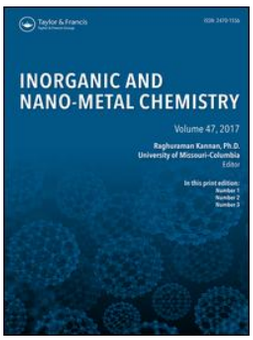

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BiOCl/FeOCl/SiO_2 nano composite as an efficacy novel catalyst toward synthesis of 2-aryl-1H-benzimidazoles in mild aerobic condition

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Abstract

BiOCl/FeOCl nano rods composited with spheres nano particles of SiO_2 as a novel nano catalyst has been synthesized by using a co-precipitation procedure and structural properties of this catalyst have been characterized by TEM, SEM, XRD, EDS as well as FT-IR spectroscopy. In addition, this nano composite was utilized to synthesis of 2-arylbenzimidazole derivatives efficiently that is described by the condensation of some aldehydes and o-phenylenediamines in present of BiOCl/FeOCl/SiO_2 nano composite as a novel nano catalyst Besides the investigated variables such as the amount of catalyst, reaction temperature, the synergistic effect of BiOCl and FeOCl, effect of various solvents, considered reusability of the catalyst are studied also. In

conclusion, synthesized BiOCl/FeOCl/SiO_2 nano composite with some several remarkable advantages like non-toxic nano catalyst, recovering and recycling for three runs minimally without significant loss of catalytic activity under aerobic mild condition, short reaction times and solvent free.

Keyword: Nanocomposite, Inorganic catalysis, Nanostructure, Catalytic properties, Benzimidazoles

1. Introduction

Over the past decade, nanomaterials have been widely investigated in the fields of chemistry, physics, electronics, biology, and medicine because of their unique chemical and physical characteristics, which are different from those of bulk materials [1]. Nevertheless, the preparation of an artificially designed structure of nanoparticles with new properties such as high surface area-to-volume ratios and tunable nanoscale sizes has attracted the attention of many researchers. [2, 3] Recently, for the synthesis of organic compounds, supported nanoparticle catalysts have been extensively studied, because the particle size decreases, relative number of surface atoms increases so that activity will increases [4]. Nanoparticle catalysts can also be easily separated and recycled with more retention of catalytic activity compare with their bulk counterparts [5].

Further, an important class of heterocyclic compounds in the pharmaceuticals as cardio tonic agents is the synthesis of potential antitumor [6], poly (ADP-ribose) phosphorilase inhibitors [7], Histamine H4 receptor binders [8], anti-parasitic [9], cardiovascular [10], anti-cancers [6], antimicrobials [11] and anti-hypertensive [11]. Moreover, due to the high importance of 2-aryl-1H-benzimidazoles for the preparation of biologically active molecules, their synthesis has received considerable attention so, many reports have been cited in the literature which describe the formation of 2-arylbenzimidazoles[12-15].

Nowadays bimetallic nanoparticles have attracted enormous attention as they provide exciting opportunities not only for developing novel catalysts with unique but also improved activities [16]. In addition, one of the bimetallic catalyst heavy post-transition elements like Bismuth, Lead, or Thallium with metallic transition elements like Pd or Pt for the selective organic reaction such as oxidation of alcohols into aldehydes and carboxylic acids and catalytic oxidation of glucose [17]. Additionally the promoting role of other post-transition elements such as Te or transition metals has also been investigated for some organic reactions [18]. Generally, bimetallic Co and Mn have been used as a catalyst for the synthesis of bis(indolyl)methanes in the past [19].

As the purpose of the present work, the innovative BiOCl/FeOCl nano rods composited with spheres nano particles of SiO_2 as a novel nano catalyst. Moreover, this study was designed with post-transition and transition elements (Bismuth and Iron) with different electronegativity to investigation catalytic synergistic effect of BiOCl and FeOCl. Additionally, SiO_2 nano particles not only play role as mediator agent for starting interactions but also as the substrate causes to increase the catalyst surface throughout the reaction. Furthermore morphology,particle size and crystal structure of nanocatalyst were explored by TEM, SEM, XRD, EDS, mapping, and FT-IR spectroscopy. In the application of this catalyst, the impressive synthesis of 2-aryl-1H-benzimidazoles has been carried out by Bi/Fe/SiO_2 nano composite.

2. Experimental

2.1. Measurement

All reagents and solvents were commercially available and were used as such. Silicon Oxide (SiO_2, 25 wt%, 20-30 nm) was purchased from Nanostructured & Amorphous Materials, Inc.

