

Imidazolium Hydrogen Sulphate Supported on Copper Oxide Nanoparticles as an efficient simple Heterogeneous Acidic Catalyst for Multi-component Synthesis of 1, 4- dihydro Pyrano [2, 3-c] pyrazoles Derivatives

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ABSTRACT

Si-Im/HSO₄(1-methyl-3-(3-(trimethoxysilyl) propyl) imidazolium hydrogen sulphate functionalized Copper oxide nanoparticles(CuO NPs) as a novel supporting ionic liquid was prepared and characterized by FT-IR spectroscopy, FE-SEM, XRD, TGA, and EDX techniques. It was used as a recyclable catalyst for the one-pot, three-component synthesis of 1, 4- dihydro Pyrano [2, 3-c] pyrazoles derivatives. The results showed that the catalyst was very efficient, and in addition, at the end of the reaction the catalyst could be easily isolated and reused for the next reaction without any appreciable loss of its catalytic activity. The reused catalyst was also characterized by the FE-SEM and EDX techniques.

Keywords: CuO NPs, functionalize, Imidazolium, Multi-component reactions

1. Introduction

The pyrazolones and bis-pyrazolones were paid much attention for their various biological activities; pyranopyrazoles are a class of heterocyclic compounds that have received significant attention from many chemists essentially because of their wide range biological and pharmaceutical attributes. Compounds including pyranopyrazoles have been found to have various biological activities, for example, antimicrobial, vasodilator, analgesic, anti-cancer, anti-inflammatory, molluscicidal, anti-fungicidal, and also as biodegradable agro-chemicals [1-5]. Different ways were developed for the synthesis of pyranopyrazoles compounds [6-8].

Metal oxides have a very important role in areas of chemistry, physics, and material science. Their surfaces play crucial roles in a wide range of phenomena [9-11]. One of the major problems of metal oxides nanoparticles is their association with different surface structures, which is represented by a high tendency of metal oxide NPs for adhesion and aggregation.

It is necessary to mention, the use of coupling agent is a good alternative to overcome this problem [12, 13]. Ionic liquids (ILs) have been used as a novel catalyst for a wide range of reactions [14-16]. Among these types of ionic liquids which are traditional, deep eutectic, and protic solvent (IL) the latter type has been proven to be an effective catalyst for a variety of reactions [17- 18]. There is an important demand for more effective and recyclable catalysts from both environmental and industrial viewpoints. ILs possesses some advantages, but their practical applications have been restricted by some degree of difficulty in their recovery, leading to economic and environmental problems. This problem can be overcome by immobilization of ILs on to solid supports to obtain heterogeneous catalysts [19-21]. Efforts at immobilizing ILs on solid supports have already been reported [22-26].

In the following, due to the specific surface properties of CuO, such as adsorption ability, high reaction activity, and good selectivity prompted us to use to this surface as carrier [27-29].

Therefore, in this work, the imidazolium hydrogen sulphate was supported on copper oxide nanoparticles and subsequently this novel core-shell acidic nanocomposite application was studied in synthesis of

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1, 4- dihydro Pyrano [2, 3-c] pyrazoles. Multi-component reactions (MCRs) have several unique benefits such as one-pot synthesis and time saving without generating by-products [30-38].

2. Experimental

2.1 Equipment

Aromatic aldehydes, 3-methyl-1-phenyl-2-pyrazolin-5-one, malononitrile and other chemical materials were purchased from Merck, Fluka and Aldrich chemical companies. Nano CuO powder was purchased from Alborz Chemical Co. (Tehran, Iran). Products were characterized of their spectroscopic data such as ^1H NMR, ^{13}C NMR, FT-IR spectra and physical properties with those reported in the literature. ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX400 spectrometer using TMS as the internal standard. Fourier transform infrared (FT-IR) spectra were recorded on a Perkin-Elmer 550 FT spectrometer in KBr pellets. The external morphology and elemental analysis of the particles were observed with a field emission scanning electron microscopy (FE-SEM) instrument model Mira 3-XMU. The TGA curve of the catalyst was recorded on Bahr SPA 503 at heating rates of $10\text{ }^\circ\text{C min}^{-1}$ under a nitrogen atmosphere. Functionalization of CuO nanoparticles was carried out in an ultrasonic liquid processor. The ultrasound was of a wave frequency of $2.25 \times 10^4 \text{ Hz}$ and power of 100W. X-ray diffraction (XRD) patterns of the samples were taken on a Philips X-ray diffractometer model PW1840. The reaction monitoring was accomplished via TLC (eluent; n-hexane: ethyl acetate; 3:1) on silica gel PolyGram SILG/UV254 plates.

