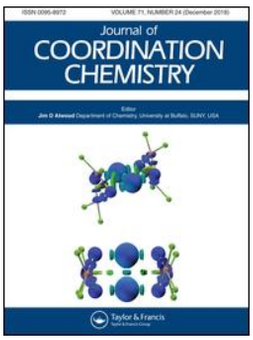

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Green synthesis of benzimidazole derivatives under ultrasound irradiation using Cu-Schiff base complexes embedded over MCM-41 as efficient and reusable catalysts

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Green synthesis of benzimidazole derivatives under ultrasound irradiation using Cu-Schiff base complexes embedded over MCM-41 as efficient and reusable catalysts

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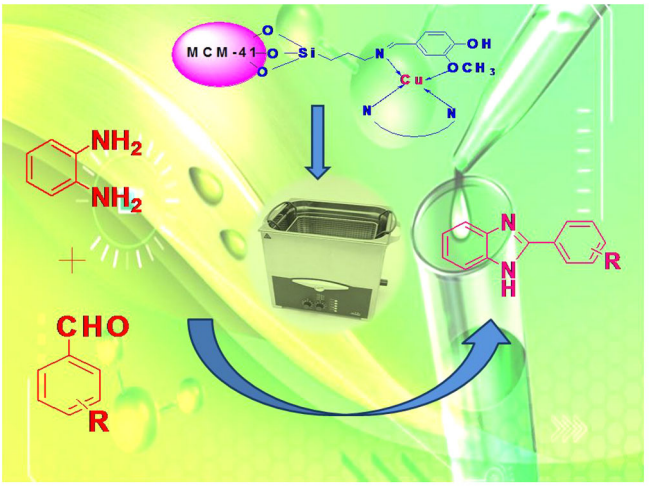
ABSTRACT

We have synthesized two recoverable catalysts by covalently attaching complexes such as Cu-complex-phen and Cu-complex-bipy on MCM-41 through a greener synthetic route. FT-IR, EDX, SEM and TEM microscopy, XRD analysis, N_2 adsorption and desorption, ICP-OES and TGA were used to characterize the heterogeneous catalysts. The catalytic functioning of Cu-complex-phen-MCM-41 (**C_1**) and Cu-complex-bipy-MCM-41 (**C_2**) were shown yield up to 95% for the synthesis of benzimidazole derivatives in ethanol/methanol solvent under ultrasonic irradiation within 90 min. The catalyst was easily recovered and reused up to three times without significant loss of its activity.

GRAPHICAL ABSTRACT



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Schiff base; MCM-41; copper catalyst; benzimidazole; ultrasonic irradiation

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1. Introduction

The goals of greener chemistry such as minimizing waste, reducing energy and time can be achieved by using ultrasonic irradiation in chemical reactions [1]. This technique has advantages like increasing the reaction rate and yield of the product. Sonication is used to promote a range of chemical reactions such as addition, substitution, coupling, condensation, oxidation, reduction, protection/deprotection, photochemical and polymerization [2–5]. Furthermore, this method is efficiently applied for homogeneous, heterogeneous and transition metal-catalyzed organic reactions [6].

Heterocyclic families are prominent in all fields of science *viz* agricultural, industrial, pharmaceutical, medicinal and material chemistry. Benzimidazoles are prominent among heterocyclic compounds, as building blocks for many bioactive compounds and structural isosteres of naturally occurring nucleotides. Hence they can readily interact with the biopolymers of living systems [7] and show enormous therapeutic applications, including anti-HIV [8], anti-cancer [9], anti-inflammatories [10], anti-bacterial [11], anti-fungal [12], anti-histaminic [13], anti-oxidant [14], anti-hypertensives [15] and anti-coagulant agents [16]. A significant number of benzimidazole-based drugs are commercially available. For example, thiabendazole, norastemizole, telmisartan and omeprazole are well-known drugs of this class as anti-parasitic, anti-histaminic, antihypertensive and anti-ulcer agents.

Benzimidazole derivatives are synthesized in two general ways. The first process is coupling of *o*-phenylenediamines and carboxylic acids [17] or their derivatives (nitriles, orthoesters or imidates) [18] under strongly acidic conditions and sometimes along with very high temperatures. The second process involves two-step synthesis consisting of formation of Schiff base by condensation of *o*-phenylenediamines with aldehyde followed by oxidative cyclodehydrogenation using oxidative and catalytic reagents such as nitrobenzene [19], 1,4-benzoquinone [20], $Ph(OAC)_2$ [21], Zn-proline [22], heteropoly acids [23], thionyl chloride-treatment [24], 2,3-dichloro-5-6-dicyanobenzoquinone (DDQ) [25], benzofuroxan [26], MnO_2 [27], oxone [28], $NaHSO_3$ [29], H_2O_2/HCl [30], $Na_2S_2O_5$ [31], air [32], copper complex [33], Hauland natural zeolite [34], NaYzeolite [35], AlKIT-5 [36], *etc*. Some of these methods suffer from major drawbacks such as low yield, expensive catalysts, prolonged reaction times, difficulty in separation of the products from the reaction mixture, use of toxic solvents and requirement of more reagent. Therefore, the focus on designing economical, stable, recoverable, reusable and eco-friendly solid-supported heterogeneous catalyst for the synthesis of benzimidazole derivatives is important.

Among mesoporous silica materials, MCM-41 has special properties like high thermal stability, high pore volume, high surface area and well-ordered hexagonal arrangement [37]. Hence MCM-41 is a suitable support for anchoring metal complexes. Metal ions such as copper, nickel [38], zinc, manganese, cobalt, *etc*., in mesoporous silica framework, have made contributions in heterogeneous catalysis due to their low toxicity and low cost. Anchoring of different ligands into the hexagonal channels can be easily modified in the walls of the porous system of MCM-41 [39, 40] and allows tuning catalytic activity.

Wanling Mo *et al.* [41] developed a heterogeneous catalyst, Cu/N,N-bidentate-ligand, that exhibits high catalytic activity, is easily recoverable and has excellent stability

in consecutive catalytic runs for the oxidative carbonylation of methanol. Mohsen Nikoorazm *et al.* [42] reported a heterogeneous catalyst, Ni-vanillin-Schiff base-MCM-41, with high catalytic activity and low leaching of metal while reusing the catalyst for the synthesis of polyhydroquinoline and 2,3-dihydroquinazolin-4(1H)-one derivatives.

Herein, we report the preparation and characterization of two heterogeneous catalysts, Cu-complex-phen/bipy-MCM-41, for the synthesis of benzimidazoles by considering the significance of N,N-bidentate ligands, vanillin and Schiff base moiety. Moreover, the catalytic reactions are carried out in a greener way *i.e.* using methanol/ethanol as solvents and with ultrasonication method.