The sample powder was analyzed by X-ray diffraction (XRD). This instrument (Philips, xpertpro, nitherland) works with voltage and current settings of 40 kV and 30 mA, respectively and uses Cu–Kα radiation (1.540510 Å). For the qualitative analysis, XRD diagrams were recorded in the interval of $0° \leq 2\theta \leq 80°$ at scan speed of 2°/min. The crystalline size of the synthesized particle was calculated following Scherrer's equation. The morphology of catalysts and their precursors were observed by means of a Philips XL30 scanning electron microscopy (SEM).

The morphology of the nano catalysts was studied by transmission electron microscopy (TEM). In addition some specimens of synthesized nano catalyst for TEM studies were prepared by ultrasonic dispersion of the catalysts in ethanol, and the suspensions were dropped onto a carbon-coated copper grid. TEM investigations were carried out using a (LEO 912 AB, 120 kV). The FT-IR spectra of the samples (as KBr pellets) were recorded using a Rayleigh WQF-510 spectrophotometer in the range of 400–4000 cm^{-1}. Melting points were determined using Electrothermal 9300 Melting Point. ^{1}HNMR spectra were recorded on Bruker 200 MHz NMR spectrometer.

2.2. Preparation of nano catalyst

First step was referred to $BiCl_3$ (0.5mol/l), $FeCl_3.6H_2O$ (0.5 mol/l) with 1/1 molar ratios [Bi/Fe] in ethanol and for different ratio of [Bi/Fe] the molars of $BiCl_3$, $FeCl_3.6H_2O$ must been changed, and amount (15 wt %) of nano SiO_2 were pre-mixed in a round-bottomed flask fitted with a condenser and the resulting solution heated. Then Aqueous Na_2CO_3 (0.5 mol/L) was added slowly to the mixed chloride solution, which was continuously stirred whilst the temperature was maintained isothermally in the range of 70–85 °C. The final pH achieved was

10; this procedure took approximately 15 min to complete and reflux for 5–6 h. The precipitate was first filtered and then washed several times with warm distilled water until no further Na^+ was observed in the washings tested by flame atomic absorption. Finally, the precipitate has been dried at 150 °C for 16 h.

2.3. Catalytic reaction procedures

A mixture of 1, 2-phenylenediamine (1mmol), aldehyde (1.1 mmol), and BiOCl/FeOCl/SiO_2 nano composite (0.015 g) as catalyst was heated at 70 °C for the appropriate time as mentioned in. After the progress of reaction was completed that monitored by TLC, then the reaction was dissolved in 10.0 mL of ethanol and transferred to a centrifuge tube and centrifuged at 4000 rpm for 10 min to precipitate and recover the BiOCl/FeOCl/SiO_2 nano composite catalyst. The clear supernatant was collected and the BiOCl/FeOCl/SiO_2 nano composite catalyst was repeatedly washed)dispersion in 3 mL of ethanol followed by centrifugation, three cycles) for recycling experiments. The reaction mixture that was dissolved in ethanol poured into ice water (30 mL). As a final point, the pure solid product was filtered, washed with ice water and subsequently dried completely.

3. Results and discussion

3.1. Characterization of nano catalyst

In this study, BiOCl/FeOCl /SiO_2 nano composite was synthesized by a mixing method through $BiCl_3$ (0.5mol/L) and $FeCl_3.6H_2O$ (0.5 mol/L) with 1/1 molar ratio [Bi/Fe] in ethanol, and 15 wt % nano SiO_2. Furthermore, the nano composite was characterized using X- XRD, TEM, SEM, EDX, mapping, and FT-IR spectra. According to the XRD patterns of Bi/Fe Nano

particles that shown in Figure1 which demonstrates the reflections characteristic of BiOCl crystal with the tetragonal structure (JCPDS Card 82 0485: a 3.888 Å and c 7.357 Å) and FeOCl crystal with the tetragonal structure (JCPDS Card 24-1005: a 3.7715 Å and c 3.3026 Å).As can be seen from XRD patterns the formation of BiOCl and FeOCl crystals have been supported on SiO_2 obviously [20, 21]. Additionally the crystal system of them were Tetragonal and Orthorhombic along with space group of P4/nmm as well as Pmnm respectively.

According to the half-height of peck list of BiOCl/FeOCl nano rods, the crystallite diameters of them were calculated using the Scherrer equation (Eq1).Therefore the estimated crystallite diameters of BiOCl/FeOCl nano rods were around 21.35 nm. In addition, Figure 1 shows X-ray pattern of BiOCl/FeOCl.

