($Co(OAc)_2.4H_2O$), copper acetate tetrahydrate ($Cu(OAc)_2.4H_2O$), polyvinylpyrrolidone (PVP, MW~10000), EtOH (99.86%), 2-methylimidazole, nitro compounds, methyl orange (MO), rhodamine B (RhB), and sodium borohydride ($NaBH_4$) were purchased from Sigma-Aldrich, Acros and Merck MilliporeSigma. Reactions were monitored by thin layer chromatography (TLC) using Merck silica gel 60F254 glass plate with 0.25 mm thickness and Varian CP-3800 gas chromatograph. UV–Vis spectra were investigated on a UV–Vis spectrophotometer (JASCO, UV-550). The morphology and microstructure of the samples were measured by a field emission scanning electron microscope (FE-SEM) JEOL JSM 840 and transmission electron microscope (TEM) EOL JEM-2010. The SEM mapping was monitored by Hitachi S3000 N. The crystallographic structures of the products were characterized by X-ray diffractometer (XRD) with Cu Kα radiation. Thermogravimetric (TG) analysis was performed on a thermogravimetric analyzer NETZSCH STA 409 PC/PG with the heating rate of 5 °C min-1 in the air atmosphere. X-ray photoelectron spectroscopy (XPS) measurements were recorded using a Kα spectrometer.

2.2 | Synthesis of Co-Cu precursors

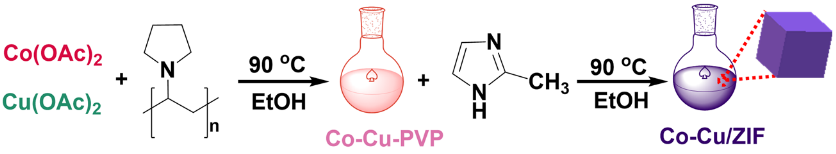
PVP (3 g), $Co(OAc)_2.4H_2O$ (0.91 g) and $Cu(OAc)_2.4H_2O$ (0.37 g) were added to 500 ml flask containing ethanol (200 ml) and the resulting solution was stirred under refluxing conditions for 8 hr. Afterwards, the obtained precipitate was separated by centrifugation (4000 rpm) and the resulting light pink solid was washed with ethanol (10 × 20 ml) and dried in oven at 60 °C.

2.3 | Synthesis of Co-Cu/ZIF

2-Methylimidazole (3 g) was dissolved in ethanol (150 ml) and the solution was stirred at 90 °C under reflux condition. Then, 50 mg of Co-Cu precursors were dispersed in ethanol (20 ml) and the mixture was added to the solution of 2-methylimidazole. Afterwards, the reaction mixture was stirred under reflux conditions for 1 hr. Finally, the purple precipitate was separated by centrifugation, washed with ethanol (5 × 20 ml) and finally dried in oven at 60 °C.

2.4 | General procedure for the reduction of nitro compounds to amines

In a 5 ml glass flask, $ArNO_2$ (0.5 mmol), $NaBH_4$ (2 mmol), catalyst (12.5 mg), and H_2O/ethanol (2 ml, 1:1) were added and reaction mixture was stirred continuously at



SCHEME 1 Schematic illustration of the formation process of Co-Cu/ZIF cubic via a two-step strategy

room temperature for the desired time. The progresses of the reactions were monitored by GC and TLC. After completion of the reaction, distilled water (2 ml) was added to the reaction mixture and the crude product was extracted with ethyl acetate (3 × 5 ml). The crude product was further purified by column or plate chromatography using n-hexane and ethyl acetate as eluents.

2.5 | Typical procedures for the reduction of nitrophenol isomers

Typically, 2 ml of a 0.15 mM aqueous solution of the nitrophenol isomers, 0.5 ml of $NaBH_4$ aqueous solution (0.5 M) and 100 μl of the catalyst (1 mg/ml) were transferred into a quartz cuvette and the mixture was stirred at room temperature. The conversion of nitrophenol isomers to corresponding aminophenol isomers were recorded by UV–Visible spectroscopy. The intensity of absorptions were centered at 415, 393 and 400 nm for the 2-NP, 3-NP and 4-NP, respectively.