2.2. Catalyst preparation

Fifty mmol of 1-methyl-imidazole (4 mL) and 50 mmol 3-chloropropyl-trimethoxy-silane (~12 mL) was stirred under reflux conditions and a nitrogen atmosphere at $95\text{ }^\circ\text{C}$ for 30 h. A yellowish viscous liquid of 1-methyl-3-(3-(trimethoxysilyl) propyl imidazolium chloride was obtained and identified by comparison of its FT-IR, ^1H NMR Spectra with those reported in the literature [34]. Then, Si-Im/Cl was suspended in dry CH_2Cl_2 (25 mL) in a three-necked round-bottomed flask equipped with stirrer and ice bath. During vigorous stirring, concentrated H_2SO_4 (98%) (50 mmol) was added drop wise at $0\text{ }^\circ\text{C}$ and in order to substitute Cl^- with HSO_4^- and the anion-exchange reaction was allowed to continue for the next 48 h.

After that, Si-Im/ HSO_4 (the silane-coupling agent attached completely with N-methylimidazolium ionic liquid) was dissolved in H_2O (solution A) and CuO nano

powder (2 g) was suspended in the de ionized (DI) water (solution B), then the mixture of Si-Im/ HSO_4 and CuO NPs (solution A and B) were immersed in ethanol and slowly stirred at room temperature for 24 h. Then, this solution subjected to ultrasonic irradiation for 30 min (**Scheme 1**). The reaction mixture was filtered and was subsequently twice washed with distilled water. Finally, the functionalized CuO nanoparticles (CuO@Si-Im/ HSO_4) were dried under the vacuum for 24 h.

2.3 Catalytic activity of the CuO@Si-Im/ HSO_4 as an environmentally friendly catalyst

A mixture, of the 3-methyl-1-phenyl-2-pyrazolin-5-one (1 mmol, 0.114 g), aromatic aldehyde (1mmol), malononitrile (1 mmol, 0.067 g) and CuO@Si-Im/ HSO_4 heterogeneous catalyst (0.05 g) was heated under reflux in ethanol for an appropriate time until the completion of the reaction (**Scheme 2**). After completion of the reaction, as monitored by TLC the filtrate mixture (crude product) was purified by recrystallization, and the nanocatalysts easily filtered, dried, and reused. The products were identified on the basis of their IR, ^1H NMR and ^{13}C NMR.

2.4. Physical data and spectral for selected product:

Table 3, entry 1: White crystals; Yield 93%, M. p.: $240\text{--}242\text{ }^\circ\text{C}$; $^1\text{H NMR}$ (δ , ppm): 2.05 (s, 3H, CH_3), 3.77 (s, 3H, OCH_3), 4.62 (s, 1H, CH), 7.14 (s, 2H, NH_2), 7.20-7.96 (m, 9H, Ar-H); $^{13}\text{C NMR}$ (δ , ppm): 11.51, 24.52, 55.32, 70.51, 114.0, 115.71, 120.0, 127.0, 129.92, 140.51, 141.0, 153.92, 159.94, 160.0.

Table 3, entry 2: Brown crystals; Yield 90 %, M. p.: $193\text{--}195\text{ }^\circ\text{C}$; $^1\text{H NMR}$ (δ , ppm): 1.88 (3H, s, CH_3), 4.85 (1H, s, CH), 4.86 (2H, s, NH_2), 7.37-8.17 (m, 9H, Ar-H); $^{13}\text{C NMR}$ (δ , ppm): 13.04, 36.73, 57.65, 98.09, 120.29, 120.52, 122.72, 126.68, 129.73, 130.69, 135.18, 137.95, 144.51, 145.63, 146.43, 148.44, 160.25.

Table 3, entry 3: Brown solid; Yield 92%, M. p.: $194\text{--}196\text{ }^\circ\text{C}$; $^1\text{H NMR}$ (δ , ppm): 1.80 (s, 3H, CH_3), 4.93 (s, 1H, CH), 6.98 (s, 2H, NH_2), 7.32-8.25 (m, 9H, Ar-H); $^{13}\text{C NMR}$ (δ , ppm): 13.63, 37.44, 57.95, 98.66, 120.79, 121.74, 121.17, 124.97, 127.40, 130.28, 130.42, 138.49, 145.08, 146.22, 147.69, 152.27, 160.78.

Table 3, entry 5: Withe crystals; Yield 96%, M. p.: $145\text{--}147\text{ }^\circ\text{C}$; $^1\text{H NMR}$ (δ , ppm): 1.89 (s, 3H, CH_3), 4.85 (s, 2H, NH_2), 5.31 (s, 1H, CH), 7.21-7.66 (m, 9H, Ar-H); $^{13}\text{C NMR}$ (δ , ppm): 12.75, 33.11, 60.92, 97.55, 118.22, 121.55, 125.85, 126.91, 128.35, 128.99, 130.56, 134.80, 134.85, 137.35, 142.90, 144.55, 156.55.

Table 3, entry 7: White crystals; Yield 95%, M. p.: 145-148 °C; $^1\text{H-NMR}(\delta, \text{ppm})$: $^1\text{H-NMR}(\delta, \text{ppm})$: 1.80 (s, 3H, CH₃), 4.56 (s, 1H, CH), 6.66 (s, 2H, NH₂), 6.80-7.23 (m, 9H, Ar-H); $^{13}\text{C-NMR}(\delta, \text{ppm})$: 11.71, 24.42, 70.44, 112.12, 126.71, 127.61, 130.11, 134.22, 141.43, 142.13, 153.60, 159.32.