Figure 1

The TEM image in Figure 2 reveals that the product consisted of nanorod structure with the average size of 10–15 nm. The characterization of new catalyst synthesized from the 1/1 sample of BiOCl/FeOCl /SiO_2 nano composite was carried out using SEM also. An additional all the electronic micrographs of SEM-EDX were obtained from the powder specimens of these materials, in addition SEM was used to obtain information on morphology and structure of products, which was shown in rod-like nanostructures (Figure 3a). In general, the SEM micrographs were in good agreement with the TEM observations. SEM-EDX aimed to obtain information on their microstructural and metal dispersion properties (Figure 3 b). Since metal

mapping studies were used to understand the dispersion of metals and their agglomeration behaviors on the support surface of nano catalyst including the Bi and Fe species over the composition process were determined by EDX so that metal mappings analysis obtained from different samples are given in Figure 3c. Overall, the EDX spectra of the nano composite has been collected to evaluate their elemental composition along with percentage distribution , to sum up Figure 3b presents a representative spectrum showing well-resolved peaks for both Bi and Fe along with Si in synthesized nano catalyst.

Figure 2

Figure 3

In particular, BiOCl and FeOCl were observed that dispersed homogeneously amongst the SiO_2 nano particles during the catalyst prepared by co-precipitations properly. As Figure 4 shows the FT-IR spectrum of the BiOCl /FeOCl among SiO_2 nano particles, where the peaks of around 660 cm^{-1} and 1400 cm^{-1} were assigned to Bi-O of BiOCl and Fe-Cl respectively. Subsequently a peak observed at 1100 cm^{-1} indicated the Si-O and the one at 3600 cm^{-1} could be attributed to the O-H bond in the nano SiO_2 surface.

Figure 4

3.2. The catalytic synergistic effect of BiOCl /FeOCl/SiO_2 nano composite

Thereafter catalytic synergistic effect of BiOCl and FeOCl in the range of 100% Bi to 100% Fe for the synthesis of 2-(4-chlorophenyl)-1H-benzo[d]imidazole was studied (Figure 5a). The result was shown that the yield of reaction for the synthesis of 2-(4-chlorophenyl)-1H-benzo[d]imidazole increased with increasing the concentration of Bi so that the maximum yield (95%) of 2- (4-chlorophenyl)-1H-benzo[d]imidazole was achieved with the ratio of [Bi]/[Fe]=3/1. Since not Bi nor Fe nanoparticles are very active for the synthesis of 2-(4-chlorophenyl)-1H-benzo[d]imidazole, it is difficult to attribute this enhancement to anything other than a synergistic modification of BiOCl by FeOCl nanoparticles through the SiO_2 nano spheres as mediator agent.

3.3. The investigated catalytic activity effect

The benzimidazole derivatives have been synthesized from the reaction of o-phenylenediamine (1 mmol) and 4-chlorobenzaldehyde (1.1 mmol) as a model in the both absence and presence of BiOCl /FeOCl nano rods, besides other catalyst such as nano-SiO_2 and SiO_2 under thermal solvent-free conditions for investigating optimum situations. As shown in table1, this transformation required amount 0.015 g of a BiOCl /FeOCl nano rods as a nano catalyst at 70°C for 17 min it has been chosen for the preparation of benzimidazole derivatives. To summarize the optimized conditions were further extended for the synthesis of benzimidazole derivatives.

3.4. The efficacy of temperature on the rate of reaction

Dependency the rate of reaction with effect of temperature were carried out at different range temperatures for the preparation of 2-(4-chlorophenyl)-1H-benzo[d]imidazole. According to the result can observe that the reaction was not completed at room temperature, yet the reaction has

been continued smoothly and almost complete conversion of the product was observed at 50°C. Further, increasing in temperature to 70, 100, and 110°C enhancement the rate of reaction (Table 1). Therefore, the reaction temperature is kept at 70°C (providing short reaction time and high yield).

3.4. The effect of solvent

Certainly, solvent plays a critical role in chemical reactions therefore, we decided to investigate the efficacy of various solvents and select an appropriate condition for the preparation of benzimidazole. Moreover, we screened different solvents such as acetonitrile, ethyl acetate, ethanol, methanol, dichloromethane, water, and solvent-free for the preparation of benzimidazole as a typical example and the 4-chlorobenzaldehyde as well as 1,2-phenylendiamine as the substrates in the presence of 0.015 g catalyst in different solvents (Table1). As a final point solvent-free was found to be the most efficient one for this conversion in which the reactions in other solvents required longer reaction time and low yield. In addition, the optimized conditions were further extended for the synthesis of substituted benzimidazole (Table 2), ^{1}HNMR and ^{13}CNMR spectra of compound was reported in supplementary information (SI).

3.5. The investigate of weight catalyst

In the next step, the effect of catalyst weight was studied to find the optimized amount of nanocomposite catalyst as shown in Table 1, which the reaction was carried out by varying the amount of the catalyst on the conversion of 2-(4-chlorophenyl)-1H-benzo[d]imidazole. As result shows, it increased linearly with the catalyst weight up to 0.015g and then became constant so that these results indicated the amount of nanocatalyst required for the conversions.