2.6 | Typical procedures for the reduction of MO and RhB

2.5 ml of MO or RhB solution (0.06 mM), 0.5 ml of $NaBH_4$ aqueous solution (0.5 M) and catalyst (1 mg) were added to a quartz cuvette and mixture was stirred at room temperature. The progress of the reaction was monitored with UV–Visible spectroscopy

3 | RESULTS AND DISCUSSIONS

3.1 | Characterization

Content of Co and Cu in the Co-Cu/ZIF were determined by atomic absorption spectroscopy to be 2.5 and 1.57 mmol/g, respectively. The morphology of the as-prepared Co-Cu precursor and Co-Cu/ZIF were investigated by different techniques. The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of Co-Cu precursor showed amorphous

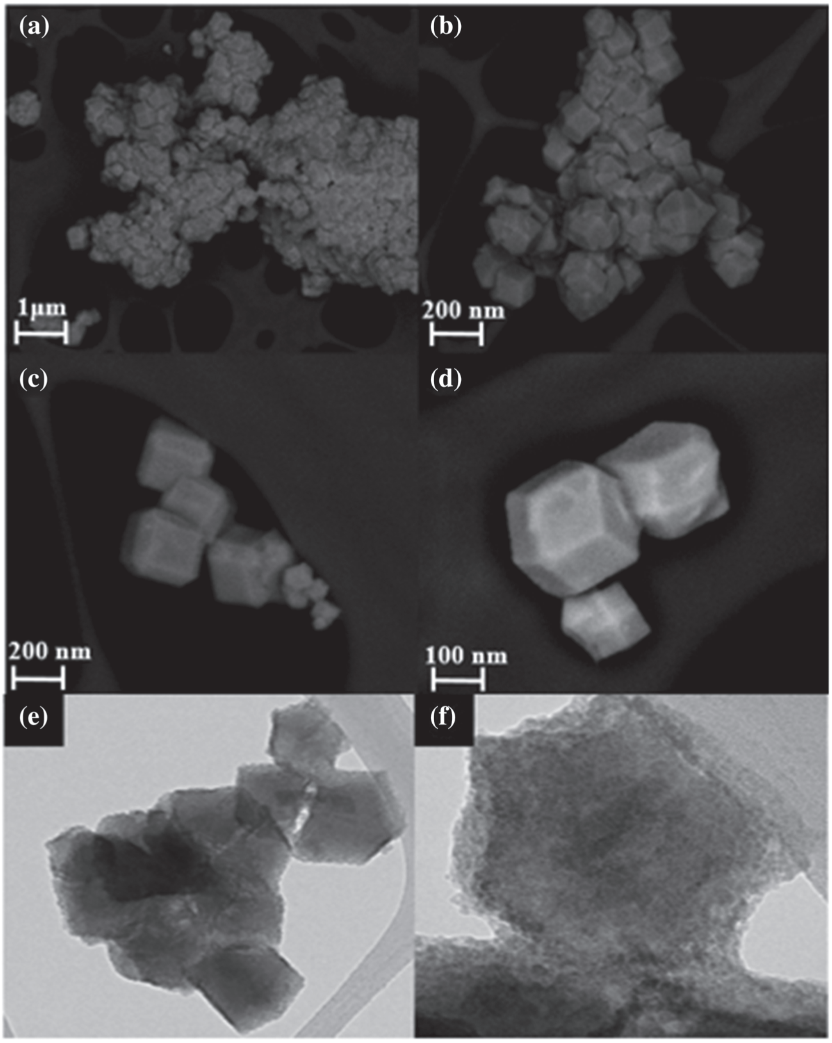


FIGURE 1 SEM images of Co-Cu/ZIF (a) low and (b, c, d) high magnification. (e, f) TEM images of Co-Cu/ZIF

sheets (Figure S1 in ESI). While, SEM and TEM images of Co-Cu/ZIF showed that the structure consists entirely of uniform cubic particles (Figure 1). Also, elemental mapping and energy dispersive X-ray spectroscopy (EDX) were carried out and proved the existence of C, Co, O, and Cu in Co-Cu precursor as well as uniform distribution of C, N, Co, O, and Cu elements in Co-Cu/ZIF structure (Figures S2-S4 in ESI).