2. Experimental

2.1. Materials and instruments

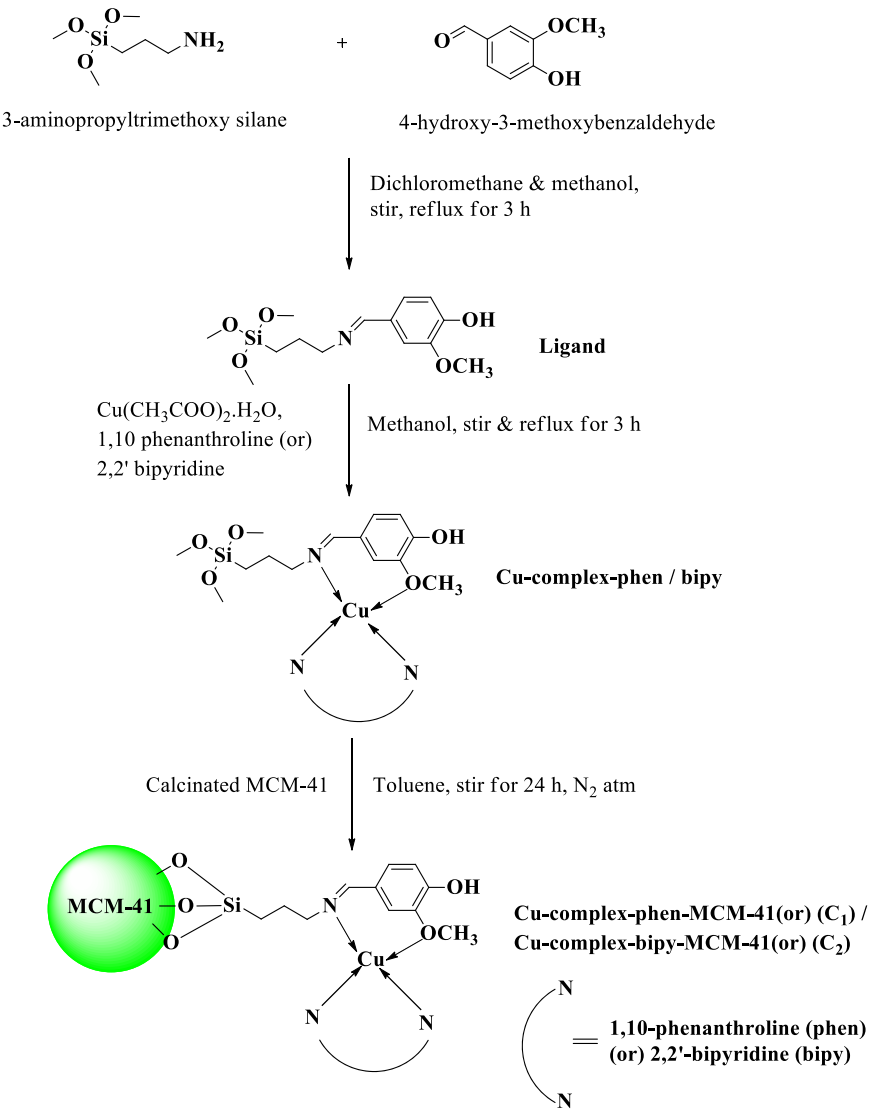
3-Aminopropyltrimethoxysilane (3-APTMS), tetraethylorthosilicate (TEOS), cetyltrimethylammoniumbromide (CTAB) and copper(II) acetate monohydrate were acquired from Aldrich and SRL. IR spectra of prepared samples were examined on an Avatar 370 model FT-IR spectrometer with KBr pellets. Powder X-ray diffraction data were recorded on a Bruker AXS D8 Advance diffractometer. Sonication was performed in an ultrasonic cleaner, Sonica 2200 MH S^3 (model no: 090.003.003). The SEM/EDX micrographs were obtained on the JEOL Model JSM 6390LV microscope. HR-TEM analysis was carried out on a JEOL JEM 2100 model. BET surface area was determined using the NOVA 1200 Quanta chrome instrument at 77 K. ICP-OES was used to analyze the Cu content in the samples. The TG/DTA micrographs were recorded on a Perkin Elmer instrument from 0-900 °C.

2.2. Preparation of MCM-41

An aqueous solution of CTAB (1 g) was added to 3.5 ml of (2 M) NaOH solution and stirred at 80 °C until the solution became uniform. Then, TEOS (5 ml) was progressively added to the solution and reacted for 2 h at the same temperature. The collected white product was washed with deionized water and dried at 70 °C. The withered powder was calcinated at 550 °C for 5 h with the rate of 2 °C/min to remove the residual surfactant and finally got the pure MCM-41 [42].

2.3. Preparation of heterogeneous Cu-complex-phen/bipy-MCM-41

1 mmol (0.17 ml) of 3-APTMS in dichloromethane was added to 1 mmol (0.15 g) of vanillin in methanolic solution, stirred and refluxed for 3 h. Then, a methanolic solution of 1 mmol (0.19 g) of $Cu(OAc)_2{\cdot}H_2O$ and 1 mmol (0.19 g) of 1,10-phenanthroline was added to the reaction mixture and continued to react for further 3 h at the same conditions. After cessation of the reaction, the Cu-complex-phen was retrieved from the reaction mixture using a rotary evaporator. 1 g of calcinated MCM-41 was added to the synthesized complex in excess of toluene and stirred for 24 h under N_2. Then, the product Cu-complex-phen-MCM-41 (**C_1**) was recovered by a rotary evaporator.

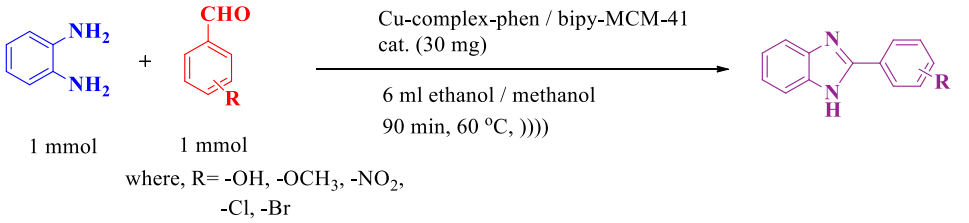


Scheme 1. Synthesis of Cu-complex-phen/bipy-MCM-41.

Cu-complex-bipy-MCM-41 (**C_2**) was prepared by following the above procedure using 1 mmol (0.15 g) of 2,2′-bipyridine instead of 1,10-phenanthroline (Scheme 1).

2.4. General procedure for the synthesis of benzimidazole derivatives under ultrasonic irradiation

30 mg of catalyst **C_1** (Scheme 2) was added to an ethanolic solution of *o*-phenylenediamine (1 mmol) and aromatic aldehyde (1 mmol) at 60 °C. Then the mixture was subjected to sonication for 90 min. After the reaction (monitored by TLC ethyl acetate:hexane = 1:2), the catalyst was separated by filtration and washed with ethanol to be reused for the next cycle. The product was obtained from the filtrate and recrystallized to get the pure compound. The compound was confirmed by ^{1}H-NMR.



Scheme 2. Synthesis of benzimidazole derivatives.