Table 3, entry 10: White crystals; Yield 96%, M. p.: 167-169 °C; $^1\text{H NMR}(\delta, \text{ppm})$: 1.90 (s, 3 H, CH₃), 4.67 (s, 1H, CH), 4.72(s, 2 H, NH₂), 7.27 – 7.68(m, 10H, Ar-H), $^{13}\text{C NMR}(\delta, \text{ppm})$: 12.93, 37.42, 63.87, 98.37, 119.13, 121.25, 126.81, 127.64, 127.92, 128.84, 129.33, 137.59, 142.05, 143.82, 146.47, 158.19.

3. Results and Discussion

In this work, the surface of CuO nanoparticles was successfully engineered by ionic liquid framework under ultrasonic irradiation at room temperature. This catalyst changes the power surface from hydrophilic to hydrophobic characteristics. The systematic steps of CuO@Si-Im/HSO₄ preparation is shown in the **Scheme 1**. The novel nanocomposite, which is easily dispersed in water or polar organic phase, is a solid acid and was used to promote the 1,4- dihydro Pyrano [2, 3-c] pyrazole synthesis under a very mild condition (**Scheme2**).

The grafting of Si-Im/ HSO₄ on the surface of CuO NPs was verified by FT-IR studies. **Fig. 1** shows the FT-IR spectra of CuO NPs, CuO@ Si-Im/HSO₄ and Si-Im /Cl in the 400 -4000 cm⁻¹. The FT-IR analysis spectra of the CuO NPs and CuO@ Si-Im/HSO₄ indicate a peak at about 529 cm⁻¹, which was attributed to the presence of Cu-O stretching vibration. In Si-Im/Cl and CuO@ Si-Im/HSO₄ spectra, the presence of a peak at 1050 cm⁻¹ is related to the vibration of the Si-O group. Characteristic peaks of Si-Im/Cl and CuO@ Si-Im/HSO₄ spectra, at about 1500 cm⁻¹ and 1600 cm⁻¹, were attributed to C=C and C=N stretching vibrations, respectively, of the imidazole ring. The C-H stretching peaks at 1200 -1400 and 2885-3090 cm⁻¹ in the CuO@ Si-Im/HSO₄ spectra exhibit that the copper oxide nanoparticles are successfully coated by imidazolium hydrogen sulphate silica hybrid.

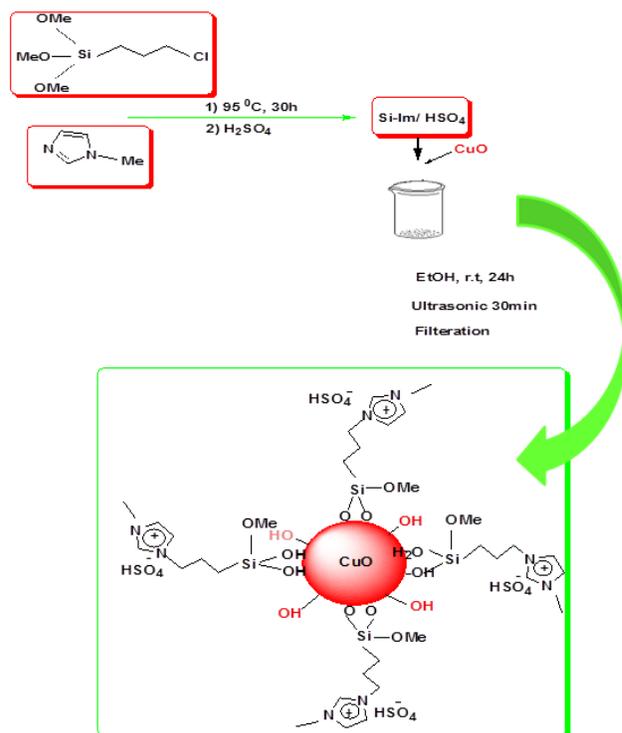
Phase investigations of the crystalline pure CuO and CuO@Si-Im/HSO₄ heterogeneous nanocatalyst were performed by XRD and the diffraction patterns are presented in **Fig. 2**. The XRD pattern of pure CuO showed intense and sharp peaks, indicating its crystalline nature. The pattern of CuO@Si-Im/HSO₄ displays a most intense peak at $2\theta=39.1$, which corresponds to the pure CuO and confirms the presence of CuO NPs. The crystallite size of CuO@ Si-Im/HSO₄

NPs can be determined from the XRD pattern and Debye-Scherrer's equation. The nanocatalyst was calculated to be 20-50 nm as a result of this line profile fitting.

