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Application of Magnetic Chicken Feather Powder-Cu to the Click Synthesis of 1,2,3-Triazoles

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ABSTRACT

A novel copper (II) decorated on Fe₃O₄-chicken feather magnetic nanoparticles, denoted as Fe₃O₄-CF-Cu, was successfully prepared and fully characterized using FT-IR, SEM, TEM, EDS, TGA, XRD, ICP, XPS and VSM techniques. The activity of the prepared catalyst was studied in the synthesis of 1,2,3-triazoles by reaction of various azides and different terminal alkynes at room temperature under mild conditions. The reusability of the prepared nanocatalyst was examined five times with only a very slight loss of catalytic activity.

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Chicken feather; click chemistry; Fe₃O₄-CF-Cu; magnetically separable; 1,2,3-triazoles

Introduction

Nanomagnetic catalysts are one of the most promising areas in organic synthesis and it has gained considerable attention in recent times. In this aspect, synthesis and use of magnetic nanoparticles (MNPs) have gained significant attention among academic and industrial community because they are non-toxic, inexpensive, easily available, recyclable and show significant enhancement in catalytic activity due to small size, high surface area, active sites. Moreover, these MNPs can be effectively recovered after completion of reaction, without any loss, which is the drawback of traditional methods like centrifugation and filtration.^{1,2}

Chicken feather (CF), a waste material is a cheapest, biodegradable and natural biopolymer produced in large amounts from poultry industries. It is mainly (>90%) composed of the protein keratin, bio polymer with a high degree of cysteine cross-linkings.³ CF has been found to be a high performance material in various fields; for instance, in making plastics, as a sorbents, feather meal and other products.⁴⁻⁶ Recently, researchers have found potential applications of waste feathers by converting them into biodegradable polymers for expanding the industrial applications.⁷⁻⁹ In addition to these applications, feather keratin has widely been used for developing water-resistant thermoplastic materials for various applications.^{10,11} It holds the potential to act as a support and also as source of various functional groups like -CO₂H, -NH₂, -SH and -OH for various important chemical reactions. However, the use of CFs in catalytic applications is rarely known in the literature.¹²

The Cu-catalyzed azide-alkyne cycloaddition (CuAAC) reaction between azide and alkyne moieties is the most successful variant, forming a 1,4-substituted 1,2,3-triazole.¹³ Due to its high regioselectivity and yield, easy reaction conditions, good reliability and tolerance to a wide range of functional groups, the CuAAC reaction has emerged as a strategy for the rapid and efficient assembly of molecules in the industrial and academic realms.¹⁴⁻¹⁶

A significant number of works have been done using copper(I) sources in regioselective azide-alkyne cycloadditions.¹⁷⁻²⁰ Copper(I) salts in the presence of a base or copper(II) salts that are coupled with

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Scheme 1. Preparation of $\text{Fe}_3\text{O}_4\text{-CF-Cu}$ MNPs.

reducing agents are commonly used catalyst systems for this reaction.^{21–24} Despite many obvious advantages, the CuAAC reaction has a non-ignorable limitation: there is a significant amount of toxic, colored and expensive copper complexes, which are difficult to remove from the end products. Immobilizing the copper catalyst on a heterogeneous support is one of the main strategies to circumvent the aforementioned problems.^{25,26}

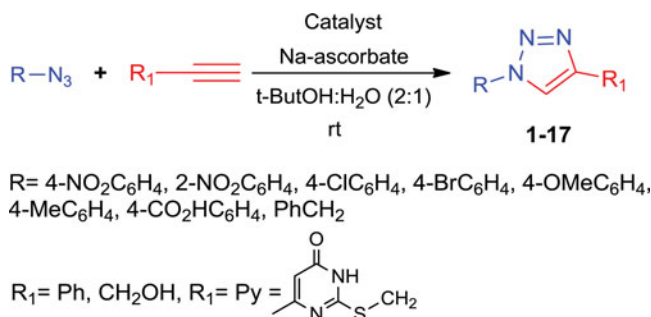
Inspired by the above facts and due to our interest in heterocycles and application of reusable catalysts in organic reactions,^{27–29} in this paper, for the first time a copper(II) immobilized on $\text{Fe}_3\text{O}_4\text{-CF}$ MNPs, containing CF was prepared (Scheme 1). The catalytic activity of this new heterogeneous catalyst which was denoted as $\text{Fe}_3\text{O}_4\text{-CF-Cu}$ was also investigated in one-pot synthesis of 1,2,3-triazoles by reaction of terminal alkynes and azides at room temperature under mild conditions (Scheme 2).