Another set of the catalytic mixture was carried out using the above procedure with 30 mg of $\mathbf{C_2}$ (catalyst) in methanol (6 ml) instead of $\mathbf{C_1}$ in ethanol.

3. Results and discussion

The new heterogeneous catalysts were characterized by FT-IR, PXRD, SEM-EDX, HR-TEM, ICP-OES, BET, TGA and analysis.

3.1. FT-IR spectroscopy

Figure 1 shows the FT-IR spectra of the synthesized ligand, Cu-complex-(phen/bipy), $\mathbf{C_1}$ and $\mathbf{C_2}$. For the MCM-41 sample (Figure 1a), the peaks at 1100, 803 and 468 cm^{-1} can be attributed to asymmetric stretching, symmetric stretching and bending vibrations of Si-O-Si, respectively [43]. In addition, the band at 3453 cm^{-1} is assigned to vibration of the hydrogen-bonding silanol groups. For the ligand, the presence of an absorption about 2900 cm^{-1} is associated with the CH_2 vibrations corresponding to the C-H stretch. The appearance of peaks at 1647 cm^{-1} and 1515 cm^{-1} are due to formation of Schiff base C=N and aromatic C=C bonds in 4-hydroxy-3-methoxybenzaldehyde (vanillin) (Figure 1b). The M-N and M-O bands, for Cu-complex-(phen/bipy), $\mathbf{C_1}$ and $\mathbf{C_2}$ are at 619 cm^{-1} and 457 cm^{-1}, respectively, which confirmed that the metal ion bonded to the ligand. C-H stretching vibrations (from phen or bipy rings) appear above 3000 cm^{-1} and characteristic C-H out of plane bending vibrations are seen at 872 and 723 cm^{-1}, indicating the presence of diimine ligands (Figures 1c-1f) [44].

3.2. PXRD

Powder XRD patterns of pure MCM-41, $\mathbf{C_1}$, $\mathbf{C_2}$ and recovered catalysts are illustrated in Figure 2. Three characteristic peaks assigned to 100, 110 and 200 reflections are observed for pure MCM-41. The intensity of the diffraction for the 100 reflection is decreased whereas 110 and 200 reflections almost disappear for both catalysts ($\mathbf{C_1}$, $\mathbf{C_2}$) and recovered catalysts when compared to that of MCM-41, revealing that the copper is highly dispersed on the inner channel pores of MCM-41 [45].

3.3. SEM, EDX and ICP-OES

SEM micrographs of MCM-41 and $\mathbf{C_1}$ and $\mathbf{C_2}$ show no significant difference in the surface morphology occurred upon inclusion of the copper complex in MCM-41 (Figure 3).

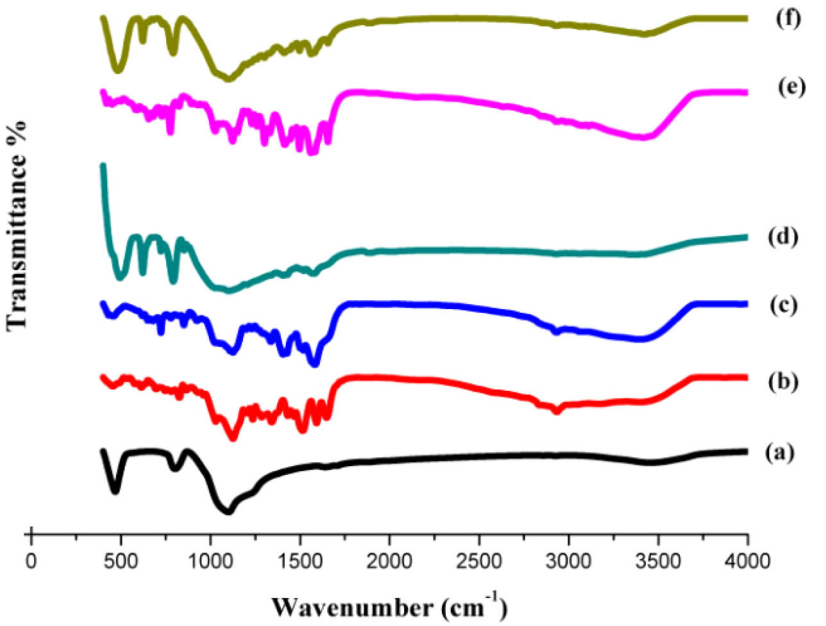


Figure 1. FT-IR spectra of (a) MCM-41, (b) ligand, (c) Cu-complex-phen, (d) Cu-complex-phen-MCM-41, (e) Cu-complex-bipy and (f) Cu-complex-bipy-MCM-41.

EDX elemental analysis indicates the presence of copper in the catalyst which is not present in the MCM-41 (Figure 3). The exact loadings of copper on **C_1** and **C_2** are 2.7×10^{-3} mol/g and 3.0×10^{-3} mol/g by ICP-OES technique.

3.4. Transmission electron microscopy

The TEM images of **C_1** and **C_2** are shown in Figure 4. **C_1** and **C_2** possess well-ordered hexagonal arrangement even after immobilization of both copper complexes onto MCM-41 [46].

3.5. N2 adsorption-desorption

The BET surface area, average pore diameter and pore volume were calculated using the BJH method for pure MCM-41 [38], **C_1** and **C_2** (see Figure 5 and Table 1). They are drastically decreased in both catalysts when compared to pure MCM-41, due to incorporation of the copper complexes in the framework of MCM-41 [47].

3.6. Thermogravimetric analysis

Figure 6 shows the TGA curves for **C_1** and **C_2**. Both have three-step weight losses. The initial weight loss up to 100 °C is due to the removal of physically adsorbed water and solvent inside the pores. Then successive weight loss in the temperature range of 150-400 °C is due to decomposition of organic groups. Upon further heating, final weight loss to 700 °C could correspond to decomposition of silanol groups [48].

