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Copper Supported Hematite NPs as Magnetically Recoverable Nanocatalysts for One-Pot Synthesis of Aminoindolizines and Pyrrolo[1,2-a]quinolines

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The Cu NPs such as CuO and Cu_2O mixed oxides supported on hematite (Cu@Fe_2O_3) surface was achieved by a facile hydrothermal method in a single step. The various techniques such as X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electronic microscopy (SEM), transmission electron microscopy (TEM), EDAX elemental analysis, Inductively coupled plasma atomic emission spectroscopy (ICP-AES) and X-ray photoelectron spectra (XPS) were used for the characterization of synthesized Cu@Fe_2O_3 MNPs. The catalytic potential of Cu@Fe_2O_3 NPs was explored for the synthesis of aminoindolizines and pyrrolo[1,2-a]quinolines *via* A3 coupling reaction. The present catalytic system offers advantages such as high catalytic activity in short reaction time, recovered the catalyst by external magnetic field and recycled for six times without significant loss in its activity.

Introduction

Recently, magnetically recoverable nanocatalysts (MRNCs) have attracted the attention of scientists working in the area of green and sustainable chemical processes in view of minimizing the costs of manufacturing and waste disposal.[1] MRNCs deals with the design and development of nanomaterials by tailoring size, shape and morphology which enhance catalytic activity with minimum waste generation, and also recoverable by external magnetic field with maximum number of catalyst recycles.[2] Till date, several MNPs such as Fe_3O_4 and MFe_2O_4 (M = Cu, Mn, Zn, Co etc.) and Fe_2O_3 (hematite) have been reported as either catalysts or catalyst supports for the sustainable organic synthesis.[3] Among these, hematite (Fe_2O_3) is the most thermodynamically stable species with perceptual magnetic properties.[4] The most fascinating properties and green aspects of hematite makes it a potential candidate in various fields including gas sensors,[5] magnetic storage media,[6] electromagnetic devices, solar cells,[7] water splitting,[8] environmental treatment,[9] optical devices and lithium-ion batteries.[10] However, ferrite alone has attracted significant attention in the field of catalysis for various organic transformations including A3 coupling reaction.[11] Hematite (Fe_2O_3) alone has not been studied as catalyst, and very limited reports found on Cu supported Fe_2O_3 based materials as catalysts for organic transformations.[12]

Indolizine and Pyrrolo[1,2-a]quinolines are most significant structural frameworks found in various natural products such as swainsonine, amorine, erythraline, cryptaustoline, slaframine, cryptowoline, crepidine, gephyrotoxin.[13] These moieties have been known to exhibit wide range of biological activities such as antibacterial, antifungal, anticonvulsant, anti-inflammatory, antibacterial, antileukamic, apoptosis, tumor inhibitor against P388 leukemia, Histamine H3 receptor antagonist etc. (Figure 1).[14]

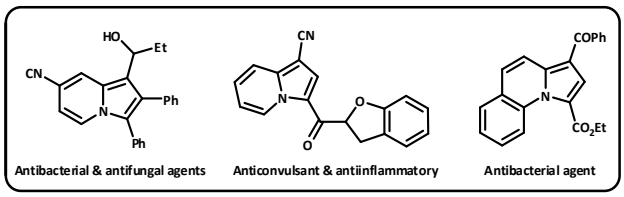

Figure 1: Biological significance of indolizine and pyrrolo[1,2-a]quinolines

Till date, various methodologies have been developed for the construction of indolizine and pyrrolo[1,2-a]quinolines such as [3+2] cycloaddition of pyridinium/quinolinium ylides with activated olefins/alkynes,[15] alkenylation of heterocycles followed by cyclization via C-H activation,[16] Au(I) catalyzed cascade reactions,[17] Cu catalyzed cycloisomerization of propargyl mesylates/propargylic acetates,[18] iodine-promoted cascade reactions,[19] transition metal promoted A3 coupling followed by cycloisomerization.[20] Among these methods, the A3 coupling reaction of 2-pyridinecarbaldehydes/quinolin-2-carboxaldehyde, secondary amines, and alkynes followed by cycloisomerization to afford

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aminoindolizines/pyrrolo[1,2-a]quinolines has become versatile protocol. However, various transition metals such as gold, copper, silver, iron and zinc have employed as catalysts,[20] but most of these suffers from drawbacks such as complicate work up procedures, usage of toxic organic solvents, expensive and non-recyclable metal catalysts. To overcome the aforementioned drawbacks, we reported CuI/CSP nanocomposites as recyclable catalyst for the synthesis of aminoindolizines and chalcones under green conditions.[21] With the inspiration of green chemistry principles and in continuation of our efforts toward nanocatalysis,[22] we report herein Cu@Fe_2O_3 as a novel and efficient magnetically recyclable nanocatalyst for the synthesis of aminoindolizines and pyrrolo[1,2-a]quinolines.

Results and discussion

The stabilization of Cu NPs as CuO and Cu_2O mixed oxides on hematite (Cu@Fe_2O_3) was achieved from the one-step hydrothermal treatment of $FeCl_3$, $CuCl_2$, urea and aqueous NH_3 in the presence of 10 mol% of glucose as a reducing agent at 180 ^oC for 8h. The usage of glucose in catalytic amount (10 mol%) has significant role in reduction of some of Fe^{3+} to Fe^{2+}, which enhance the formation of α-Fe_2O_3 NPs.[23] Moreover, glucose may also participated in partial reduction of CuO (Cu^{2+}) to Cu_2O (Cu^{+1}) and their stabilization on hematite as shown in Figure 2. The synthesized Cu@Fe_2O_3 MNPs were characterized by using various techniques such as X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electronic microscopy (SEM), transmission electron microscopy (TEM), EDAX elemental analysis, Inductively coupled plasma atomic emission spectroscopy (ICP-AES) and X-ray photoelectron spectra (XPS) etc.