Results and discussion

Preparation and characterization of the catalyst

The schematic synthesis of catalyst is depicted in Scheme 1. The catalyst was prepared by sonicating CF powder in deionized water, and then adding iron salts including $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and aqueous ammonia to form nanomagnetic Fe_3O_4 in matrix CF ($\text{Fe}_3\text{O}_4\text{-CF}$), followed by the addition of copper acetate in ethanol to get Cu(II) immobilized magnetic CF $\text{Fe}_3\text{O}_4\text{-CF-Cu}$ catalyst in excellent yield. After preparation, the catalyst fully characterized using different techniques including Fourier transform infrared spectroscopy (FT-IR), transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy-dispersive X-ray (EDS), thermogravimetric analysis (TGA), X-ray powder diffraction (XRD), inductively coupled plasma (ICP), vibrating sample magnetometry (VSM) and X-ray photoelectron spectroscopy (XPS).

The FT-IR spectra of Fe_3O_4 , CF, $\text{Fe}_3\text{O}_4\text{-CF}$ and $\text{Fe}_3\text{O}_4\text{-CF-Cu}$ MNPs are compared in Figure 1. The FT-IR spectrum for the naked Fe_3O_4 (Figure 1 (violet line)) shows a stretching vibration at 3415 cm^{-1} , which incorporates the contributions from both symmetrical and asymmetrical modes of the O–H bonds, which are attached to the surface iron atoms. The bands at low wave numbers (595 cm^{-1}) come from vibrations of Fe–O bonds of iron oxide skeleton. In FT-IR spectrum of CF (Figure 1 (green line)), the absorption peaks at 1657 , 1530 and 3315 cm^{-1} are attributed to the characteristic absorption bands of the amide I and amide II and (–NH, –OH) stretching, respectively. Coating Fe_3O_4 MNPs with CF



Scheme 2. Synthesis of 1,2,3-triazoles catalyzed by $\text{Fe}_3\text{O}_4\text{-CF-Cu}$ MNPs.

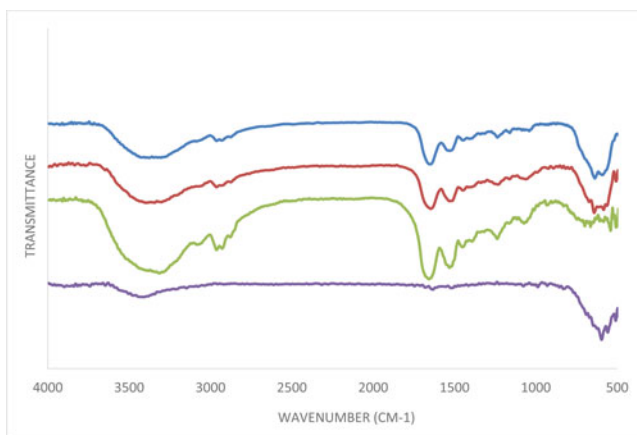


Figure 1. FT-IR spectra of (violet line) Fe_3O_4 MNPs, (green line) CF, (red line) Fe_3O_4 -CF MNPs and (blue line) Fe_3O_4 -CF-Cu MNPs.

is confirmed by appeared peaks at 1645, 1530 and 3397 cm^{-1} assigned to the amide and (-NH, -OH) stretching vibrations of CF, respectively (Figure 1 (red line)). The peak shifting of bending vibration of amide I and amide II from 1645, 1530 and 3397 cm^{-1} to 1650, 1527 and 3378 cm^{-1} was most likely due to the interaction of amide and OH groups of feather with copper(II) (Figure 1 (blue line)).^{30,12} These results confirm the good immobilization of Cu(II) on Fe_3O_4 -CF MNPs.