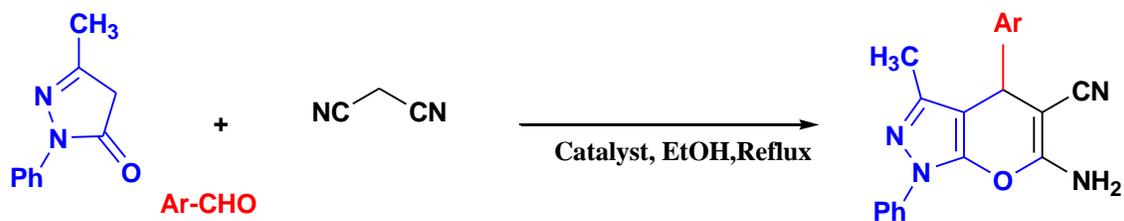
The size and shape of catalyst were investigated by scanning electron microscopy (FE-SEM) technique. **Fig. 3** shows the photographs of the surface CuO@Si-Im/HSO₄ NPs, which have a needle shape with nano thickness ranging from 20 nm to 50 nm.

Nanocatalyst (CuO@Si-Im/HSO₄) was analyzed by EDX **Fig. 4**. The analysis indicates the presence of all expected elements in the structure of the catalyst **Scheme 1**

The thermal stability of the nanocomposite was also investigated by thermo gravimetric analysis (TGA). **Fig. 5** shows the TGA Curve for nanocomposite t (CuO@Si-Im/HSO₄). The 17% weight loss at temperatures <160 °C might be due to the loss of the adsorbed water as well as dehydration of the surface-OH groups. The TGA profile results revealed that the nanocatalyst was completely stable below about 300 °C and, therefore, could be applied without any danger of degradation. After 300 °C, it seems that the organic layers start to decompose and a mass loss at temperatures >300°C (about 20%) was reported. Thus, the TGA curve also conveys the obvious information that the CuO particles are successfully coated by imidazolium hydrogen sulphate silica hybrid.



Scheme 1. Surface functionalized CuO nanoparticles



Scheme 2. Synthesis of 1, 4- dihydro Pyrano [2, 3-c] pyrazoles catalyzed by CuO@ Si-Im/ HSO₄