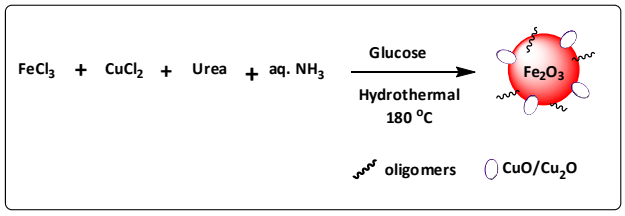


Figure 2: Schematic representation for formation of Cu@Fe_2O_3 MNPs

The powder X-ray diffraction of Cu@Fe_2O_3 MNPs revealed the presence of rhombohedral α-Fe_2O_3 with phases such as (012), (104), (110), (113), (024), (116), (018), (214), (300), (119) corresponding diffraction peaks at (2θ) 24.52, 33.52, 36.03, 41.32, 49.83, 54.39, 57.87, 62.79, 64.35, 72.14 respectively as shown in Figure 3 (JCPDS card 33-0664). The grain size of Fe_2O_3 NPs was estimated using Scherrer equation and found to be about 28 nm.

The functional groups of Cu@Fe_2O_3 MNPs were characterized by using FT-IR technique as shown in Figure 4. The characteristic bands at 452, 587 cm^{-1} corresponds to Fe-O stretching vibration of hematite.[24] The functional groups of oligomers resulted from the polymerization of glucose under hydrothermal conditions were conformed from the appearance of bands at 3340, 2908, 1625, 1401, 1057 cm^{-1} corresponds to the hydroxyl, C-H stretching, carbonyl, C-H bending, C-O stretching frequencies respectively (Figure 4).[21]

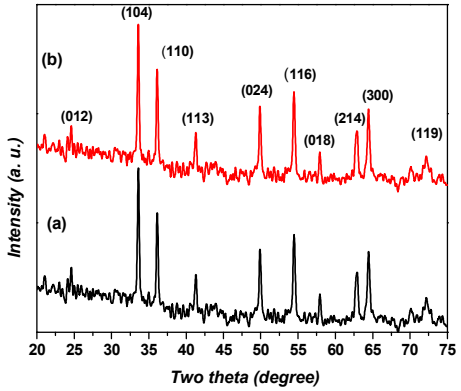


Figure 3: PXRD of (a) fresh and (b) recycled Cu@Fe_2O_3 MNPs

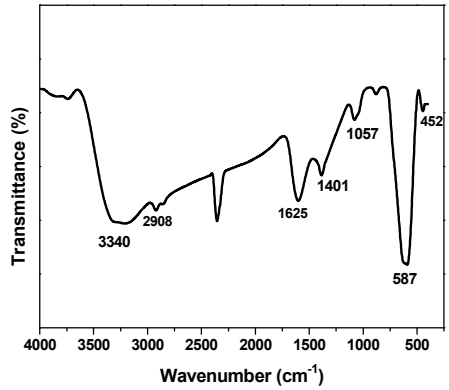


Figure 4: FT-IR spectra of Cu@Fe_2O_3 MNPs

The EDAX elemental analysis of Cu@Fe_2O_3 showed the presence of copper in 3.8 wt% and 1.7 at% (Figure 5). The sum of iron (50.4 wt%) and oxygen (35.8 wt%) was found to be 86.2 wt%. The remaining 10 wt% was belonging to carbon, which was obtained from the polymerization of glucose under hydrothermal condition (Figure 5). The 3.5 wt% of Cu was detected from ICP-AES technique was almost inconsistent with the EDAX elemental analysis.

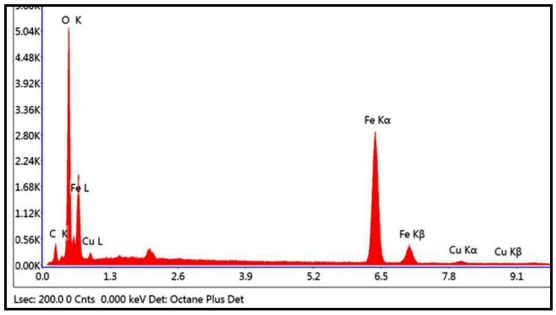


Figure 5: EDAX elemental analysis of Cu@Fe_2O_3 MNPs

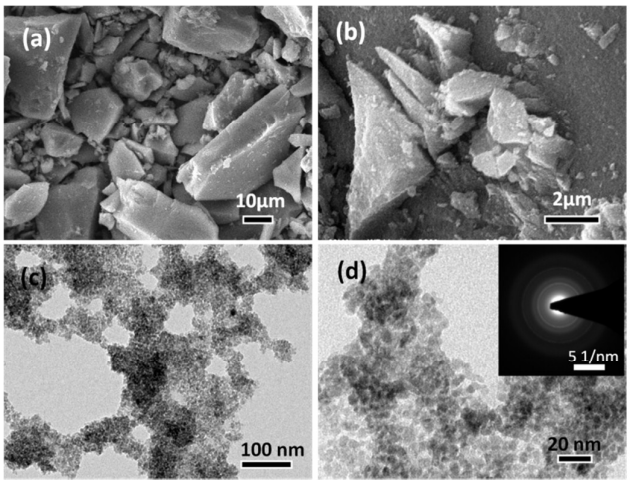


Figure 6: SEM (a, b) and TEM (c, d) images of Cu@Fe_2O_3 MNPs

The SEM images of Cu@Fe_2O_3 revealed the existence of rock like morphology in non uniform shape and size with surface covered with Cu NPs (Figure 6). The internal morphology of MNPs was characterized from transmission electron microscopy and the results showed that the existence of aggregated spheres as shown in Figure 6 (c, d).