Table 1

3.6. Plausible mechanism of the reaction

The Scheme 1 has been illustrated of proposed mechanism for the synthesis of the benzimidazoles. As the best of our knowledge, firstly the BiOCl/FeOCl /SiO_2 nano composite activated the aldehyde group through forming a coordinate bond with the Lewis acid site of a BiOCl/FeOCl over the surface of SiO_2 as mediator agent. Next step involved of nucleophilic addition by phenylene-1,2-diamine on the aldehyde produced intermediate (A). Since, ring closure provided a five-member ring by catalyst (B). Then, the oxidation of the (B) might be initiated by air as the oxidant agent for the preparation of (C) compound [20].

Scheme. 1

Table 2

3.7. Reusability of the nano catalyst

For testing the reusability, the separated catalyst was reused in four consecutive reactions between 4-chlorobenzaldehyde and o-phenylenediamine, by the way the conversion of the reactant after four cycles was almost constant and catalytic activity was observed as compared with the fresh catalyst (Figure 5b)

Figure 5

4. Conclusions

Spheres nano particles of SiO_2 composited with BiOCl/FeOCl nano rods was prepared by using a co-precipitation procedure and investigated for affecting synthesis of benzimidazole derivatives. Particularly, the optimum preparation conditions were identified with respect to catalytic performance for the conversion of synthesis benzimidazole derivatives. Furthermore, this catalyst have several advantages including short reaction times, excellent yields, inexpensiveness, mild conditions, non-toxic catalyst, as well as simple operation and work-up. Additionally, the nanocatalyst did not require volatile and hazardous organic solvents and an additional ultrasound or microwave oven. Above all elimination of the solvent has obvious environmental benefits in terms of the depletion of solvent waste. Overall, the nano catalyst could recover and recycle for three times at least without any significant loss in catalytic activity successfully.

Supporting Information

^{1}H NMR, and ^{13}C NMR of material are provided in supporting information.

Acknowledgments

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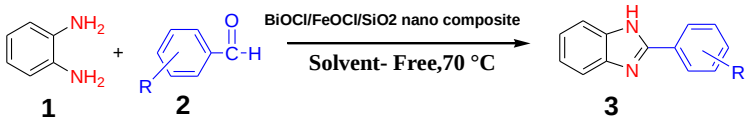
Table 1. Optimum conditions for the preparation of 2-(4-chlorophenyl)-1H-benzo[d]imidazol

Entry	Solvent	Catalyst Weight (g)	Catalyst	Temp. (°C)	Time (h)	Yield (%) [a]
			Effect of catalyst			
1	Solvent-free	——	No	70	24	___
2	Solvent-free	0.015	SiO_2	70	24	___
3	Solvent-free	0.015	SiO_2 nano particles	70	24	___
4	Solvent-free	0.015	BiOCl/FeOCl/SiO_2 nano composite	70	17	95
			Effect of temperature			
5	Solvent-free	0.015	BiOCl/FeOCl/SiO_2 nano composite	25	24	90
6	Solvent-free	0.015	BiOCl/FeOCl/SiO_2 nano composite	50	45	95
7	Solvent-free	0.015	BiOCl/FeOCl/SiO_2 nano composite	70	17	95
8	Solvent-free	0.015	BiOCl/FeOCl/SiO_2 nano composite	100	10	95
9	Solvent-free	0.015	BiOCl/FeOCl/SiO_2 nano composite	110	9	95
			Effect of solvent			
10	CH_3CN	0.015	BiOCl/FeOCl/SiO_2 nano composite	Refluxed	25	90
11	AcOEt	0.015	BiOCl/FeOCl/SiO_2 nano composite	Refluxed	20	95
12	CH_2Cl_2	0.015	BiOCl/FeOCl/SiO_2 nano composite	Refluxed	25	90
13	MeOH	0.015	BiOCl/FeOCl/SiO_2 nano composite	Refluxed	28	90
14	EtOH	0.015	BiOCl/FeOCl/SiO_2 nano composite	Refluxed	25	90
15	Solvent-free	0.015	BiOCl/FeOCl/SiO_2 nano composite	70	17	95
16	H_2O	0.015	BiOCl/FeOCl/SiO_2 nano composite	Refluxed	25	95
			Effect of catalyst weight			
17	Solvent-free	0.005	BiOCl/FeOCl/SiO_2 nano composite	70	17	40
18	Solvent-free	0.01	BiOCl/FeOCl/SiO_2 nano composite	70	17	80
19	Solvent-free	0.015	BiOCl/FeOCl/SiO_2 nano composite	70	17	95

19	Solvent-free	0.025	$BiOCl/FeOCl/SiO_2$ nano composite	70	17	95

[a] Isolated yield.