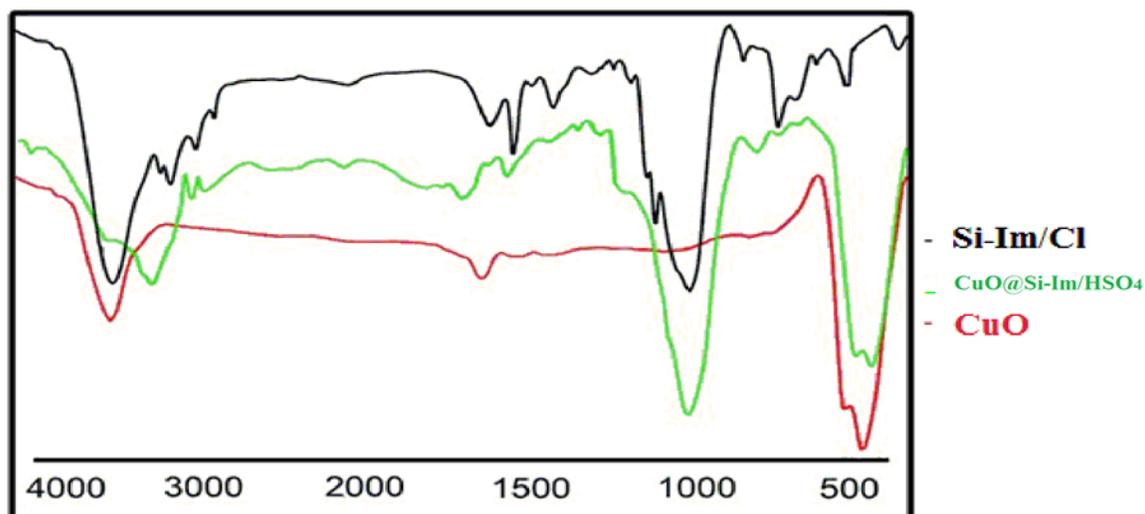


Fig. 1. FT-IR spectra of CuO NPs, CuO@Si-Im/ HSO₄ and Si-Im/Cl

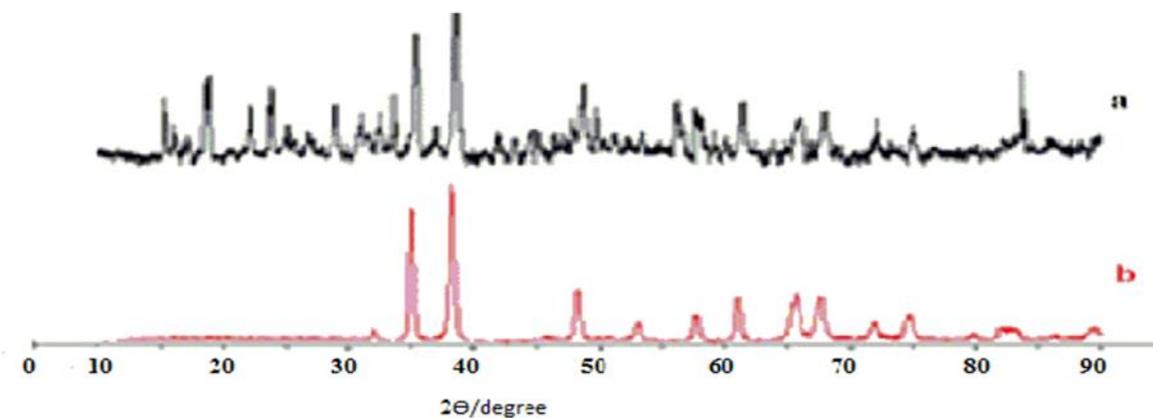


Fig. 2. XRD pattern a) CuO@ Si-Im/HSO₄ nanocatalyst, b) pure CuO

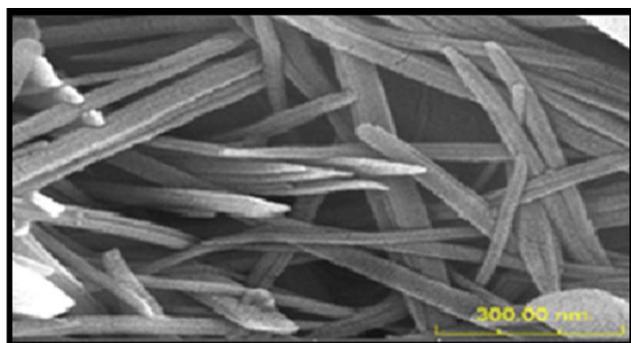


Fig. 3. FE-SEM images of CuO@ Si-Im/ HSO₄

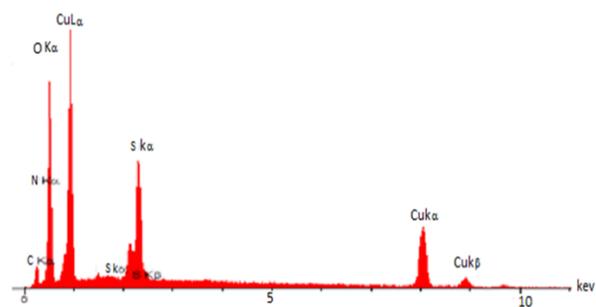


Fig. 4. EDX of CuO@ Si-Im/HSO₄

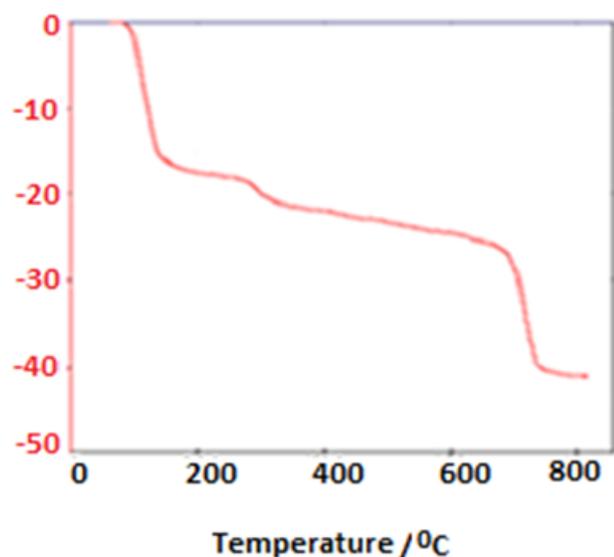


Fig. 5. TGA curve CuO@ Si-Im/ HSO₄

After the characterization of catalyst with FT-IR, XRD, EDX, TGA and Fe-SEM techniques, we decided to use CuO@Si-Im/HSO₄ nanocatalyst as a new catalyst for the one-pot multicomponent synthesis of 1,4- dihydro

Pyrano [2, 3-c] pyrazoles heterocyclic compounds (**Scheme 2**). In the first set of experiments, we focused on different conditions for the synthesis of 1,4- dihydro Pyrano [2, 3-c] pyrazoles derivatives in the model three-component condensation of benzaldehyde, malonitrile and 3-methyl-1-phenyl-2-pyrazolin-5-one, and the nanocatalyst compared with some of those reported in the literature. Various solvents and temperatures were screened to test the efficiency of the catalyst and the obtained results are summarized in **Tables 1** and **2**. After some experiments, the best condition that was found to produce a very clean reaction was the use of CuO@ Si-Im/HSO₄ (0.05gr, 0.037 mmol g⁻¹ of H⁺) [39] in EtOH as solvent at 80°C. As can be seen in Table 2, higher yields and shorter reaction time of products were obtained when CuO@ Si-Im/HSO₄ was utilized as the catalyst for the synthesis of 6-Amino-1, 4-diphenyl-5-cyano-3-methyl -1, 4-dihydropyrano [2, 3-c]pyrazole (entry 9). Also, the higher activity of the immobilized catalyst compared with its bare CuO NPs could be attributed to the participation of Si-Im/HSO₄ in the catalytic process (**Table 1**)

Table 1 Optimization of reaction conditions for the synthesis 6-Amino-1, 4-diphenyl-5-cyano-3-methyl -1, 4-dihydropyrano [2, 3-c]pyrazole in the presence of CuO@ Si-Im/HSO₄