The oxidation state of Cu and Fe in Cu@Fe_2O_3 MNPs was analyzed by using X-ray photoelectron spectra (XPS) technique (Figure 7). The survey spectra showed the presence of Cu 2p, Fe 2p, O 1s, C 1s photoelectrons from the peaks with binding energies 932, 710, 530 and 285 eV respectively as shown in Figure 7.

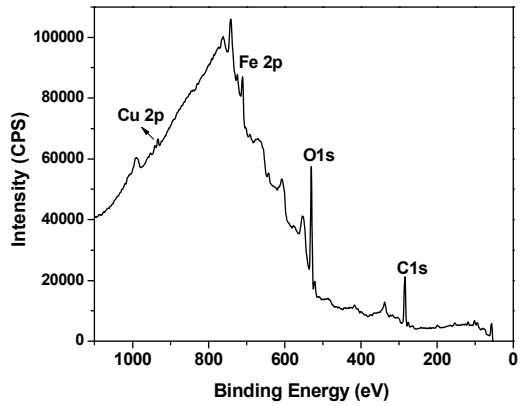


Figure 7: Survey X-ray photoelectron spectra of Cu@Fe_2O_3 MNPs

The high resolution spectra of Cu 2p region revealed the presence of CuO with the Cu $2p_{1/2}$ and Cu $2p_{3/2}$ peaks of binding energies 954.2 and 933.8 eV and their corresponding satellite peaks at 961.7 and 942.5 eV respectively as shown in Figure 8.[25] However, the peak intensity and shape was not in uniform manner, which may be due to the presence of Cu_2O by partial reduction of CuO (Figure 8).[26] In the region of Fe 2p, the peaks with binding energies 710.7 and 724.5 eV corresponds to Fe $2p_{3/2}$ and Fe $2p_{1/2}$ of α-Fe_2O_3 NPs respectively (Figure 9).[27] The presence of satellite peak at 718.5 eV was conformed the presence of Fe^{3+} ions and the additional satellite peak at higher binding energy 741.9 eV was responsible due to the charge transfer and shake-up processes in α-Fe_2O_3 (Figure 9).[28] All the assinged peaks in XPS spectra are in well agreement with the reported data. (see SI for high resoluation XPS spectra of O1s and C1s).

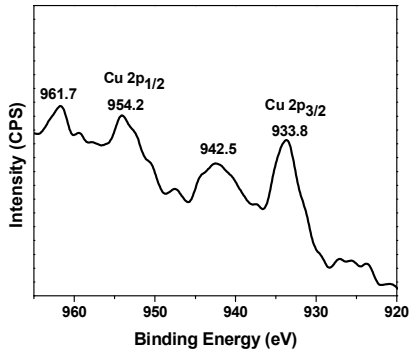


Figure 8: High resolution XPS of Cu 2p region in Cu@Fe_2O_3 MNPs

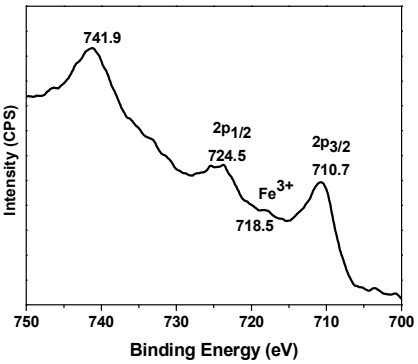


Figure 9: High resolution XPS of Fe 2p region in Cu@Fe_2O_3 MNPs

Cu@Fe_2O_3 MNPs catalyzed synthesis of aminoindolizines and pyrrolo[1,2-a]quinolines:

The reaction conditions were optimized for a model reaction among pyridine-2-carboxaldehyde (**1a**), morpholine (**2a**), and phenylacetylene (**3a**) in the presence of 5 mg of Cu@Fe_2O_3 catalyst using various solvents at different temperatures as depicted in Table 1. The reaction was not proceeded in the presence of toluene, 1,4-dioxane and DMF (entries 1, 2 and 8, Table 1). In the presence of EtOH, MeOH, CH_3CN, THF and DMSO, the 2-pyridinyl propargyl amine (**5**) was observed in 20-70% conversions (entries 3-7). The desired aminoindolizine (**4aaa**) was obtained in poor yield in the presence of water (entry 9). Interestingly EG, PEG and glycerin were found to be appropriate solvents to afford the product (**4aaa**) in 88-100% conversions at 110 ^{o} C (entries 10-12). Glycerin was found to be superior to obtain the isolated pure product (**4aaa**) in 87% yield (entry 12).