Table 2. Synthesis of benzimidazole derivatives



ENTRY	R	Time (min)	Yield(%) [a,b]	
1	4- OH	25	96	3a
2	4-Me	18	95	3b
3	4- Cl	17	95	3c
4	4- $(CH_3)_2N$	20	80	3d
5	H	20	95	3e
6	2-OH	25	93	3f
7	4- MeO	23	90	3g
8	4-Ph	20	95	3h
9	4-CHO	50	95	3i
10	3-NO2	50	95	3j
11	4-NO_2	50	95	3k
12	2-Cl	17	94	3l
13	4-F	20	96	3m

[A] THE PRODUCTS WERE CHARACTERIZED BY COMPARISON OF THEIR SPECTROSCOPIC AND PHYSICAL DATA WITH AUTHENTIC SAMPLES SYNTHESIZED BY REPORTED PROCEDURES.

[B] YIELDS REFER TO PURE ISOLATED PRODUCTS.

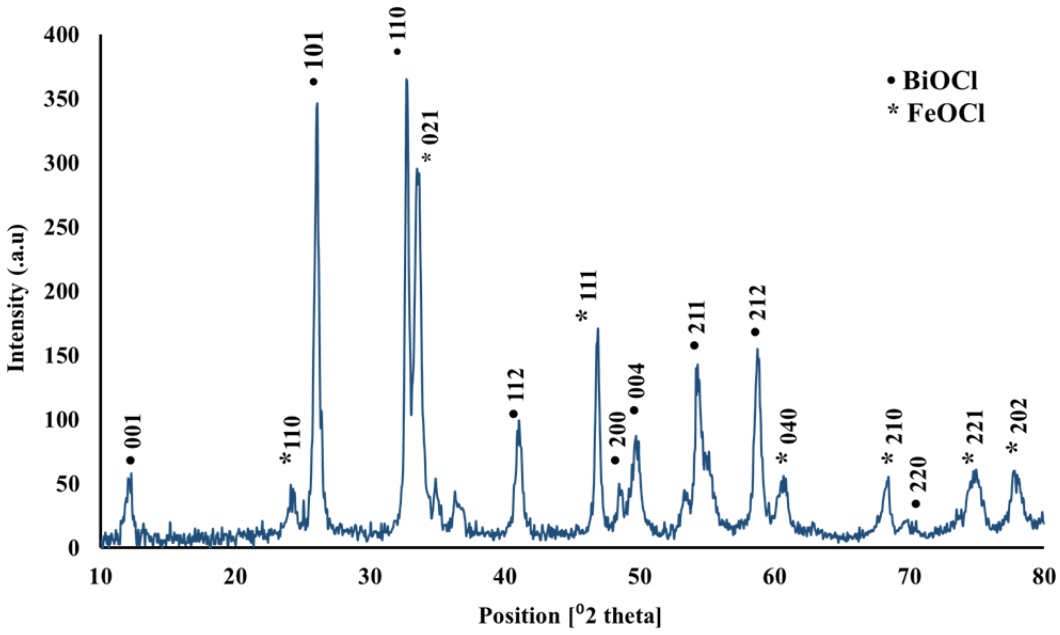


Figure 1. XRD pattern of BiOCl/FeOCl nano rods.