In order to find more information about oxidation states of elements, X-ray photoelectron spectroscopy (XPS) of Co-Cu/ZIF in Co 2p, Cu 2p, C 1 s, and N 1 s regions were studied (Figure 2). From the XPS spectra it can be realized that peaks centered at 932.8 and 935.08 are related to Cu $2p_{3/2}$ and peak at 953.0 eV is related to Cu $2p_{1/2}$ of Cu (II) (Figure 2a). It should be noted that three small peaks at 941.2, 943.8 and 955.2 are shake-up satellites related to Cu (II) (Figure 2a).[31] Also, peaks centered at 284.78 and 285 eV were attributed to C-C and C-N bonds in Co/Cu-ZIF (Figure 2b).[32,33] The Co 2p spectra exhibited four peaks at a binding energy of 780.8, 782.5, 796.7 and 798.3 eV, which are assigned to Co^{3+} $2p_{3/2}$, Co^{2+} $2p_{3/2}$, Co^{3+} $2p_{1/2}$ and Co^{2+} $2p_{1/2}$, respectively (Figure 2c).[34–37] It should be noted that two peaks at 786.78 and 804.28 eV are ascribed to shake-up satellite peaks of Co^{2+}.[38–40] Also, the peak located at 398.7 eV represented the tertiary N bonded to carbon atoms (Figure 2d).[41] It is worth mentioning that presence of N 1 s of imidazole peak in Co-Cu/ZIF compared to Co-Cu precursor confirm successful formation of ZIF framework (Figure S5 in ESI).

The crystal structure and phase composition of Co-Cu/ZIF were characterized by X-ray diffraction (XRD).