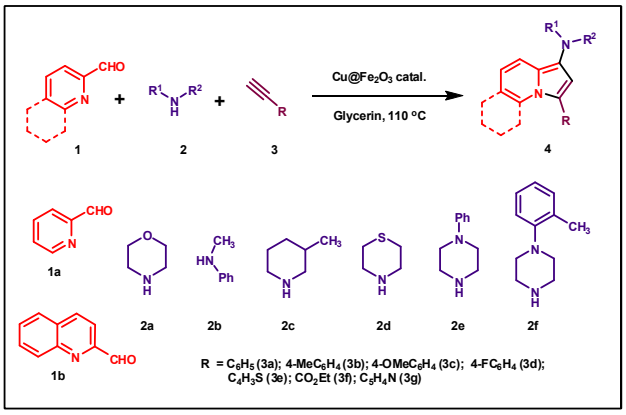
Table 1: Optimization study for $Cu@Fe_2O_3$ MNPs catalyzed synthesis of aminoindolizine (**4aaa**).[a]

Entry	Catalyst (mg)	Solvent	Temp (^oC)	Time (h)	Conv. of A3 (%)[b]	Conv. of **4aaa** (%)[c]	Yield of **4aaa** (%)[d]
1	$Cu@Fe_2O_3$ (5)	Toluene	110	6	NR	NR	NR
2	$Cu@Fe_2O_3$ (5)	1,4-dioxane	100	6	NR	NR	NR
3	$Cu@Fe_2O_3$ (5)	EtOH	80	6	40	-	-
4	$Cu@Fe_2O_3$ (5)	MeOH	60	6	42	-	-
5	$Cu@Fe_2O_3$ (5)	CH_3CN	80	6	70	-	-
6	$Cu@Fe_2O_3$ (5)	THF	65	6	20	-	-
7	$Cu@Fe_2O_3$ (5)	DMSO	110	6	40	-	-
8	$Cu@Fe_2O_3$ (5)	DMF	110	6	NR	NR	NR
9	$Cu@Fe_2O_3$ (5)	water	100	6	-	30	10
10	$Cu@Fe_2O_3$ (5)	EG	110	4	-	90	75
11	$Cu@Fe_2O_3$ (5)	PEG	110	2	-	88	80
12	**$Cu@Fe_2O_3$ (5)**	**Glycerin**	**110**	**2**	**-**	**100**	**87**
13	$Cu@Fe_2O_3$ (5)	Glycerin	90	2	-	75	68
14	$Cu@Fe_2O_3$ (5)	Glycerin	70	6	-	50	40
15	$Cu@Fe_2O_3$ (5)	Glycerin	rt	24	NR	NR	NR
16	$Cu@Fe_2O_3$ (10)	Glycerin	110	2	-	100	87
17	$Cu@Fe_2O_3$ (15)	Glycerin	110	2	-	100	86
18	$Cu@Fe_2O_3$ (20)	Glycerin	110	2	-	100	87
19	Fe_3O_4 (5)[e]	Glycerin	110	6	65	-	-
20	neat	Glycerin	110	6	NR	NR	NR

[a]Reaction conditions: Pyridine-2-carboxaldehye **1a** (1 mmol), morpholine **2a** (1 mmol), phenylacetylene **3a** (1 mmol), $Cu@Fe_2O_3$ catalyst (5mg), solvent (4 mL) were stirred at appropriate temperature. [b,c]Conversions were calculated from the ^1H NMR of crude reaction mixture. [d]isolated yields. [e]2-pyridinyl propargyl amine (A3) was obtained in 65% conversion and 45% isolated yield. NR = no reaction; (-) represents no product formed.

With these results in hand, we further studied the effect of temperature and catalyst loading on the yield of product (**4aaa**) in the presence of glycerin as a solvent (entries 13-18). As temperature decreased from 110 ^oC to 70 ^oC, the yield of product dropped from 87% to 40% (entries 12-14). At room temperature, there was no progress in the reaction even after prolonged reaction time (entry 15). Upon increasing the catalyst loading from 5 mg to 20 mg, there was no change in the conversion of product (**4aaa**) (entries 12 and 16-18). When the model reaction was performed using Fe_2O_3 MNPs alone as catalyst, there was no product formation observed even in trace amount but the intermediate 2-pyridinyl propargyl amine (**5**) was observed in 65% conversion (entry 19, Table 1). There was no product formation in the absence of catalyst under optimized conditions (entry 20). Thus, the optimized reaction condition was found to be usage of 5 mg of $Cu@Fe_2O_3$ catalyst in the presence of glycerin as a solvent at 110 ^oC in 2 h to afford product (**4aaa**) in 87% yield.

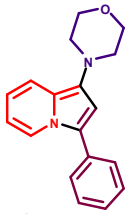
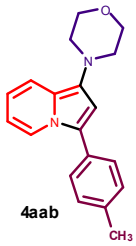
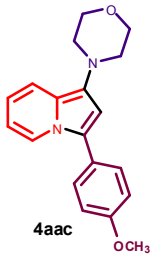
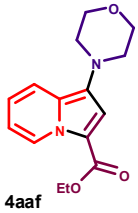
Next, the wide applicability of $Cu@Fe_2O_3$ nanocatalyst was studied for the synthesis of aminoindolizine and pyrrolo[1,2-a]quinoline derivatives from 2-pyridinecarbaldehyde (**1a**) and quinolin-2-carboxaldehyde (**1b**), various secondary amines such as morpholine (**2a**), N-methylaniline (**2b**), 3-metylpiperidine (**2c**), thiomorpholine (**2d**), phenylpiperazine (**2e**), 1-(o-tolyl)piperazine (**2f**) and aromatic alkynes bearing electron donating and withdrawing substituent (**3a-3d**), heteroatom aromatic alkynes such as 2-ethynylpyridine, 3-ethynylthiophene and activated aliphatic alkyne such as ethyl propiolate (**3e**) as shown in Scheme 1. In general, all the screened substrates underwent smooth cycloisomerization to afford the desired products such as aminoindolizines and pyrrolo[1,2-a]quinolines in good yields in short reaction time as depicted in Table 2.



Scheme 1: One-pot synthesis of aminoindolizine and pyrrolo[1,2-a]quinoline derivatives

The present catalytic system found to be superior to the all known methods in terms of catalyst recover and reusability, simple work up procedures, wide substrate scope and usage of green solvent such as glycerin. After completion of reaction, the $Cu@Fe_2O_3$ catalyst was recovered by using external magnet. The comparison of present $Cu@Fe_2O_3$ catalyst with the reported catalysts is as shown in the Table 3.