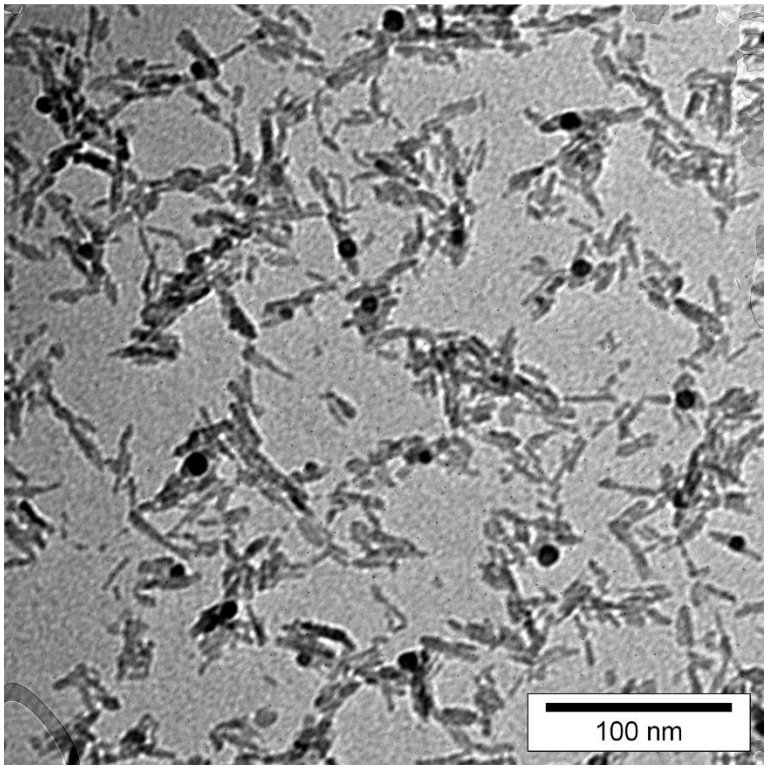
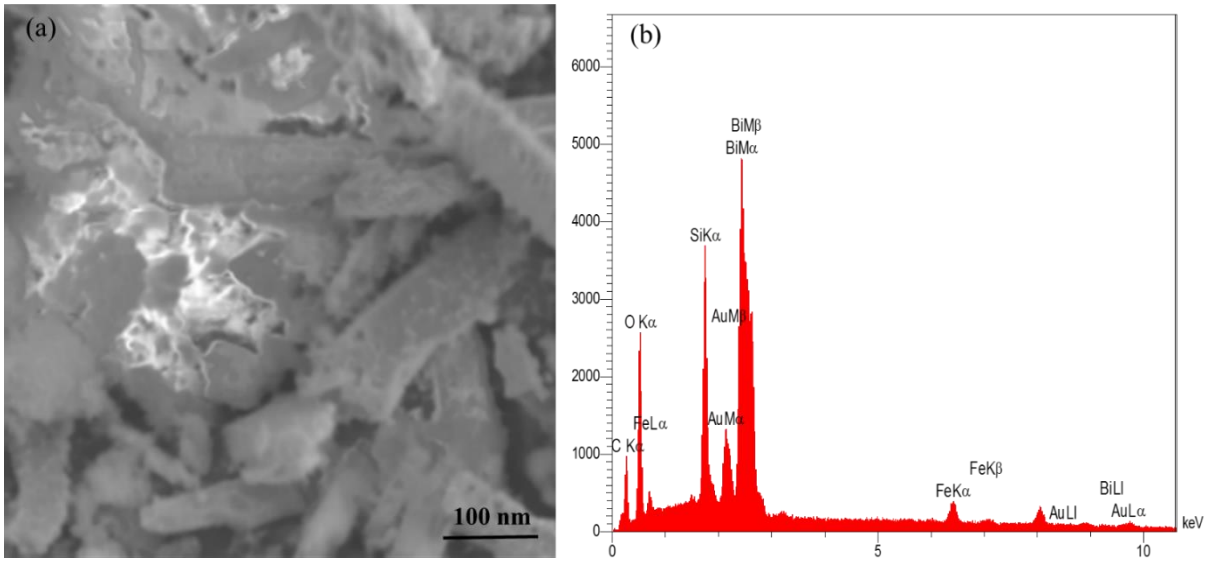


Figure 2. TEM images of the catalyst BiOCl/FeOCl/SiO_2 nano composite.