The morphological features were studied by SEM technique. The SEM image of Fe_3O_4 -CF-Cu (Figure 2a) demonstrates that these modified copper CF coated Fe_3O_4 MNPs are almost spherical, narrowly distributed and well dispersed. Also, the particle size of nanocatalyst was investigated by TEM technique. The TEM photograph of sample (Figure 2b) shows average size of Fe_3O_4 -CF-Cu magnetic nanocatalyst is approximately between 10 and 20 nm in the diameter.³⁰

The existence of Cu element along with other elements containing Fe, O, S, N and C in EDS spectrum of the Fe_3O_4 -CF-Cu catalyst shows the successful immobilization of Cu(II) on Fe_3O_4 -CF MNPs. As can be seen in Figure 3, no additional peak related to other impurities was appeared in the spectrum.

The TGA of Fe_3O_4 -CF-Cu was also investigated in air from room temperature to 1000°C and used to determine the thermal stability and content of organic functional groups on the surface of the MNPs (Figure 4). TGA curve of Fe_3O_4 -CF-Cu showed the initial weight loss about 100°C, which was related to the adsorbed water molecules on the support. The organic parts were decomposed completely in the

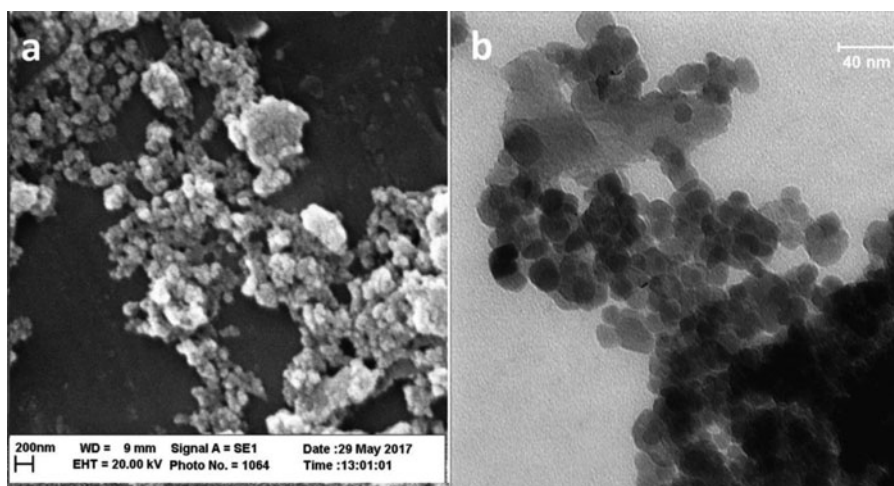


Figure 2. SEM (a) and TEM (b) images of Fe_3O_4 -CF-Cu MNPs.

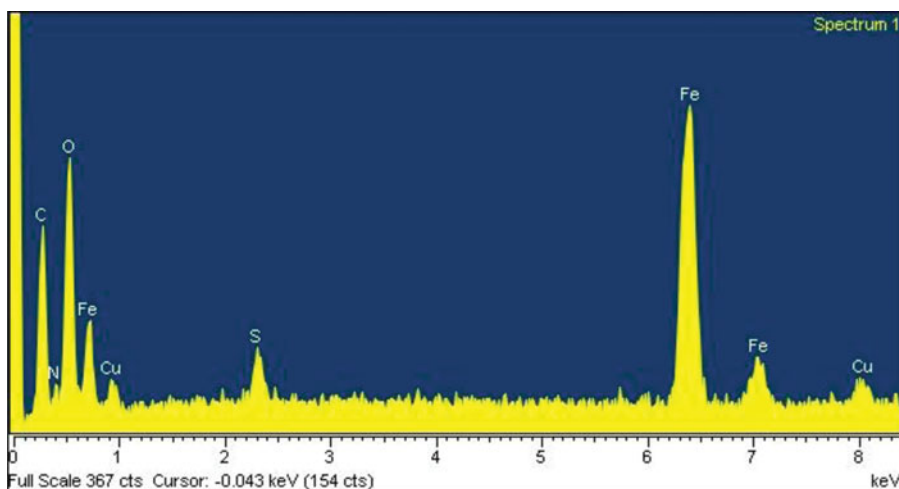


Figure 3. EDS pattern of $\text{Fe}_3\text{O}_4\text{-CF-Cu}$ MNPs.

temperature range of 250–450°C. Thus, the catalyst is stable up to 200°C and can be used in organic reactions below this temperature.