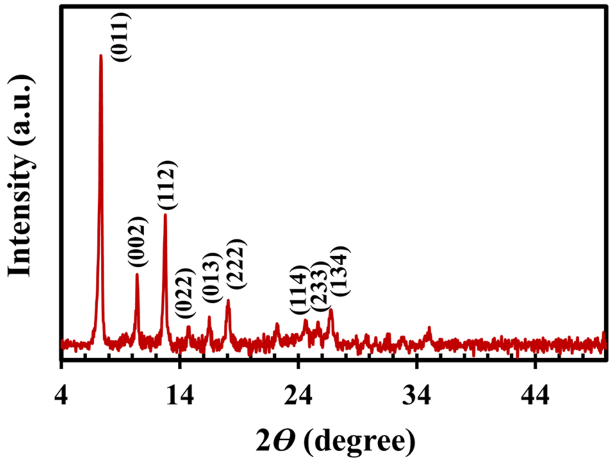


FIGURE 3 XRD spectrum of Co-Cu/ZIF

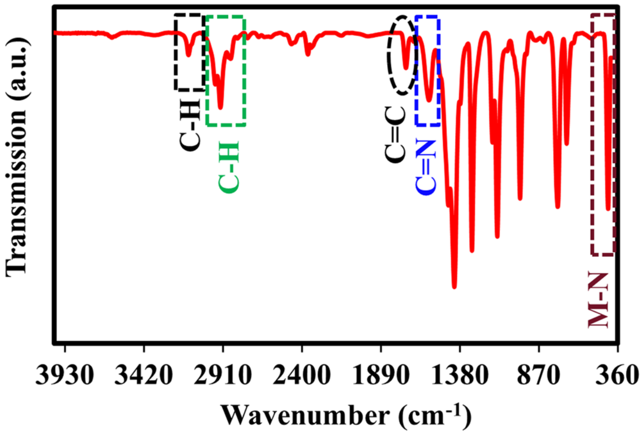


FIGURE 4 FT-IR spectra of the Co-Cu/ZIF

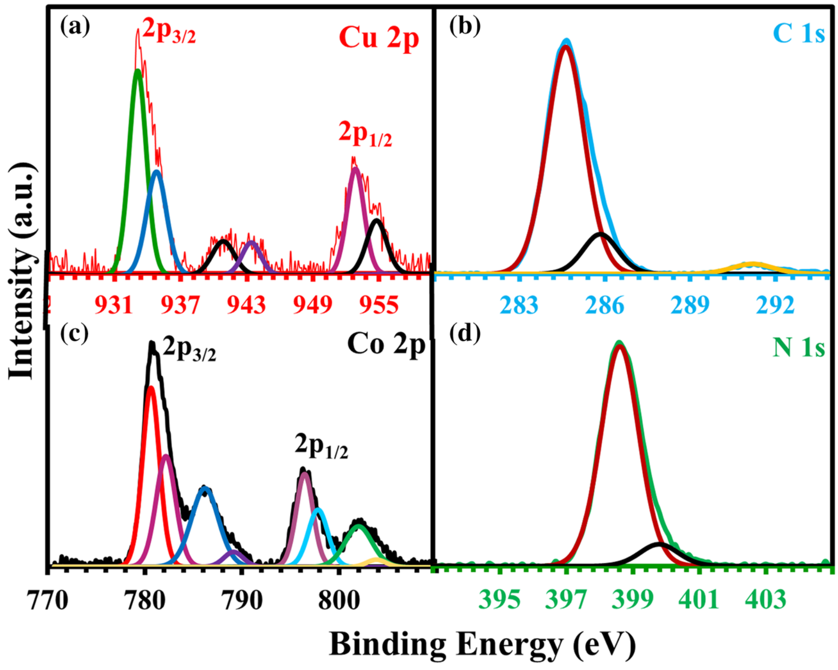


FIGURE 2 High resolution XPS spectra of (a) Cu 2p, (b) C 1s, (c) Co 2p and (d) N 1s for Co-Cu/ZIF

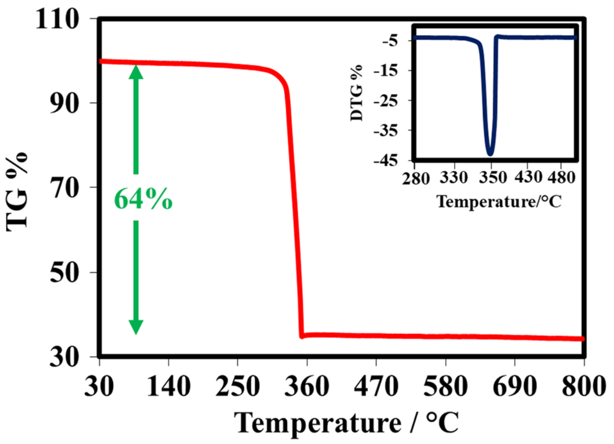


FIGURE 5 TGA curve of the Co-Cu/ZIF

Results showed the stronger peaks at 2θ = 7.35° and 12.8° corresponding to (011) and (112) planes indicating high crystallinity of synthesized Co-Cu/ZIF and confirmed the crystalline phases of prepared ZIF (Figure 3).[6,42]

FT-IR spectrum of Co-Cu/ZIF showed two peaks located at 3130 and 2927 cm^{-1} distinguishing the stretching vibrations of C-H bonds in the imidazole ring and the methyl group, respectively (Figure 4). Also, the absorption bands at 1610 cm^{-1} and 1580 cm^{-1} can be attributed to stretching vibration of C=C and C=N respectively. The peaks in the range of 1350–1500 cm^{-1} are correspond to the entire imidazole ring stretching. In addition, peaks in the region between 900–1350 cm^{-1} indicated to the in-plane bending of the ring and the peaks at 600–800 cm^{-1} exhibited the out-of-plane bending. Finally, the band at 420 cm^{-1} shows the metal-N stretching mode.[14,43]

The thermogravimetric analysis (TGA) indicates that Co-Cu/ZIF has high thermal stability and negligible organic compounds leaching up to 360 °C (Figure 5).

3.2 | Catalytic performance

To investigate the catalytic activity of the Co-Cu/ZIF, initially the reduction of 4-nitrophenol (4-NP) to 4-aminophenol in the presence of $NaBH_4$ was selected as a model reaction and progress of the reaction was monitored by UV–visible spectroscopy (Figure 6). Results indicated that after the addition of catalyst and $NaBH_4$, absorption spectra of 4-NP which is centered at 317 nm, was shifted to 400 nm, indicating formation of 4-nitrophenolate ion. Then, the peak intensity at 400 nm was remarkably decreased and new absorption peak was appeared at 300 nm denoting the formation of 4-aminophenol.[44,45] The complete reduction of 4-nitrophenols to 4-aminophenol was achieved within 4 min. To ensure the accuracy of the results, yield of reaction was checked by gas chromatography (GC). Result indicated that obtained GC yield is in line with UV–visible spectroscopy results.