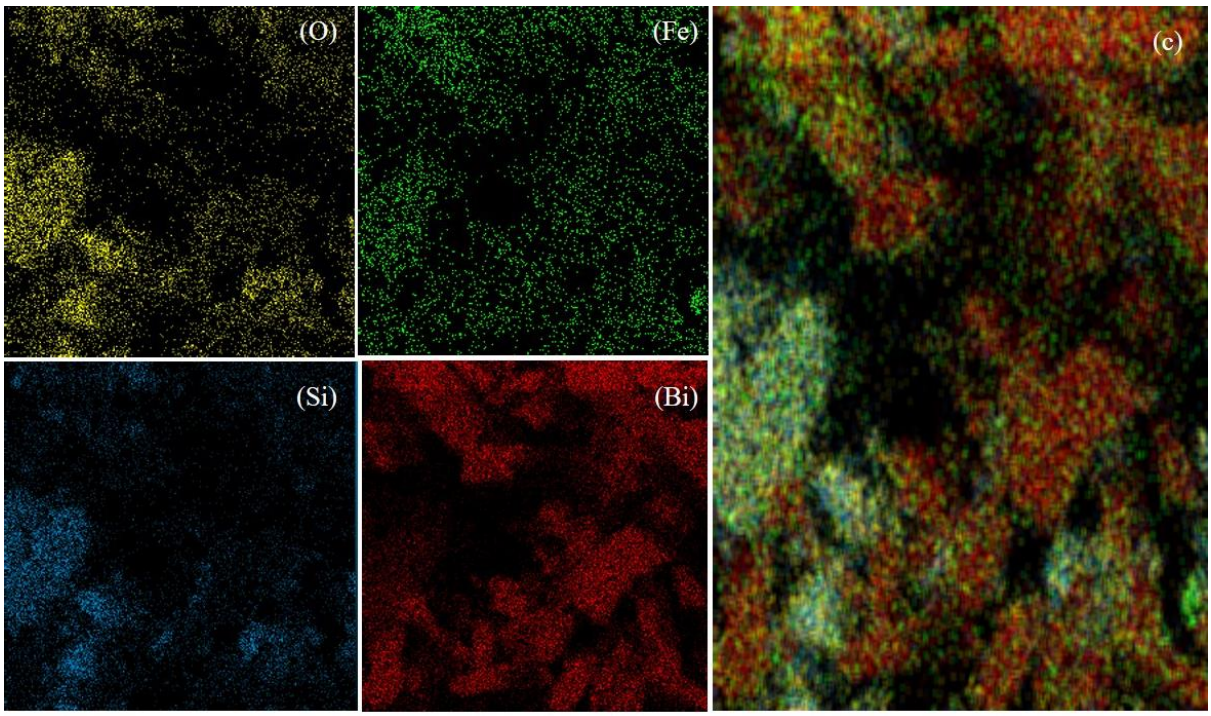


Figure 3. a) SEM images of the catalyst, b) EDX spectrum, c) mapping graph of BiOCl/FeOCl / SiO_2 nano composite.

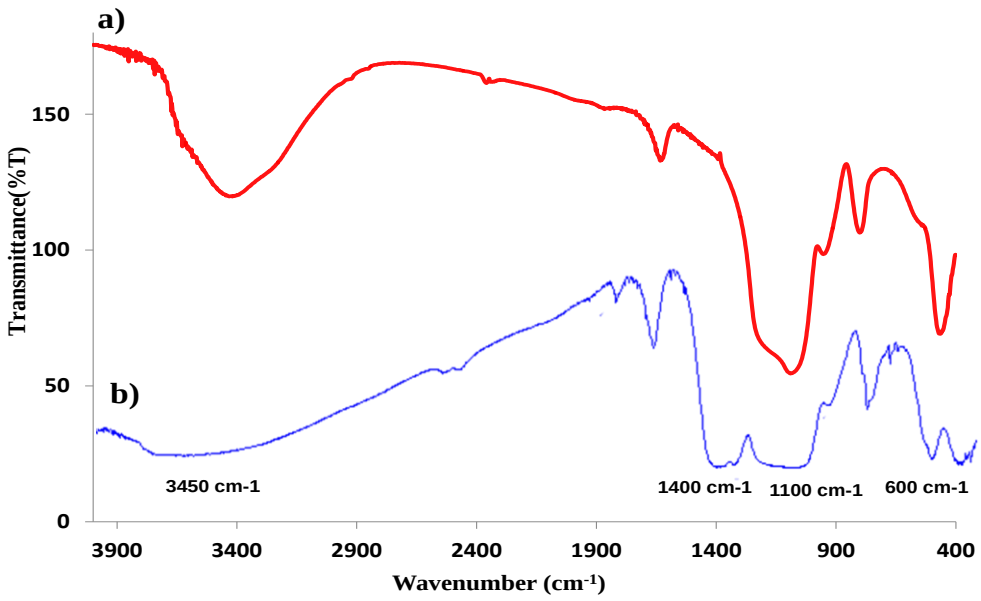
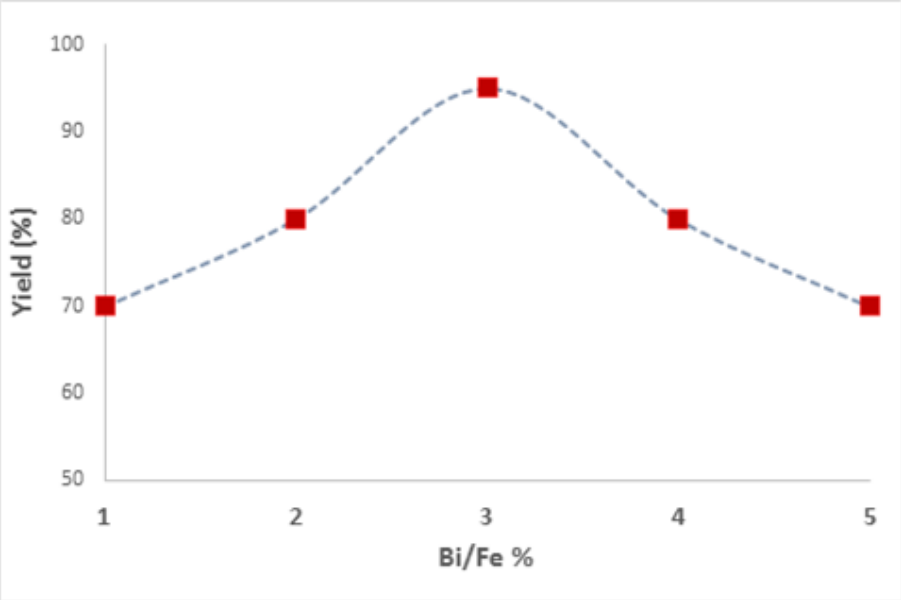


Figure 4. a) FT-IR spectrum of SiO_2 nano particles, b) BiOCl/FeOCl/SiO_2 nano composite.