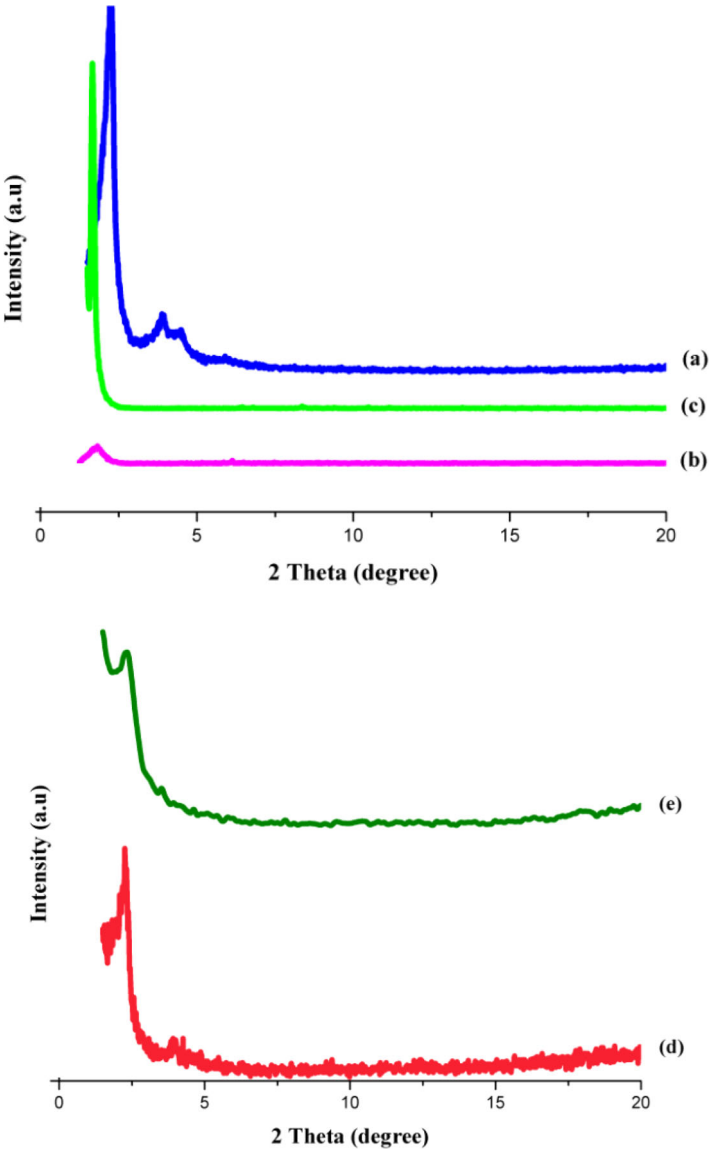


Figure 2. PXRD patterns of (a) MCM-41, (b) Cu-complex-phen-MCM-41, (c) Cu-complex-bipy-MCM-41, (d) recovered catalyst Cu-complex-phen-MCM-41 and (e) recovered catalyst Cu-complex-bipy-MCM-41.

3.7. Catalytic activity

The catalytic activities of $\mathbf{C_1}$ and $\mathbf{C_2}$ have been carried out in the synthesis of benzimidazole derivatives from *o*-phenylenediamine and with various substituted aldehydes under ultrasonic irradiation.

In order to optimize the reaction conditions, benzaldehyde has been selected as a model substrate and it was subjected to different reaction conditions such as the amount of catalyst, time, solvent and temperature. To find the appropriate solvent, we

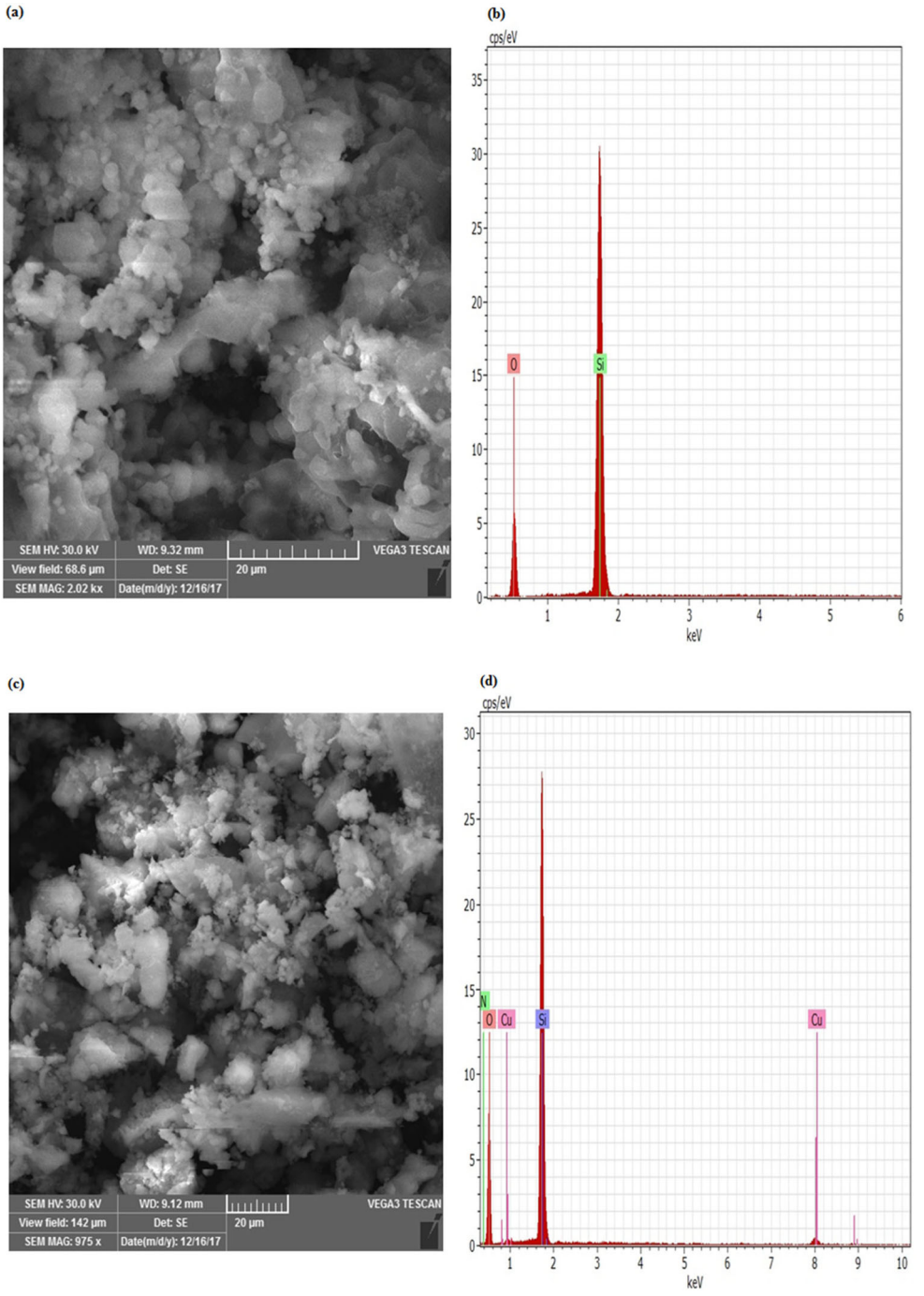


Figure 3. SEM images and EDX spectra of (a) (b) MCM-41, (c) (d) Cu-complex-phen-MCM-41 and (e) (f) Cu-complex-bipy-MCM-41.