Table 2: $Cu@Fe_2O_3$ catalyzed synthesis of aminoindolizine and pyrrolo[1,2-a]quinoline derivatives

 4aaa	 4aab	 4aac	 4aaf
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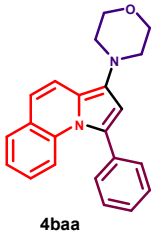
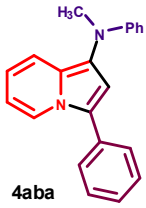
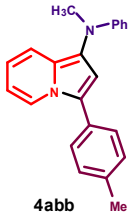
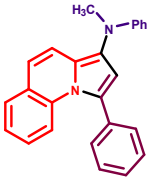
 4baa	 4aba	 4abb	 4bba
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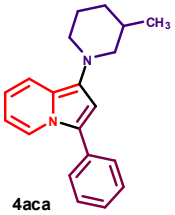
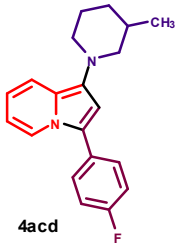
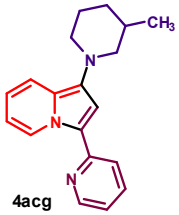
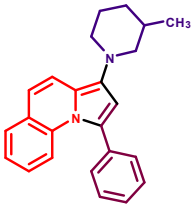
 4aca	 4acd	 4acg	 4bca
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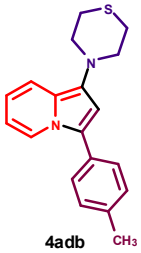
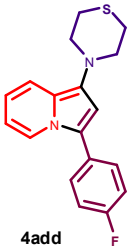
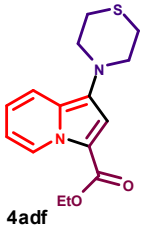
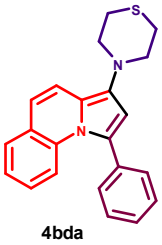
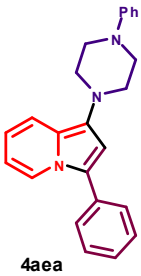
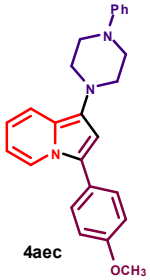
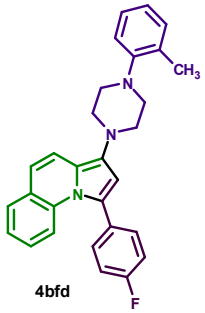
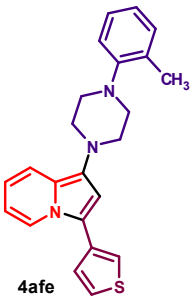
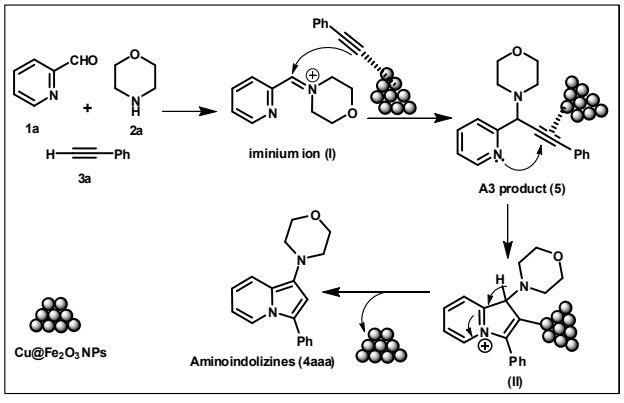
 4adb	 4add	 4adf	 4bda
2 h, 87%	3 h, 82%	2 h, 87%	4 h, 84%
 4aea	 4aec	 4bfd	 4afe
2 h, 90%	2 h, 81%	5 h, 85%	2 h, 86%

Table 3: Comparison of present method with the reported catalysts for the synthesis of aminoindolizine (**4aaa**)

S. No	Catalyst	Solvent	Yield of **4aaa** (%)	[Ref]	Catal. recycle
1	**$Cu@Fe_2O_3$**	**Glycerin**	**87**	**present**	**yes**
2	CuI/CSP	EG	92	[21]	yes
3	ZnI_2	Toluene	90	[20a]	No
4	Cu NPs/C	DCM	74	[20f], [20g]	No
5	CuCl	PEG	96	[20b]	No
6	$Fe(acac)_3$	TBAOH, DMSO	83	[20c]	No
7	$AgBF_4$	Toluene	89	[20d]	No
8	$NaAuCl_4$	Neat	95	[20e]	No

The plausible mechanism for the formation of aminoindolizine *via* propargyl amine (A3 product) intermediate followed by cycloisomerization was demonstrated in the literature.[20] On the basis of these reports, we proposed the mechanism for $Cu@Fe_2O_3$ catalyzed synthesis of aminoindolizine as shown in Scheme 2. To understand the role of Fe_2O_3 support, we performed model reaction using Fe_2O_3 NPs alone as catalyst under optimized reaction conditions. The reaction mixture was analyzed by ^1H NMR spectroscopy technique, the result showed that the formation of 2-pyridinyl propargyl amine (**5**) in 65% conversion *via* A3 coupling reaction and there was no cycloisomerized product in the mixture. The presence of low-coordinated sites, and surface vacancies, Lewis acidic Fe^{3+} sites of Fe_2O_3 was responsible for its high catalytic activity in A3 coupling reaction. It gives clear idea about the role of Fe_2O_3 support to promote the A3 coupling and also Cu NPs on its surface enhance the A3 coupling as well as cycloisomerization to afford the aminoindolizine (**4aaa**) as show in Scheme 2. The excellent catalytic activity of $Cu@Fe_2O_3$ MNPs was due to the synergistic effect of both Fe_2O_3 and Cu NPs.