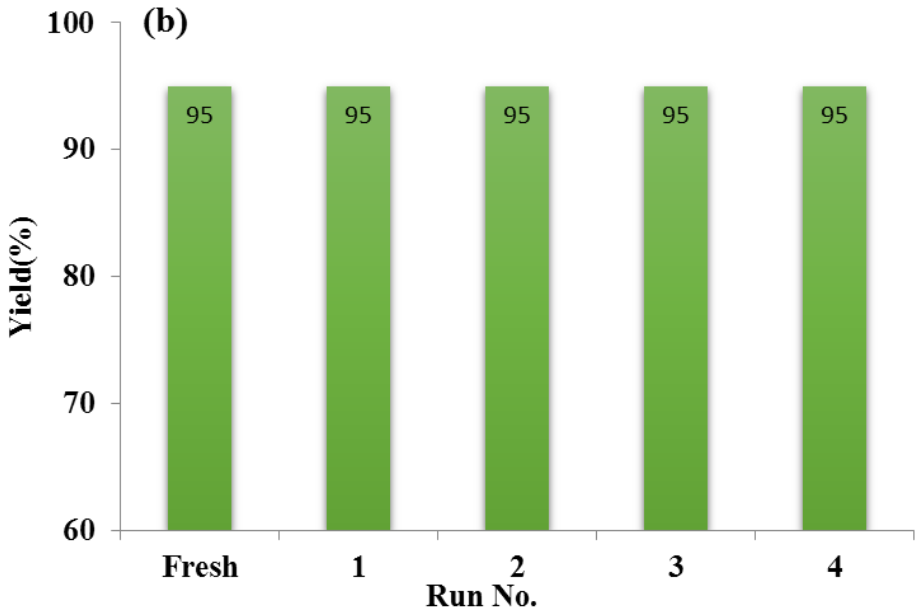
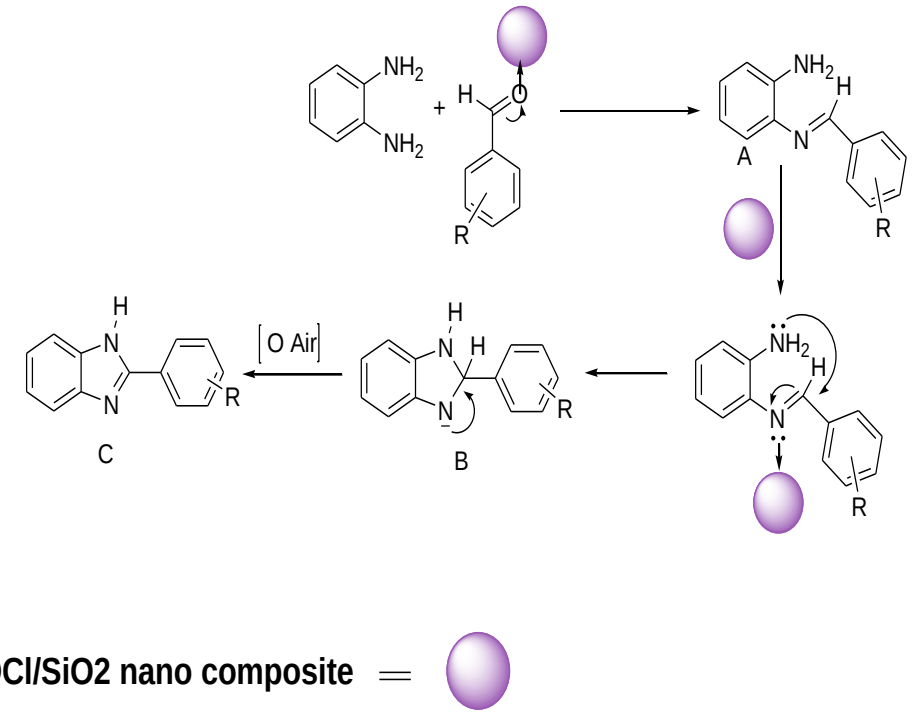


Figure 5. a) Effect of Bi/Fe molar ratio on the catalytic performance 1=0/100%, 2=50/50%, 3=75/25%, 4=25/75%, 5=100/0% of Bi/Fe, b) Reusability of the BiOCl/FeOCl nano rods.



Scheme. 1. The proposed mechanism for the synthesis of the benzimidazoles by BiOCl/FeOCl /SiO_2 nano composite.