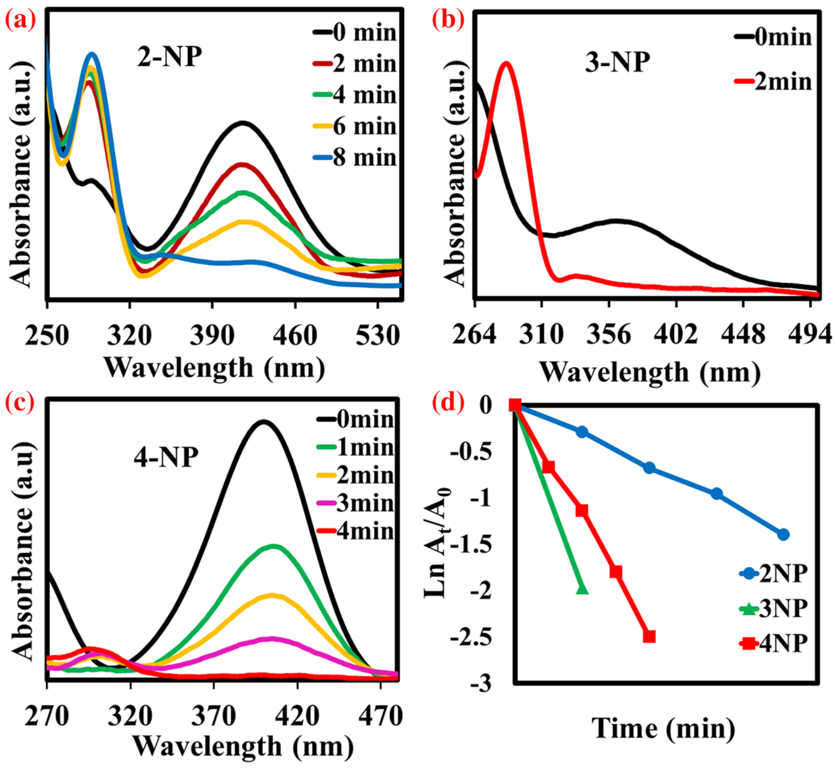
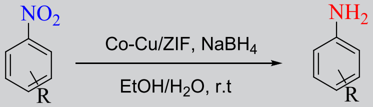
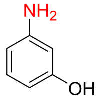
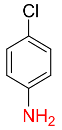
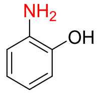
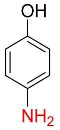
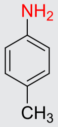
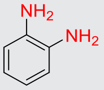
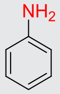
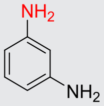
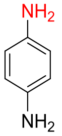
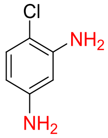
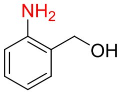
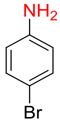
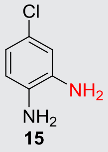
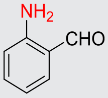


FIGURE 6 UV–Vis absorption spectra of nitrophenol compounds reduction in the presence of $NaBH_4$. Spectra showing the reduction of nitrophenol catalyzed by Co-Cu/ZIF

The reduction of 2-NP and 3-NP was also performed under the same reaction conditions and investigated by the similar methodology (Figure 6). Results showed that the absorption peak of 2-NP was emerging at 417 nm in the UV–visible spectrum. With the addition of the catalyst and $NaBH_4$, the intensity of this peak was decreased and the new peak became visible at the 291 nm indicating formation of corresponding amine product.[46,47] Similarly, 3-NP shows the peak absorption at 368 nm in UV–visible spectrum and the new peak absorption appeared at 288 nm confirming the formation of 3-AP.

TABLE 1 The reduction of structurally different nitro compounds using Co-Cu/ZIF as the catalyst[a,b]



 **3** 100% (5min)	 **1** >99% (5min)	 **2** 100% (10min)	 **4** 100% (5min) **5** 0% (24h)[c]
 **7** 94% (17%)[d] (26%)[e](5min)	 **8** 100% (5min)	 **6** 100% (5min)	 **9** 100% (5min)
 **10** 100% (5min)	 **13** 100% (5min)	 **12** 80% (5min)	 **11** 99% (5min)
	 **15** 100% (5min)	 **14** 100% (5min)	