Scheme 2: The plausible mechanism for $Cu@Fe_2O_3$ catalyzed synthesis of aminoindolizine (**4aaa**)

The $Cu@Fe_2O_3$ nanocatalyst recycle study was performed using model reaction under optimized conditions to obtain aminoindolizine (**4aaa**) as shown in Figure 10. After completion of reaction, glycerin was removed by addition of water followed by decanting the reaction mixture. Ethanol was added to the obtained mixture, and the catalyst was recovered by external magnet. The catalyst was washed with ethanol and dried at 90 ^oC in oven for 4 h. The organic layer was subjected to ICP-AES analysis, to check the loss of catalyst during washings and metal contamination in the final product. The negative results reveal that neither catalyst loss nor metal contamination was observed. The combined organic layers were evaporated to afford the crude product, which was purified by flash column chromatography technique. The recovered catalyst was successfully recycled for five times more without significant loss in its catalytic activity by following same procedure as shown in Figure 10.

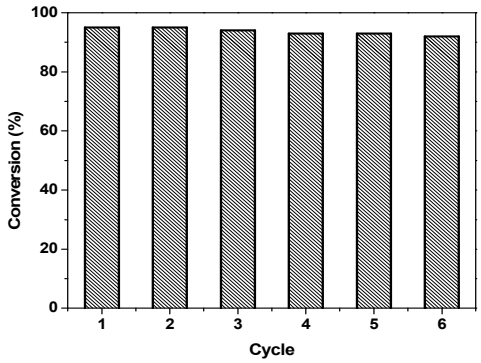


Figure 10: Recyclability of $Cu@Fe_2O_3$ catalyst for the synthesis of (**4aaa**)

Next, we studied the heterogeneity of $Cu@Fe_2O_3$ nanocatalyst for a model reaction to afford aminoindolizines (**4aaa**) in glycerine and water (1:1) mixture as solvent at 110 ^oC by hot filtration test experiment. The model reaction was monitored at 50% conversion of starting materials and filtered out the $Cu@Fe_2O_3$ catalyst from the reaction mixture. The reaction was further continued with filtrate under optimized conditions and there was no progress of reaction even after 12 h. The negative results were indicating that the absence of active Cu in the filtrate and no leaching of CuO NPs from Fe_2O_3 support.

Conclusions

We developed an efficient protocol for synthesis of $Cu@Fe_2O_3$ MNPs *via* hydrothermal method in a single step for the first time. The characterization studies revealed the presence of CuO/Cu_2O mixed oxides on hematite supporting material. The synthesized MNPs were found to be efficient catalyst for one-pot synthesis of aminoindolizines and pyrrolo[1,2-a]quinolines via A3 coupling reaction. Interestingly, hematite showed catalytic activity in A3 coupling reaction to afford the 2-pyridinyl propargyl amine intermediate, which supported proposed mechanism. The study revealed the synergistic effect of both Fe_2O_3 and Cu NPs of catalyst

was responsible for its excellent catalytic activity. The present method offers advantages over the reported methods such as easy recoverability of catalyst by external magnetic field, recyclability for six times, green reaction conditions, wide substrate scope, high catalytic activity, short reaction time etc. The further study on catalytic potential of $Cu@Fe_2O_3$ is underway in our laboratory.

Experimental Section

Typical procedure for the synthesis of $Cu@Fe_2O_3$ MNPs: The synthesis of $Cu@Fe_2O_3$ MNPs was achieved by hydrothermal method. Typically, 10 mL of 0.2 M $FeCl_3$ aqueous solution (2 mmol, 0.324 g) and 10 mL of 2.0 M aqueous urea solution (20 mmol, 1.2 g) were mixed in 10 mL of ethylene glycol. To this mixture, 10 mL of 0.2 M $CuCl_2$ aqueous solution (2 mmol, 0.27 g) and glucose (10 mol%) and 5 mL of 20.6 M (40 %) aqueous NH_3 were mixed successively and sonicated for 15 min to form a homogeneous mixture. The resulted mixture was transferred into a 100 ml Teflon-lined stainless-steel autoclave and heated at 180 ^oC for 8h. The autoclave was allowed to cool naturally to room temperature. The resulting solid nanoparticles were washed several times with water followed by final wash with acetone and recovered by using external magnetic field. The obtained MNPs were collected and dried in oven at 70 ^oC for 6 h.

General Procedure for synthesis of aminoindolizines and pyrrolo[1,2-a]quinolines (4): A mixture of pyridine-2-carboxaldehye/quinolin-2-carboxaldehyde **1** (1 mmol), amines **2** (1 mmol), phenylacetylenes **3** (1 mmol) and $Cu@Fe_2O_3$ catalyst (5 mg) were stirred at 110 ^oC in glycerin (2 mL). The progress of reaction was monitored by TLC until the reaction was completed. After completion of reaction, the glycerin was removed by addition of water followed by decanting the reaction mixture. Ethanol was added to this mixture followed by recovery of $Cu@Fe_2O_3$ catalyst by external magnet. The recovered catalyst was washed with ethanol for 3-4 times and dried at 80 ^oC in oven to reuse it for further. The combined organic layers were evaporated and the obtained crude products were purified by flash column chromatography.