Entry	Solvent	Temperature (°C)	Catalyst loading (g)	Time (min)	Yield (%)
1	-	r.t	0.1 (0.078 mmol of H ⁺)	240	30
2	EtOH	r.t	-	240	Trace
3	EtOH	Reflux	0.05(0.037 mmol of H ⁺)	35	96
4	CHCl ₃	Reflux	0.1(0.078 mmol of H ⁺)	55	60
5	CH ₂ Cl ₂	Reflux	0.1(0.078 mmol of H ⁺)	60	70
6	CH ₃ CN	Reflux	0.1(0.078 mmol of H ⁺)	90	68
7	H ₂ O	Reflux	0.1(0.078 mmol of H ⁺)	110	71
8	EtOH	Reflux	bare CuO 0.10	140	55

Table 2 Comparison of CuO@ Si-Im/HSO₄ in the synthesis of 1, 4 dihydropyrano [2, 3-c]pyrazoles with previously reported catalysts

Entry	Catalyst	Time (min)	Yield (%)
1	SPPyNs	30-60	50-92[28]
2	DBSA	180	82-94[29]
3	palladium nanoparticles	4-43 h	85-90[40]
4	PVPy	18-65	89-92[41]
5	SB-DABCO	25-60	93-97[42]
6	NMPyTS	30-60	79-82[43]
7	Ni-MP(AMP) ₂ @Fe-biochar	60-560	90-98[31]
8	Cu-Cytosine@MCM-41	15-120	90-95[44]
9	CuO@Si-Im/HSO ₄	30-35	86-96 [This work]

In the next step, our work was developed with a wide range of various benzaldehyde with malononitrile and 3-methyl-1-phenyl-2-pyrazolin-5-one in the presence of synthesized nanocatalysts and the results are summarized in **Table 3**.

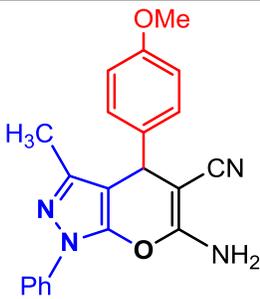
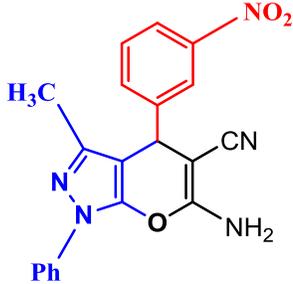
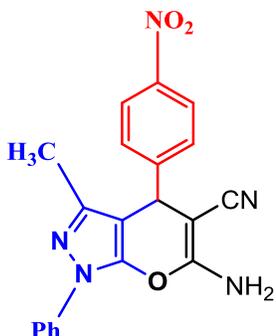
Benzaldehyde and aromatic aldehydes including electron-donating groups or electron- withdrawing functional groups were successfully converted to corresponding products in excellent yields under reaction conditions. Also aliphatic aldehydes were studied, but were discarded because of their low yields.

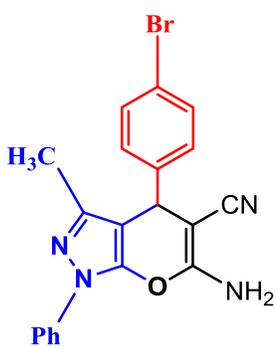
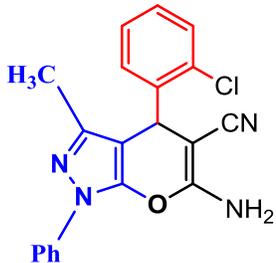
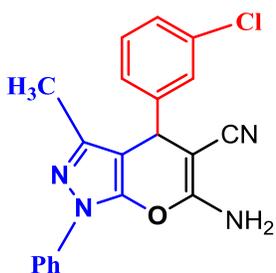
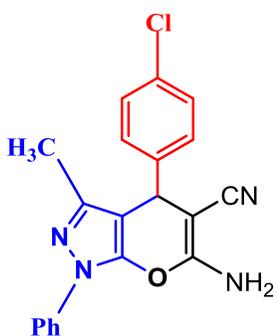
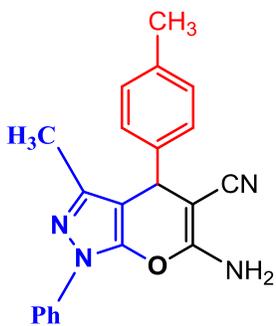
The mechanism proposed for the catalytic effect of nanocomposite in one pot preparation of 1, 4- dihydro