The magnetization curve of $\text{Fe}_3\text{O}_4\text{-CF-Cu}$ was measured at ambient temperature with a VSM. As illustrated in Figure 5, the value of saturation magnetic moment of catalyst is 22.10 emu g^{-1} which indicates the catalyst is superparamagnetic. XRD measurement was applied to identify the crystalline structure of $\text{Fe}_3\text{O}_4\text{-CF-Cu}$ MNPs. As shown in Figure 6, six characteristic diffraction peaks ($2\theta = 30.2^\circ, 35.6^\circ, 43.3^\circ, 53.8^\circ, 57.3^\circ$ and 63°) corresponding to the (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) reflections of inverse spinel Fe_3O_4 were in well accordance with the previous literatures. According to XPS result, there are both oxidation states of Cu(0) and (II) in catalyst, and most of them is Cu(II). Three weak diffraction peaks ($2\theta = 43.2^\circ, 50.8^\circ$ and 74.6°) corresponding to the (1 1 1), (2 0 0) and (2 2 0) are belonged to Cu(0) that anchored on $\text{Fe}_3\text{O}_4\text{-CF}$ MNPs and the peaks related

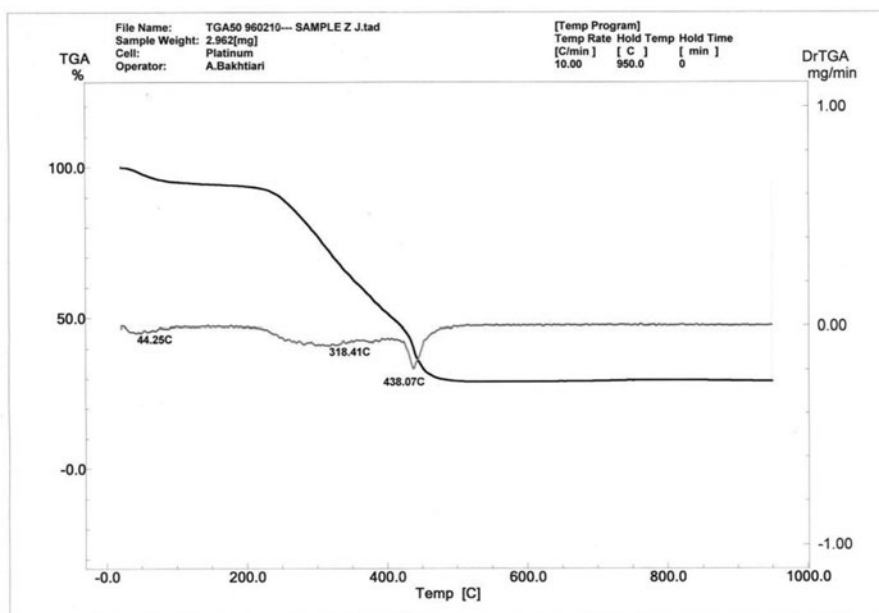


Figure 4. TGA curve of $\text{Fe}_3\text{O}_4\text{-CF-Cu}$ MNPs.

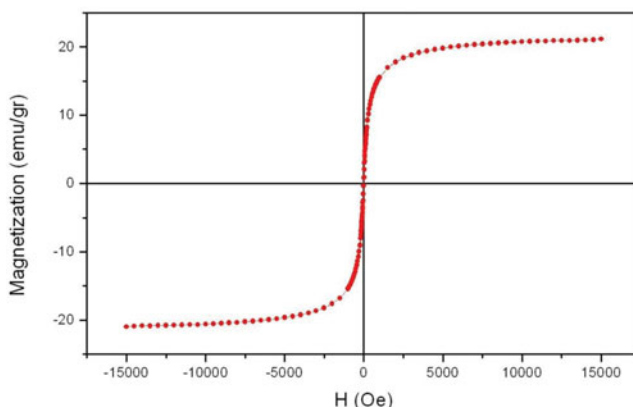


Figure 5. Hysteresis loops of $\text{Fe}_3\text{O}_4\text{-CF-Cu}$ MNPs at room temperature.