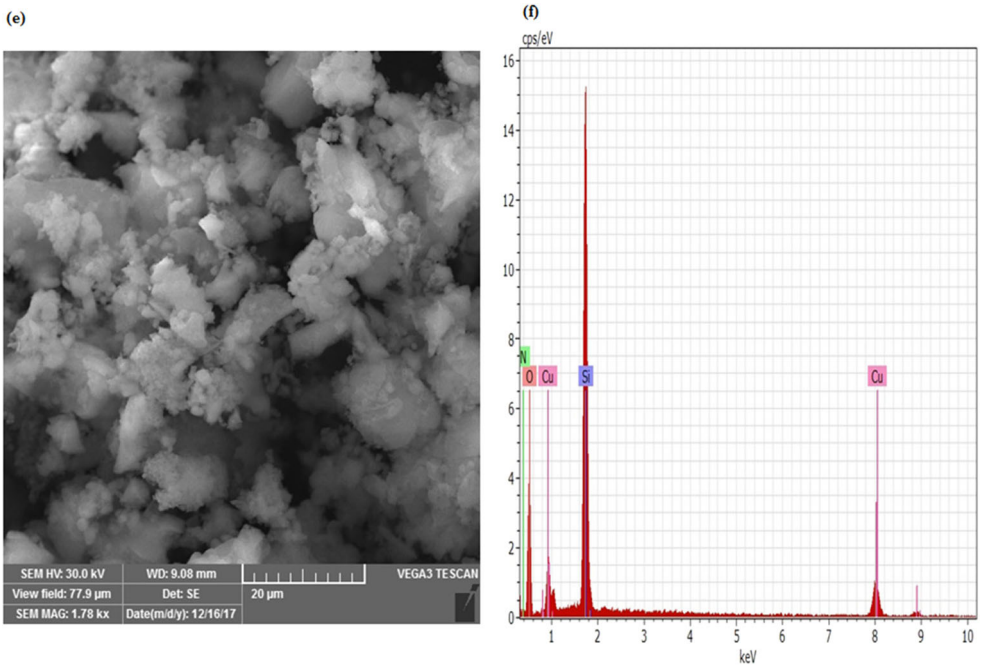


Figure 3. (Continued)

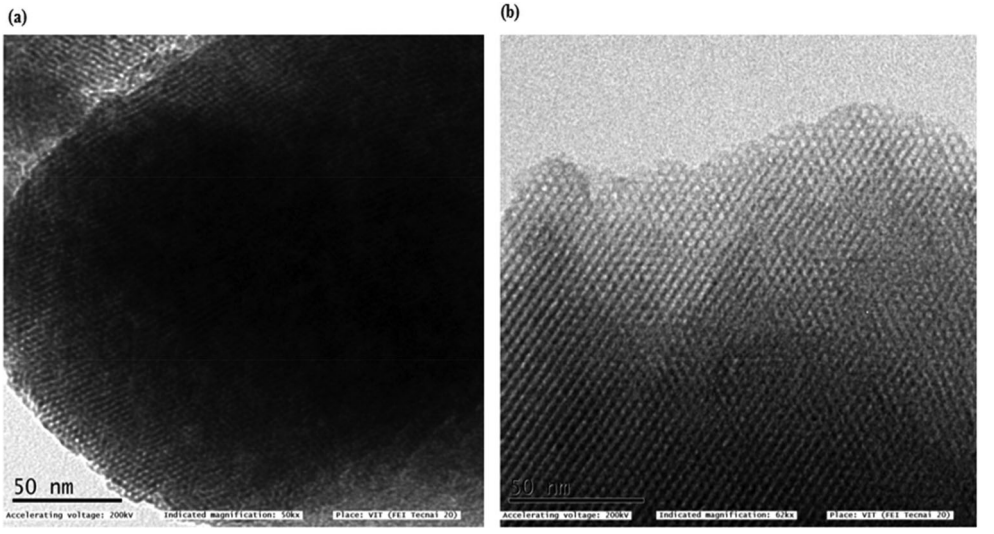


Figure 4. TEM images of (a) Cu-complex-phen-MCM-41 and (b) Cu-complex-bipy-MCM-41.

carried out the reaction in different solvents in the presence of $\mathbf{C_1}$/$\mathbf{C_2}$ (Table 2, entries 1-6). Ethanol and methanol were the best solvents (Table 2, entries 1 and 2) while using $\mathbf{C_1}$ and $\mathbf{C_2}$, respectively. We carried out the reaction in neat ethanol/methanol for 90 min. The reaction was very sluggish and gives only a small amount of product (Table 2, entries 9 and 10). The reaction temperature was optimized as 60 °C (Table 2, entries 1 and 2).

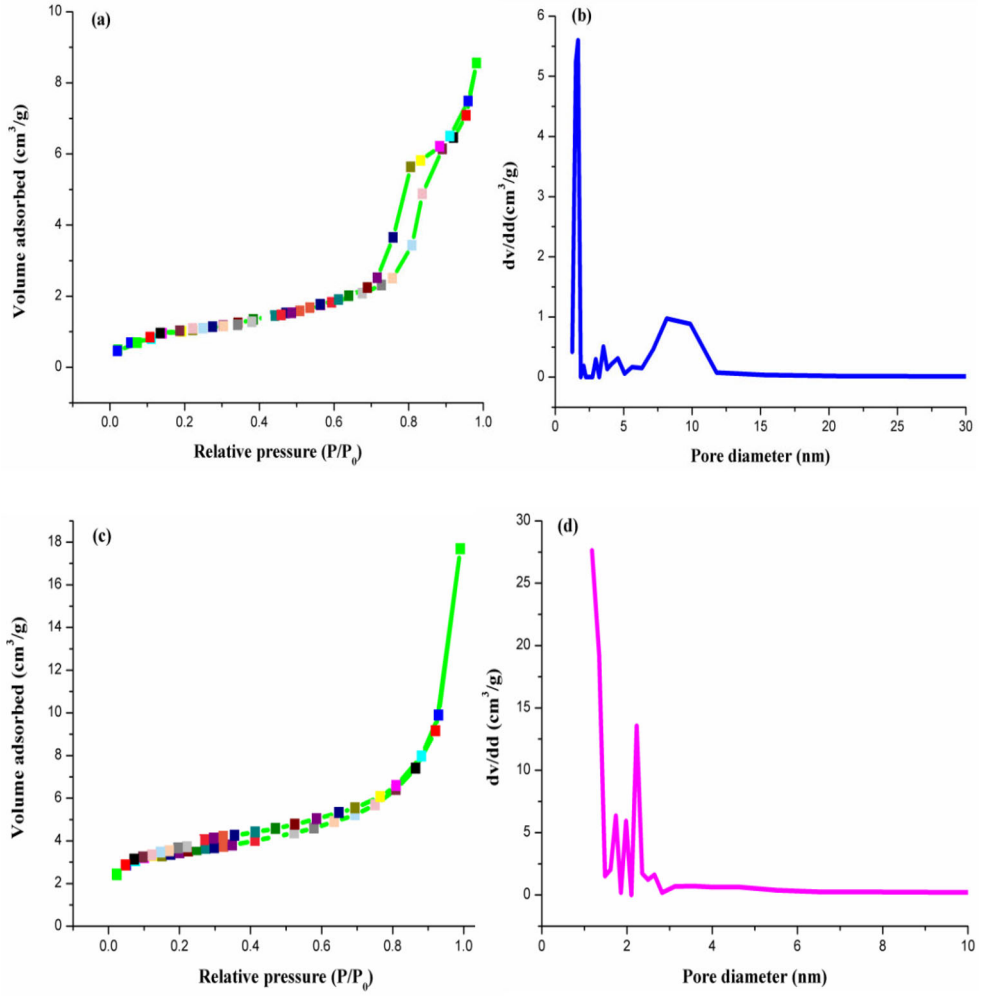


Figure 5. BET images of (a) (b) Cu-complex-phen-MCM-41 and (c) (d) Cu-complex-bipy-MCM-41.