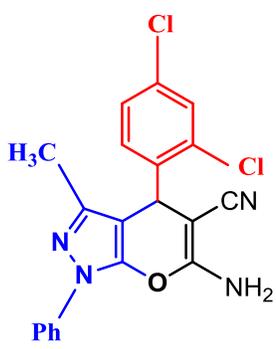
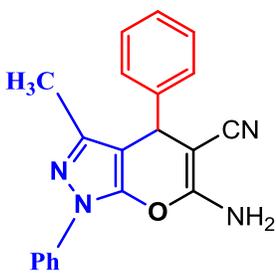
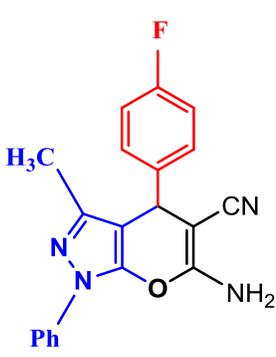
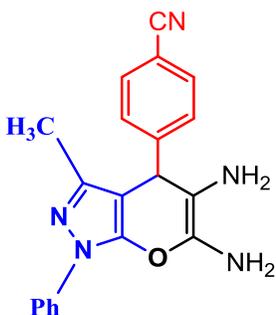
Pyrano [2, 3-c] pyrazoles compounds is shown in **Scheme 3**. First, the intermediate (**A**) is created upon initial condensation of aryl aldehyde with malononitrile under the catalytic activity of CuO@ Si-Im/HSO₄. Afterwards, nucleophilic addition of compound (**B**) to the intermediate (**A**) created intermediate (**C**). Intermediate (**C**) undergoes intramolecular cyclization followed by tautomerization furnishing 1,4- dihydro pyrano[2, 3-c]pyrazoles derivatives (**E**) and the CuO@ Si-Im/HSO₄ was released for further reactions.

The structures of products were determined by comparison of their spectral (IR, ¹H & ¹³C NMR) data, melting points and TLC with the authentic samples prepared by reporting methods.

Table 3 Synthesis of 1, 4- dihydro Pyrano [2, 3-c] pyrazoles derivatives in the presence of CuO@Si-Im/HSO₄ nanoparticles in EtOH

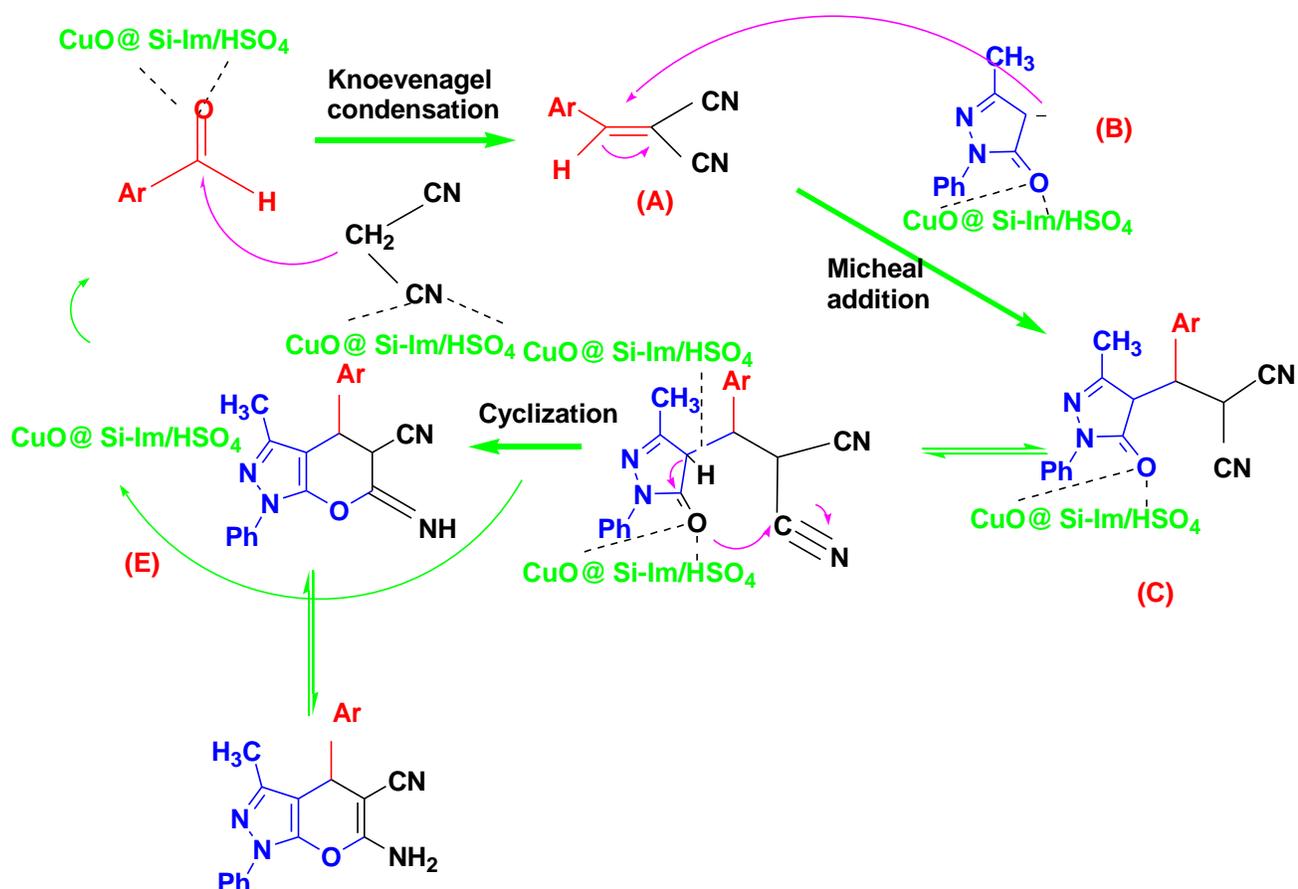
Entry	Product	Time (min)	Yield (%)	M. P. °C	
				Found	Reported
1		35	93	240-242	241-243[28]
2		35	90	193-195	190-192 [28]
3		32	92	194-196	195-196 [29]