Experimental data for unknown compounds

1-(3-Methylpiperidin-1-yl)-3-(pyridin-2-yl)indolizine **(4acg)**: Yellow oil. IR (υ_{max}/cm^{-1}, $CHCl_3$): 2936, 2842, 1734, 1628, 1531, 1448, 1309, 956, 745; ^1H NMR (400 MHz, C_6D_6) δ = 10.37 (d, J = 6.9 Hz, 1H), 8.45 (d, J = 6.1 Hz, 1H), 7.55 (d, *J* = 9.2 Hz, 1H), 7.27 (d, *J* = 8.4 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 7.06 (s, 1H), 6.52 (t, *J* = 6.1 Hz, 1H), 6.47 (t, *J* = 7.6 Hz, 1H), 6.35 (t, J = 6.9 Hz, 1H), 3.22 (d, J = 7.6 Hz, 2H), 2.59 (t, *J* = 11.4 Hz, 1H), 2.34 (t, *J* = 10.7 Hz, 1H), 1.92-1.64 (m, 5H), 0.88 (d, *J* = 6.7 Hz, 3H) ppm; ^{13}C NMR (100 MHz, C_6D_6) δ = 153.31, 148.44, 135.73, 132.22, 127.29, 119.86, 118.66, 117.45, 116.92, 111.81, 107.17, 62.68, 54.98, 33.31, 31.96, 26.41, 19.74 ppm; HRMS (ES): Calcd 291.1735, found 291.1721; Anal. calcd for C19H21N3: C, 78.32; H, 7.26; N, 14.42; found C, 78.22; H, 7.41; N, 14.24.

3-(Thiophen-3-yl)-1-(4-o-tolylpiperazin-1-yl)indolizine (**4afe**): Yellow oil; IR (υ_{max}/cm^{-1}, $CHCl_3$): 2930, 2816, 1599, 1549, 1498, 1434, 1366, 1259, 1137, 1025, 938, 807, 732; ^1H NMR (400 MHz, C_6D_6) δ = 7.93 (d, *J* = 7.6 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 1H), 7.19-7.16 (m, 2H), 7.16-7.13 (m, 2H), 7.10 (t, *J* = 7.6 Hz, 1H), 7.04-7.01 (m, 2H), 6.76 (s, 1H), 6.38 (t, *J* = 6.8 Hz, 1H), 6.10 (t, *J* = 6.8 Hz, 1H), 3.11 (t, *J* = 4.6 Hz, 4H), 3.08 (t, *J* = 4.6 Hz, 4H), 2.34 (s, 3H) ppm; ^{13}C NMR (100 MHz, C_6D_6) δ = 150.92, 131.99, 131.48, 130.02, 128.92, 125.62, 124.55, 122.19, 120.97, 119.01, 118.14, 116.83, 113.12, 109.69, 105.14, 53.31, 51.34, 16.70 ppm; HRMS (ES): Calcd 373.1613, found 373.1609; Anal. calcd for $C_{23}H_{23}N_3S$: C, 73.96; H, 6.21; N, 11.25; S, 8.58: found C, 73.78; H, 6.42; N, 11.04; S, 8.38:

N-Methyl-N,1-diphenylpyrrolo[1,2-a]quinolin-3-amine (**4bba**)*:* Yellow oil. IR (υ_{max}/cm^{-1}, $CHCl_3$): 2926, 2809, 2359, 1598, 1496, 1449, 1320.39, 1114, 796, 751; ^1H NMR (400 MHz, C_6D_6) δ = 7.63 (d, *J* = 8.3 Hz, 1H), 7.32 (d, *J* = 7.6 Hz, 2H), 7.27 (d, *J* = 7.6 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 2H), 7.12-709 (m, 3H), 6.90 (d, *J* = 7.6 Hz, 2H), 6.82 (t, *J* = 6.8 Hz, 1H), 6.77 (d, *J* = 8.3 Hz, 1H), 6.63 (d, *J* = 9.1 Hz, 1H), 6.52 (s, 1H), 3.12 (s, 3H) ppm; ^{13}C NMR (100 MHz, C_6D_6) δ = 150.54, 135.86, 134.62, 129.52, 129.28, 128.73, 126.69, 126.15, 123.63, 119.05, 117.98, 117.63, 117.33, 114.60, 113.85 ppm; HRMS (ES): Calcd 348.1626, found 348.1624; Anal. calcd for $C_{25}H_{20}N_2$: C, 86.17; H, 5.79; N, 8.04; found C, 86.15; H, 5.81; N, 8.16.

*3-(3-Methylpiperidin-1-yl)-1-phenylpyrrolo [1,2-a]quinoline (**4bca**):* Yellow oil. IR (υ_{max}/cm^{-1}, $CHCl_3$): 3059, 2926, 2850, 1607, 1492, 1451, 1374, 1317, 1190, 1126, 791, 755, 700; ^1H NMR (400 MHz, C_6D_6) δ = 7.59 (t, *J* = 9.1 Hz, 2H), 7.36 (d, *J* = 7.6 Hz, 2H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.12-7.09 (m, 2H), 6.93 (t, *J* = 7.6 Hz, 1H), 6.78 (t, *J* = 6.8 Hz, 1H), 6.71 (d, *J* = 9.2 Hz, 1H), 6.58 (s, 1H), 3.24 (t, *J* = 10.7 Hz, 2H), 2.64 (t, *J* = 11.4 Hz, 1H), 2.36 (t, *J* = 10.6 Hz, 1H), 1.83-1.76 (m, 1H), 1.69-1.58 (m, 2H), 0.96-0.89 (m, 1H), 0.85 (d, *J* = 6.8 Hz, 3H) ppm. ^{13}C NMR (100 MHz, C_6D_6) δ = 136.43, 134.80, 134.09, 129.44, 128.69, 128.59, 127.50, 126.68, 126.27, 124.83, 123.39, 118.06, 116.79, 109.49, 62.93, 55.25, 33.20, 31.88, 26.39, 19.68 ppm. HRMS (ES): Calcd 340.1939, found 340.1940; Anal. calcd for $C_{24}H_{24}N_2$: C, 84.67; H, 7.11; N, 8.23; found C, 84.57; H, 7.16; N, 8.28.