To investigate the effect of the catalysts, systematic studies were carried out in the presence of different amounts of catalyst (20, 30, 40 and 50 mg) (Table 3). By increasing the catalyst amount above 30 mg, there was a slight decrease in the yield of the product (Table 3, entries 1 and 2). Thus, the best yield was found using 30 mg of catalysts. In the next step, the influence of time in the presence of catalysts was examined. When the reaction time was increased gradually from 30 min to 90 min, the rate of the reaction increased (Table 4, entries 1 and 2). Optimization results reveal that 30 mg of catalysts at 60 °C for 90 min was most suitable for this reaction.

Comparative studies between pure MCM-41, pure complexes (Cu-complex-phen/bipy) and catalysts ($\mathbf{C_1}$ and $\mathbf{C_2}$) were performed for the synthesis of benzimidazole derivative; 2-nitro benzaldehyde in ethanol and vanillin in methanol were selected as model substrates for $\mathbf{C_1}$ and $\mathbf{C_2}$, respectively (Figure 7). The yield of product is remarkably increased while using $\mathbf{C_1}$ and $\mathbf{C_2}$ when compared to pure MCM-41 and pure complexes.

Table 1. Surface properties of MCM-41, Cu-complex-phen-MCM-41 and Cu-complex-bipy-MCM-41.

Entry	Materials	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
1	MCM-41	1091.165	0.805	2.7
2	Cu-complex-phen-MCM-41	3.719	0.013	1.6
3	Cu-complex-bipy-MCM-41	10.883	0.016	1.1

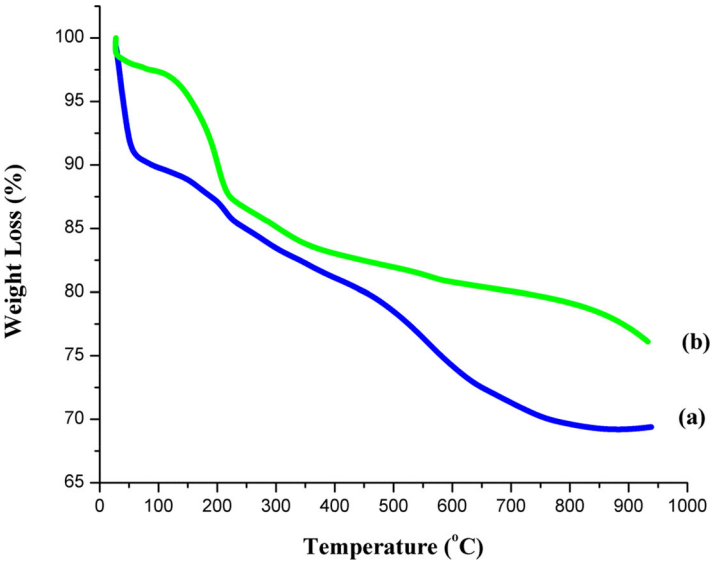


Figure 6. TGA curves of (a) Cu-complex-phen-MCM-41 and (b) Cu-complex-bipy-MCM-41.

Table 2. Effect of solvent and temperature for the synthesis of benzimidazole derivatives reaction.[a]

			Yield %	
Entry	Solvent	Temperature (°C)	Cu-complex-phen-MCM-41	Cu-complex-bipy-MCM-41
1	Ethanol	60	95	89
2	Methanol	60	55	93
3	Water	60	65	76
4	DCM	60	67	72
5	Toluene	60	39	75
6	Acetonitrile	60	80	68
7	Ethanol	RT	66	-
8	Methanol	RT	-	65
9	Ethanol[b]	RT	42	-
10	Methanol[b]	RT	-	46

[a]Reaction conditions: 1 mmol of *o*-phenylenediamine, 1 mmol of benzaldehyde, Cu-complex-phen/bipy-MCM-41 (30 mg) as catalyst in (6 ml) of solvent for 90 min under ultrasonic irradiation.
[b]Reaction was carried out under neat condition (without catalyst).

Under optimized conditions, we have carried out the catalytic reactions with *o*-phenylenediamine and a range of aldehydes bearing various electron donating (Table 5, entries 2, 7 and 10)/electron withdrawing (Table 5, entries 4-6) and sterically hindering groups. Good to excellent yields of products for all types of aldehydes were obtained (Table 5). Our catalysts have also given good yields with the disubstituted aldehydes (Table 5, entries 3 and 9) and the catalytic reaction of fused ring aldehyde

Table 3. Effect of catalyst amount.[a]

Entry	Catalyst	Solvent	Amount of catalyst (mg)	Yield (%) [b]
1	Cu-complex-phen-MCM-41	Ethanol	20 / **30** / 40 / 50	78 / **95** / 87 / 90
2	Cu-complex-bipy-MCM-41	Methanol	20 / **30** / 40 / 50	87 / **93** / 90 / 92

[a]Reaction conditions: 1 mmol of o-phenylenediamine, 1 mmol of benzaldehyde, catalyst in 6 ml of solvent at 60 °C for 90 min under ultrasonic irradiation.
[b]Isolated yield.

Table 4. Effect of time.[a]

Entry	Catalyst	Solvent	Time (min)	Yield (%)[b]
1	Cu-complex-phen-MCM-41	Ethanol	30 / 60 / **90**	57 / 75 / **95**
2	Cu-complex-bipy-MCM-41	Methanol	30 / 60 / **90**	52 / 69 / **93**

[a]Reaction conditions: 1 mmol of o-phenylenediamine, 1 mmol of benzaldehyde, (30 mg) catalyst in 6 ml of solvent at 60 °C under ultrasonic irradiation.
[b]Isolated yield.