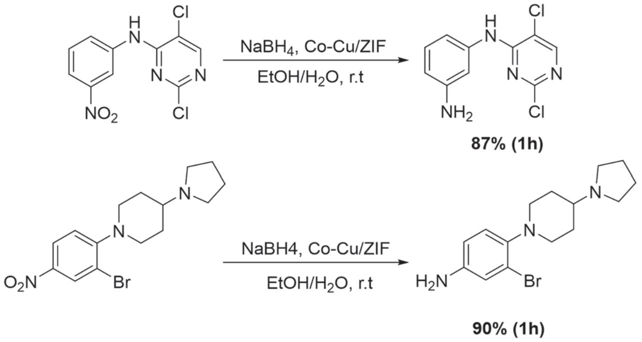
[a] Reaction conditions: $ArNO_2$ (0.5 mmol), $NaBH_4$ (2 mmol), catalyst (12.5 mg) in H_2O/ethanol (1:1) at room temperature.

[b] Yields determined by GC.

[c] Reduction of 4-nitrophenol in the absence of $NaBH_4$ using Co-Cu/ZIF under optimized reaction conditions.

[d] Reaction performed using Co/ZIF.

[e] Reaction performed using $Cu(OAc)_2$.



SCHEME 2 The reduction of 2,5-dichloro-N-(3-nitrophenyl) pyrimidin-4-amine and 3-bromo-4-(4-(pyrrolidin-1-yl)piperidin-1-yl)aniline

Using the UV–visible spectra, the percentage of conversion for reduction of three nitrophenol isomers was calculated [Equation (1)].

$$\mathrm{Ln}\frac{C_t}{C_0} = \mathrm{Ln}\frac{A_t}{A_0} = -k_{app}t \tag{1}$$

In addition, the apparent rate constants (k_{app}) for the reduction of 2-NP, 3-NP and 4-NP are computed [Equation (2)].

$$\%\mathrm{Conversion} = \frac{A_0 - A_t}{A_0} \times 100 \tag{2}$$

Where A_t and A_0 are the absorbance of nitrophenol at time (t) and the time of initial absorbance, respectively. The conversion percentage, completion time of reactions and the apparent rate constant (K_{app}) for the reduction of all three nitrophenol isomers to aminophenol using Co-Cu/ZIF as a catalyst are exhibited (Table S1 in ESI). Results showed that the complete reduction of 4-NP, 3-NP and 2-NP were achieved in 4 min, 2 min and 8 min, respectively and reduction rates of nitrophenols follow 3-NP > 4-NP > 2-NP order. This order can be explained by conjugation, inductive and steric effects. The 2-NP and 4-NP can be stabilized under the conjugation effect and the negative charge in the phenoxide ion delocalizes onto the nitro group resulted their lower reactivity than 3-NP. Also, the inductive effect of 2-NP is higher than 4-NP, that produced more positively charged nitrogen atom expecting higher reactivity of 2-NP. However, lower reactivity of 2-NP than 4-NP indicated that the steric effect plays an important role and reduce activity.

Activity of Co-Cu/ZIF catalyst is compared with other catalysts reported previously using the normalized rate constant ($k_{nor} = k_{app}/m$, where m is total weight of catalyst) confirming higher efficiency of Co-Cu/ZIF catalyst (Table S2 in ESI).[48–58]

We also studied application of the Co-Cu/ZIF catalyst in the reduction of structurally different aromatic nitro compounds (Table 1). Results indicated that nitroarenes having electron donating and electron withdrawing groups were reduced very efficiently and produced amines in excellent yields. For highlighting advantage of using bimetallic Co-Cu/ZIF in the reduction of nitroarenes, reduction of 4-nitrotoluene using Co/ZIF[59] under optimized reaction conditions was studied. However, results showed formation of desired amine in very low yield (Table 1, entry 7). Furthermore, reduction of 4-nitrotoluene using $Cu(OAc)_2$ afforded very low yield demonstrating advantage of using bimetallic Co-Cu/ZIF in this reaction (Table 1, entry 7). These results confirmed presences of synergetic effect in bimetallic Co-Cu/ZIF catalysts compared to monometallic analogies. We have also studied reduction of 4-nitrophenol in the absence of $NaBH_4$ using Co-Cu/ZIF under optimized reaction conditions. In this case result showed that reaction did not proceed and starting material was intact (Table 1, entry 5).