to Cu(II) acetate were appeared between 10° to 25° theta, but because of the overlap with CF peaks in these regions, the characterization of mentioned peaks is hard.³¹

Figure 7 shows the XPS spectra of the deconvoluted Cu analysis in term of $\text{Cu}^0/\text{Cu}^{1+}$, Cu^{2+} and Cu^{3+} component. The envelope of Cu^0 and Cu^{1+} component at 933.1 eV could not be unambiguously deconvolute without introducing a large approximation when assigning the separate peaks for Cu^0 and Cu^{1+} .³² The copper spectrum shows a broad Cu $2p_{3/2}$ signal that can be attributed to the corresponding shake-up satellite peak contribution at 934.2 eV.³³ The various redox potential available at the Cu surface are due to the different oxidation state for Cu. The intensity ratio of the shake-up satellite and the intensity of the Cu $2p_{3/2}$ peak revealed that the most of the copper is as Cu^{2+} /acetate (Table 1). Moreover, the carbon spectrum showed an important peak located at 288.2 eV, which according to the standard corresponds to copper acetate (Figure 8).³³

Finally, the copper content of the prepared $\text{Fe}_3\text{O}_4\text{-CF-Cu}$ was analyzed by ICP. According to ICP analysis, 2.307% of catalyst is copper NPs. These results show the good immobilization of Cu(II) on $\text{Fe}_3\text{O}_4\text{-CF}$ MNPs.

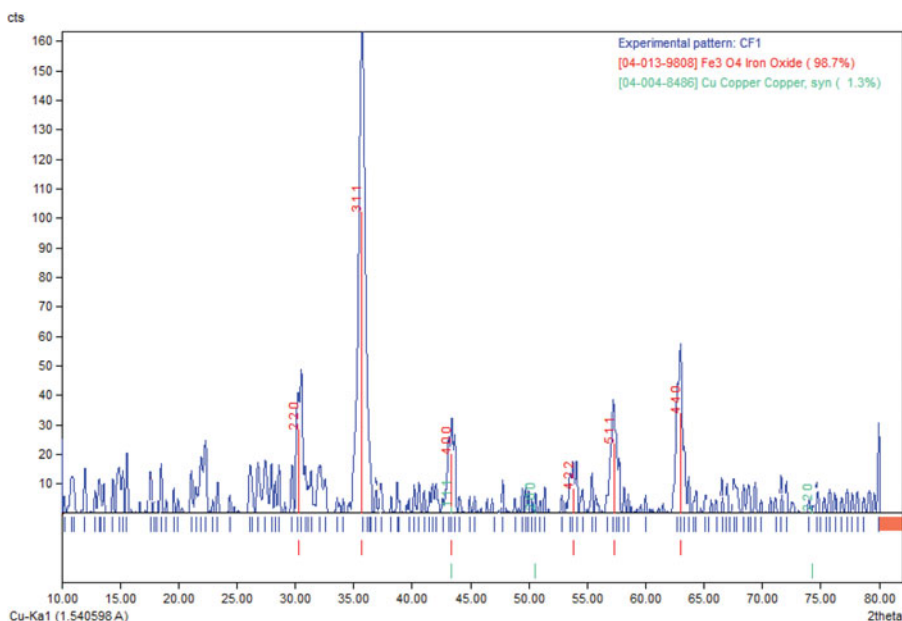


Figure 6. The XRD pattern of $\text{Fe}_3\text{O}_4\text{-CF-Cu}$ MNPs.

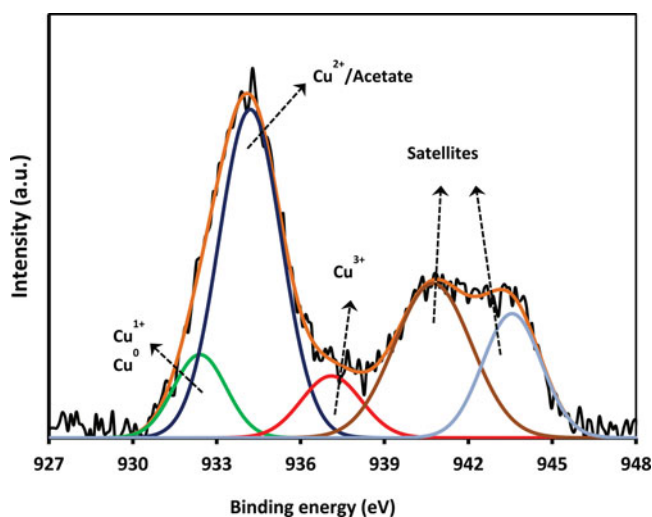


Figure 7. High-resolution Cu 2p_{3/2} XPS spectra for Fe₃O₄-CF-Cu MNPs.