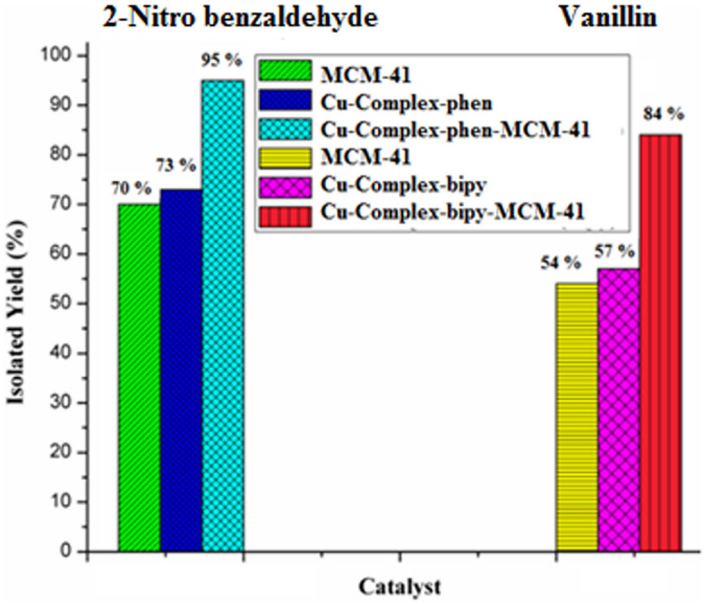
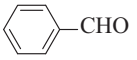
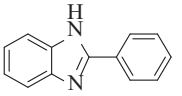
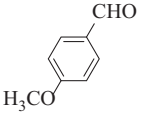
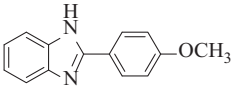
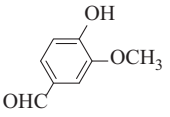
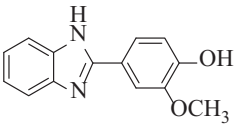
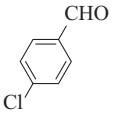
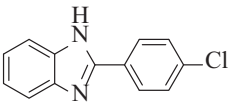
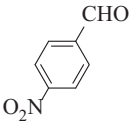
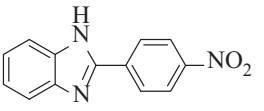
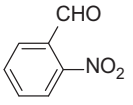
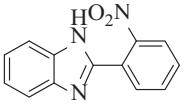
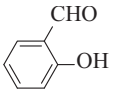
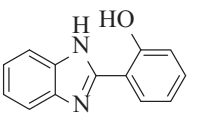
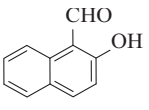
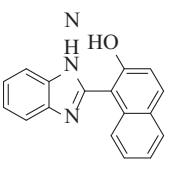
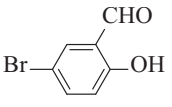
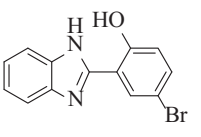


Figure 7. Catalytic performance of the benzimidazole derivatives reaction.

(Table 5, entry 8) has also gone well. Steric hindrance of the catalyst and the substituent of the substrate affect the yield of the catalytic reaction. $\mathbf{C_1}$ gives higher yield while using ortho-substituted aldehydes (Table 5, entries 6-8) whereas $\mathbf{C_2}$ gives higher yield while using para-substituted aldehydes (Table 5, entries 2, 4, 5 and 10) as substrates.

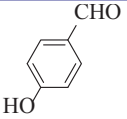
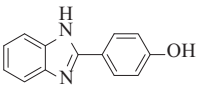
We have also compared the activity of our catalysts with some previously reported homogeneous/heterogeneous catalysts (Table 6). The activity of our catalyst is much better than entries 2, 3, 5, 6 and 8. Although the catalysts in entries 1, 4, 7 and 9 gave similar or slightly higher yields when compared to our catalysts, they possess some crucial disadvantages. Our catalyst overcomes those disadvantages and has given better yields. In entry 1, TBAF (tetrabutylammonium fluoride) has been used as a

Table 5. Synthesis of various aryl benzimidazole derivatives by Cu-complex-phen/bipy-MCM-41 catalyst.[a]

			Cu-complex-phen-MCM-41[b]			Cu-complex-bipy-MCM-41[c]		
Entry	Aldehyde	Product	Yield (%)[d]	TON[e]	TOF (h^{-1})[f]	Yield (%)[d]	TON[e]	TOF (h^{-1})[f]
1			95	115	77	93	100	67
2			64	77	51	69	74	49
3			81	98	65	83	90	60
4			57	69	46	59	64	43
5			51	61	41	76	82	55
6			95	115	77	73	79	51
7			43	52	35	40	44	29
8			62	75	50	60	65	43
9			55	66	44	61	66	44

(*continued*)

Table 5. Continued.

Entry	Aldehyde	Product	Cu-complex-phen-MCM-41[b] Yield (%)[d]	TON[e]	TOF (h^{-1})[f]	Cu-complex-bipy-MCM-41[c] Yield (%)[d]	TON[e]	TOF (h^{-1})[f]
10			70	85	57	75	81	54

[a]Reaction conditions: 1 mmol of o-phenylenediamine, 1 mmol of aldehyde (30 mg, 0.824%, 0.921% Cu) catalyst in (6 ml) solvent under ultrasonic irradiation at 60 °C for 90 min.
[b]In ethanol (6 ml).
[c]In methanol (6 ml).
[d]Isolated Yield.
[e]Turnover number (TON) = (mmol of product)/(mmol of catalyst) after time t.
[f]TOF = TON/time.

Table 6. Comparison of the different procedures with some reported catalysts, which has been applied for the synthesis of benzimidazole derivative.[a]

Entry	Catalyst	Condition	Yield (%)	References
1	Tetrabutylammonium fluoride (TBAF)	Water, RT, ultrasonic irradiation, 30 min	94	[51]
2	Graphene-oxide	Methanol, 35 °C, ultrasonic irradiation, 70 min	86	[52]
3	Ammonium nickel sulphate	Water, RT, ultrasonic irradiation, 135 min	80	[53]
4	$NiEuFe_2O_4$	Water, RT, ultrasonic irradiation, 20 min	95	[54]
5	Sulfonated graphene oxide	Solvent free, RT, 7 h	89	[55]
6	HPFP-1(NP)	Ethanol, RT, 3 h	90	[56]
7	AlKIT-5	Acetonitrile, reflux, 4 h	95	[36]
8	Ni-MCM-41	Glycerol, 90 °C, 4 h	75	[38]
9	Co/SBA-15	Ethanol, 60 °C, 4 h	98	[57]
10	Cu-complex-phen-MCM-41	Ethanol, 60 °C, ultrasonic irradiation, 90 min	95	This work
11	Cu-complex-bipy-MCM-41	Methanol, 60 °C, ultrasonic irradiation, 90 min	93	This work

[a]Benzimidazole derivatives of o-phenylenediamine and benzaldehyde.

homogeneous catalyst. Hence, it is very difficult to recover and reuse. Although $NiEuFe_2O_4$ has been used as a heterogeneous catalyst in entry 4, the cost of one of the reactants (rare earth europium salt) is much higher than that of the simple copper acetate, that we have used. Moreover, the calcination of their catalyst required much-elevated temperature (800 °C) over our MCM-41 (550 °C). In entries 7 and 9, heterogeneous catalysts AlKIT in acetonitrile under reflux for 4 h and Co/SBA-15 in ethanol at 60 °C for 4 h were used, respectively. From an environmental perspective, acetonitrile is not a green solvent [49]. Our catalysts give the same/competitive yield by using alcohols (ethanol/methanol) as solvents, in a shorter reaction time of 90 min under ultrasonic irradiation.