We also studied reduction of pharmaceutical type nitroarenes such as 2,5-dichloro-N-(3-nitrophenyl) pyrimidin-4-amine and 3-bromo-4-(4-(pyrrolidin-1-yl) piperidin-1-yl)aniline to corresponding amines (Scheme 2). Results showed desired amine products were obtained in 87–90 isolated yields.

Recovery and recyclability of the catalyst is important from industrial and economical standpoints. Therefore, we investigated the reusability of Co-Cu/ZIF catalyst in a reduction of 4-nitrophenol. Result of this study showed that the Co-Cu/ZIF reused for ten successive reaction cycles with small decrease in activity (Figure S6 in ESI). Structure of reused catalyst was studied by SEM and FT-IR in which SEM images (Figures S7a and S7b in ESI) and FT-IR spectrum (Figure S8 in ESI) of reused catalyst after 3 and 5 runs showed that structure of Co-Cu/ZIF is almost preserved with partial destruction. However, SEM image (Figure S7c in ESI) after 10 runs showed complete distortion of the ZIF structure. This result was confirmed by FT-IR study in which spectrum after 10 run showed absence of related peaks to imidazole moiety confirming destruction of the ZIF structure (Figure S8 in ESI).

Finally, the catalytic activity of Co-Cu/ZIF was investigated in the reduction of dyes, including methyl orange (MO) and rhodamine B (RhB). These reactions were monitored using UV–visible spectra in which in the presence of Co-Cu/ZIF the absorbance of MO ($\lambda_{max} = 467$ nm) and RhB ($\lambda_{max} = 556$ nm) decrease with time (Figure 7). The K_{app} values of MO and RhB dyes are calculated to be 2.52 and 1.34 min^{-1}, respectively indicating that Co-Cu/ZIF can be employed as an efficient catalyst for the reduction of organic dyes.[60,61] The proposed mechanism

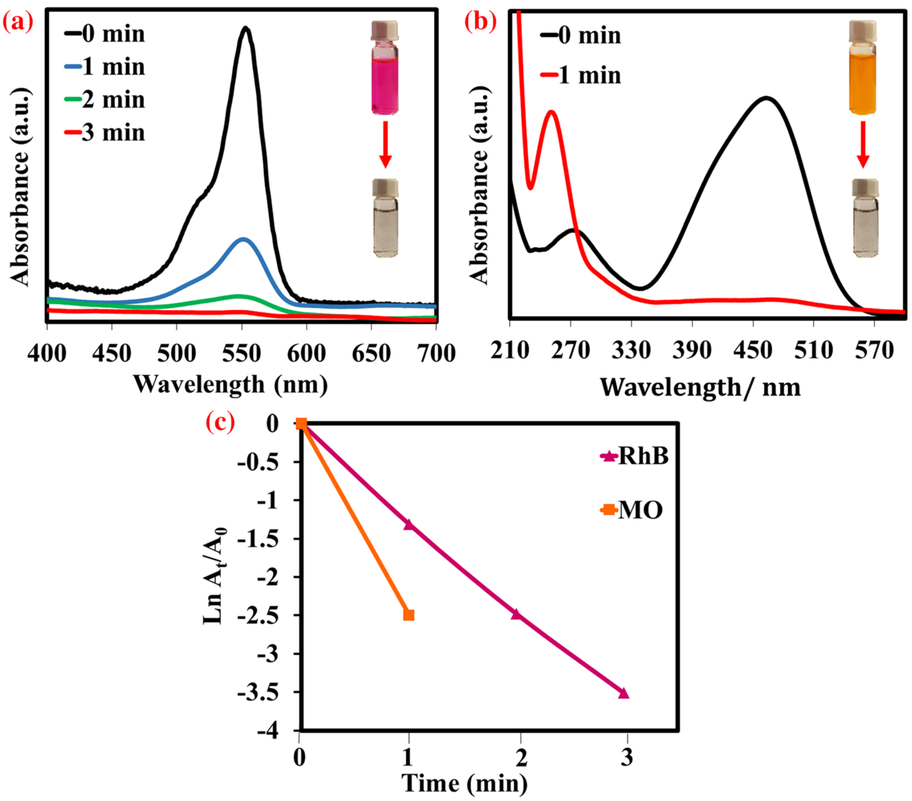


FIGURE 7 Time-dependent UV–visible absorption spectra for the catalytic reduction of (a) RhB and (b) MO using Co-Cu/ZIF catalyst