4		30	86	184-186	184-185 [43]
5		35	96	145-147	145-146 [29]
6		35	96	157-161	158-160 [29]
7		35	95	145-148	144-146 [29]
8		35	92	176-179	177-178 [29]

9		32	91	186-188	185-186 [29]
10		36	96	167-169	168-170 [29]
11		33	83	169-172	170-172 [39]
12		35	89	215-218	217-219- [41]

The TGA curve of the nanocatalyst showed that the catalyst did not suffer from extensive mechanical degradation and was reused. Also the reusability of the catalyst was investigated and the synthesized catalyst was reused in the one-pot three-component condensation of 2-chlorobenzaldehyde, malononitrile and 3-methyl-1-phenyl-2-pyrazolin-5-one under the optimized conditions. After completion of reaction, the catalyst was recovered and washed with distilled water and acetone and dried at 80°C and reused for subsequent runs. **Table 4** clearly indicates the practical reusability of CuO@ Si-Im/ HSO₄.

In order to show the stability of CuO@Si-Im/HSO₄ under organic reactions, the recycled catalyst has been characterized by scanning electron microscopy and EDX techniques. The FE-SEM images of reused catalyst are shown in **Fig. 6**. The scanning electron microscopy images of reused catalyst show a good agreement with scanning electron microscopy images of fresh catalyst in term of particle size and shape. As shown in EDX analysis of the catalyst after recycling, the element content of reused CuO@ Si-Im/ HSO₄ is formed from Si, O, N, S, Cu element (**Fig. 7**).



Scheme 3. Postulated roles of CuO@ Si-Im/ HSO₄ in the 1, 4- dihydro Pyrano [2, 3-c] pyrazoles synthesis

Table 4 Catalyst reusability study

No. Cycle	Catalyst Recovery (%)
1	96
2	95
3	91
4	88

The EDX analysis of the recovered catalyst (**Fig. 7**) show good agreement with fresh catalyst (**Fig. 4**). Therefore, these results indicate that this catalyst can be reused for next runs under organic reaction without any change.

4. Conclusions

In this study, a novel solid acid catalyst was successfully prepared through the support of acidic ionic liquid onto the surface of CuO NPs. The catalytic activity of this

environmentally safe nanocomposite was probed through the one-pot synthesis of 1, 4- dihydro Pyrano [2, 3-c] pyrazoles derivatives via three-component coupling of aromatic aldehydes, malononitrile and 3-methyl-1-phenyl-2-pyrazolin-5-one. In these reactions CuO@Si-Im/HSO₄ shows a highly catalytic nature, easy to handle procedure, facile reaction work-up, short reaction time and high yield of the products. Subsequent reuse of catalyst, without significant loss in catalytic activity showed that the catalysis was precisely heterogeneous.

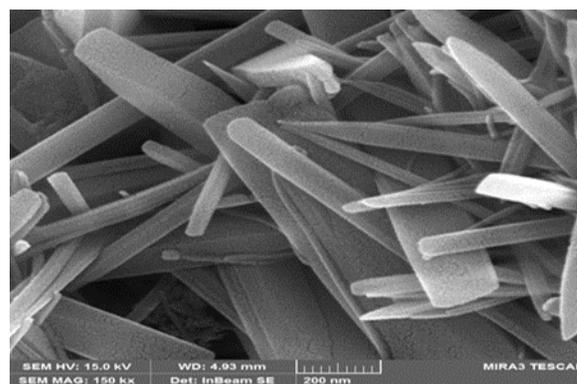


Fig. 6 FE-SEM images of CuO@ Si-Im/ HSO₄ after recycling

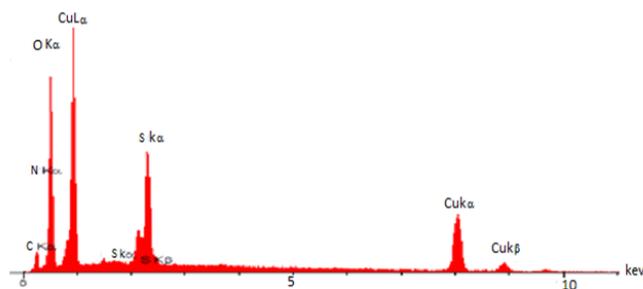


Fig. 7 EDX spectrums of reused CuO@ Si-Im/ HSO₄

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