Overall, our catalysts are more promising than others due to their following factors: i) heterogeneous nature, reusability, ii) greener catalytic conditions (ultrasonication, ethanol/methanol) and iii) low-cost catalyst. Above all, we have used a new class of mixed ligand complexes as catalysts in order to enhance the activity by "synergistic effect".

Finally, the reusability of $\mathbf{C_1}$ and $\mathbf{C_2}$ was checked in 2-nitro benzaldehyde in ethanol and vanillin in methanol, respectively, at 60 °C for 90 min under ultrasonic irradiation.

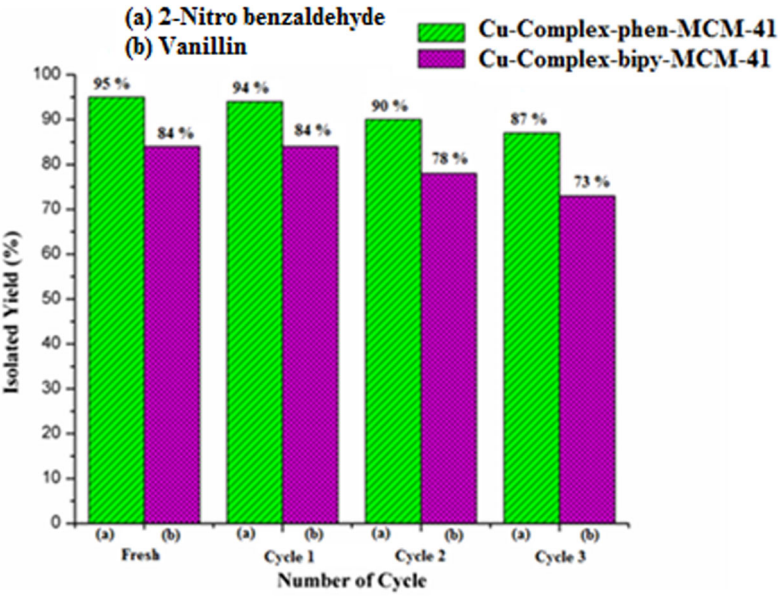
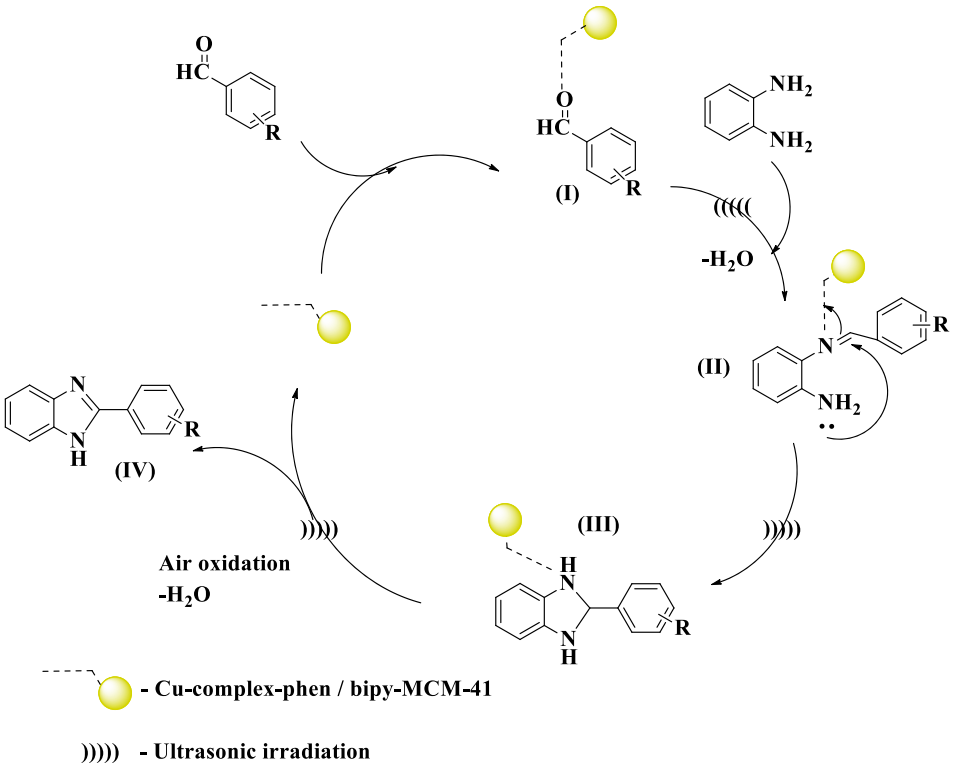


Figure 8. Reusability of catalyst Cu-complex-phen/bipy-MCM-41 for benzimidazole derivatives reaction.



Scheme 3. Plausible mechanism for the synthesis of benzimidazole derivatives.

The catalysts were separated by simple filtration after each cycle, washed with ethanol/methanol and then subjected to the next cycle. The catalysts were reused up to three cycles without any significant loss of activity (Figure 8).

The proposed mechanistic path for the formation of benzimidazoles in the presence of a catalyst is shown in Scheme 3 [50]. The catalyst coordinates with the carbonyl group of aldehyde to assist the nucleophilic addition of *o*-phenylenediamine to the activated aldehyde (I) and gives the intermediate (II). Then the intermediate (II) undergoes intramolecular Michael-type addition to give intermediate III, which is oxidized in air and gives the desired products.

3.8. Hot filtration test

To examine the leaching of metal from solid catalyst during the reaction, hot filtration test was performed. In this test, a mixture of 2-nitro benzaldehyde and *o*-phenylenediamine with $\mathbf{C_1}$ (30 mg) in ethanol was heated at 60 °C for 90 min under ultrasonic irradiation. Then, the catalyst was removed from the reaction mixture and the reaction was continued with the filtrate for further 90 min at same conditions. It was observed that the yield of the product was not increased after the removal of catalyst (95% and 94% yield for before and after the test). A similar result was obtained while using $\mathbf{C_2}$ with the substrate vanillin (84% and 83.5% yield before and after the test), confirming that there is no leaching of metal during the catalytic reaction and the heterogeneous nature of the catalyst.

4. Conclusion

We have synthesized and characterized two heterogeneous catalysts, Cu-complex-phen/bipy-MCM-41. The catalysts were used for synthesis of benzimidazole derivatives under a green pathway *i.e.*, using methanol/ethanol as a solvent and ultrasonic irradiation. We have also discussed the influence of the steric factor based on the position of the substituent in the substrates on the yield of the catalytic product with good to excellent yields and also easy recovery. Hot filtration test confirmed that there is no leaching of the metal from the catalyst even after the third cycle which shows the stability and purity of the catalyst. Hence, the catalysts were successful for the catalytic reaction up to three cycles without any significant loss in the yield of the product. In particular, the new class of mixed ligand complexes have shown a new path in the heterogeneous catalysis and enhance the activity by the synergistic effect.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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