for the Co-Cu/ZIF reduction of MO and RhB is the same as the known mechanism for the metal catalyzed reduction reactions of MO and RhB. On the basis of common analogies, produced H_2 from the reaction of $NaBH_4$ and H_2O in the presence of ZIF catalyst reduce Methyl Orange to N^1,N^1-dimethylbenzene-1,4-diamine and sodium 4-aminobenzenesulfonate and Rhodamine B to leuco rhodamine B (Figure 8).[62–70]

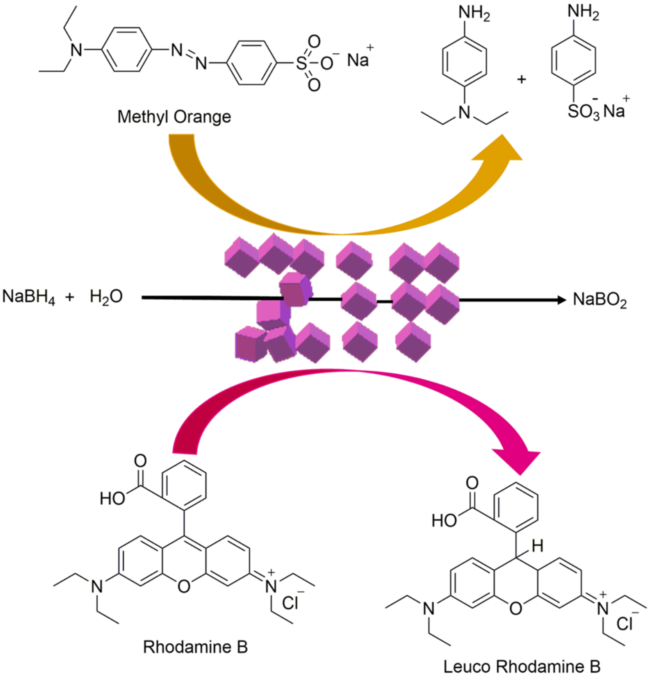


FIGURE 8 Possible mechanism for the reduction of methyl orange (MO) and rhodamine B (RhB) by the Co-Cu/ZIF catalyst using $NaBH_4$

4 | CONCLUSION

In conclusion, we introduced efficient strategy for the synthesized of cubic Co-Cu/ZIF using mild reaction conditions and characterized by different techniques. The Co-Cu/ZIF exhibits high catalytic activity in the reduction of nitro compounds and organic dyes at room temperature. The presence of Cu was proved to be crucial to obtain excellent yields. This catalyst was recovered and recycled using simple centrifugation and reused several times with small decrease in activity. SEM and FT-IR studies of reused catalyst proved that structure of the catalyst was preserved until three recycling runs.

ASSOCIATED CONTENT

Supporting Information. Further SEM, XPS, Map, EDX, TGA, FT-IR of Co-Cu precursor and Co-Cu/ZIFs, recycling diagram, comparison Tables, GC spectra reduction reactions, and ^{1}H NMR and ^{13}C NMR of amine products.

ACKNOWLEGMENT

The authors are grateful to Institute for Advanced Studies in Basic Sciences (IASBS) Research Council and Iran National Science Foundation (INSF-Grant number of 97021804) for support of this work. José M. Sansano is also thankful for financial support to the Spanish Ministerio de Economía y Competitividad (MINECO) (projects CTQ2013–43446-P and CTQ2014–51912-REDC), the Spanish Ministerio de Economía, Industria y Competitividad, Agencia Estatal de Investigación (AEI) and Fondo Europeo de Desarrollo Regional (FEDER, EU) (projects CTQ2016–76782-P and CTQ2016–81797-REDC), the Generalitat Valenciana (PROMETEOII/2014/017) and the University of Alicante. Special thanks to Ms. Dehghan Hesami for her technical assistant.

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How to cite this article: Gholinejad M, Naghshbandi Z, Sansano JM. Co/Cu bimetallic ZIF as New heterogeneous catalyst for reduction of nitroarenes and dyes. *Appl Organometal Chem*. 2020;e5522. https://doi.org/10.1002/aoc.5522