4-(1-Phenylpyrrolo[1,2-a]quinolin-3-yl)thiomorpholine (**4bda**)*:* Yellow oil. IR (υ_{max}/cm^{-1}, $CHCl_3$): 2923, 2854, 2358, 1600, 1459, 1374, 1075, 966, 760; ^1H NMR (400 MHz, C_6D_6) δ = 7.57 (d, *J* = 8.3 Hz, 1H), 7.38 (d, *J* = 9.1 Hz, 1H), 7.34-7.31 (m, 3H), 7.12-7.10 (m, 3H), 6.92 (t, *J* = 7.6 Hz, 1H), 6.77 (t, *J* = 8.3 Hz, 1H), 6.71 (d, *J* = 9.9 Hz, 1H), 6.47 (s, 1H), 3.11 (t, *J* = 5.3 Hz, 4H), 2.58 (t, *J* = 4.5 Hz, 4H) ppm; ^{13}C NMR (100 MHz, C_6D_6) δ = 136.00, 134.41, 133.53, 129.26, 128.51, 128.45, 126.25, 124.82, 123.33, 117.84, 117.31, 117.13, 109.58, 56.30, 28.44 ppm; HRMS (ES): Calcd 344.1347, found 344.1341; Anal. calcd for $C_{22}H_{20}N_2S$: C, 76.71; H, 5.85; N, 8.13; S, 9.31; found C, 76.68; H, 5.79; N, 8.19; S, 9.30.

1-(4-Fluorophenyl)-3-(3-methylpiperidin-1-yl)pyrrolo[1,2-a]quinoline (**4bfd**): Yellow oil. IR (υ_{max}/cm^{-1}, $CHCl_3$): 2945, 2817, 2359, 1601, 1493, 1371, , 1225, 1146, 969, 794, 757; ^1H NMR (400 MHz, C_6D_6) δ = 7.48 (d, *J* = 9.1 Hz, 1H), 7.38 (d, *J* = 8.3 Hz, 1H), 7.30 (d, *J* = 8.3 Hz, 1H), 7.14 (d, *J* = 7.6 Hz, 2H), 7.04-7.01 (m, 3H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.90 (t, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 7.6 Hz, 1H), 6.73 (t, *J* = 8.3 Hz, 2H), 6.68 (d, *J* = 9.1 Hz, 1H), 6.43 (s, 1H), 3.06 (t, *J* = 4.5 Hz, 4H), 2.92 (t, *J* = 4.5 Hz, 4H), 2.29 (s, 3H) ppm; ^{13}C NMR (100 MHz, C_6D_6) δ

= 163.99, 161.49, 152.26, 134.66, 133.03, 132.86, 132.17, 131.47, 131.31, 131.24, 128.80, 127.10, 126.55, 126.48, 124.87, 123.11, 123.65, 119.55, 117.92, 117.83, 117.18, 115.82, 115.61, 109.46, 54.78, 52.65, 18.13 ppm; HRMS (ES): Calcd 435.2111, found 435.2109; Anal. calcd for $C_{29}H_{26}FN_3$: C, 79.97; H, 6.02; N, 9.65; found C, 79.87; H, 6.32; N, 9.51.

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Graphical Abstract

Copper Supported Hematite NPs as Magnetically Recoverable Nanocatalysts for One-Pot Synthesis of Aminioindolizines and Pyrrolo[1,2-a]quinolines

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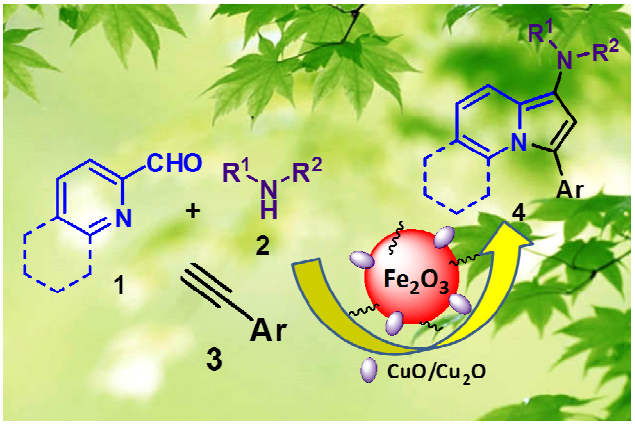

The Cu NPs such as CuO and Cu_2O mixed oxides supported on hematite ($Cu@Fe_2O_3$) surface was achieved by a facile hydrothermal method in a single step. The various techniques such as X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electronic microscopy (SEM), transmission electron microscopy (TEM), EDAX elemental analysis, Inductively coupled plasma atomic emission spectroscopy (ICP-AES) and X-ray photoelectron spectra (XPS) were used for the characterization of synthesized $Cu@Fe_2O_3$ MNPs. The catalytic potential of $Cu@Fe_2O_3$ NPs was explored for the synthesis of aminoindolizines and pyrrolo[1,2-a]quinolines *via* A3 coupling reaction. The present catalytic system offers advantages such as high catalytic activity in short reaction time, recovered the catalyst by external magnetic field and recycled for six times without significant loss in its activity.