Table 1. XPS analysis for the fresh catalyst.

Peak label/ID	BE (eV)	FWHM (eV)	Height	Norm. area	Rel. area %
Cu(0)	932.4	2.21	3134.44	7397.91	9.10
Cu(2+)/acetate	934.2	2.63	12401	34711.4	42.90
Cu(3+)	937.1	2.53	2335.1	6287.29	7.80
Satellites	940.7	3.25	5828.88	20179.2	24.90
Satellites	943.57	2.48	4690.05	12369.1	15.30

Catalytic synthesis of 1,2,3-triazoles

After the successful preparation and full characterization of the Fe₃O₄-CF-Cu, its catalytic activity was examined for the green one-pot synthesis of 1,2,3-triazoles from the reaction of various terminal alkynes and different azide (1,3-dipolar Huisgen cycloaddition reaction) at room temperature (Scheme 1).

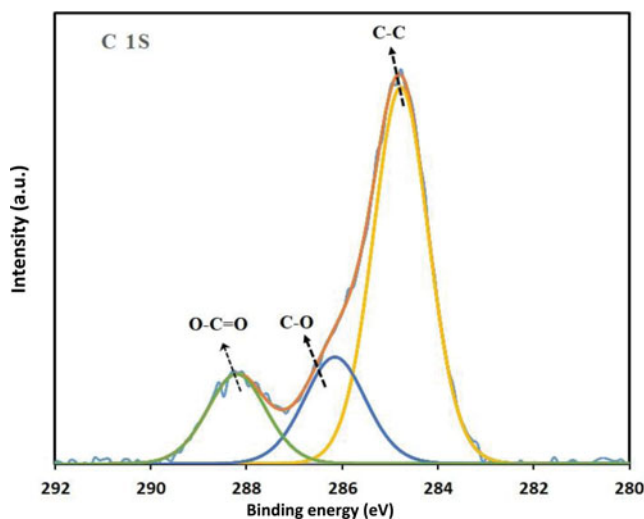


Figure 8. High-resolution C 1s XPS spectra for Fe₃O₄-CF-Cu MNPs.

Table 2. Screening of the amount of the catalyst and molar ration of 4-nitrophenyl azide/phenyl acetylene for the formation of compound 1.

Entry	Catalyst (mol%)	4-nitrophenyl azide/phenyl acetylene	Na ascorbate	T (°C)	Time (min)	Isolated yield ^a (%)
1	—	1.5/1	10	rt	240	Trace
2	5	1.5/1	10	rt	120	70
3	10	1.5/1	10	rt	120	81
4	15	1.5/1	10	rt	120	92
5	20	1.5/1	10	rt	120	93
6	15	1/1	10	rt	120	80
7	15	1.5/1	—	rt	120	40
8	15	1.5/1	5	rt	120	85

^aIsolated yields.

The reaction of 4-nitro-phenylazide (1.5 mmol), phenylacetylene (1.0 mmol) and sodium ascorbate (10 mol%) for the synthesis of compound **1** was selected as a model, to optimize the reaction conditions. This reaction was carried out in the absence and presence of different amount of catalyst (Table 2). No product was obtained in the absence of the catalyst after 240 min (entry 1). Increasing the amount of the catalyst improved the yield of **1** (entries 2–4), with the use of 15 mol% of catalyst resulted in the highest yield in 2 h (entry 4). Further increase of the amount of the catalyst failed to affect the yield noticeably (entry 5). When we used the equal amount of azide and phenylacetylene (1/1), the yield of the product is decreased to 80% (entry 6). Also, the reaction was performed in the presence and absence of sodium ascorbate (entries 4, 7, 8). In the absence of sodium ascorbate, the reaction was done with low yield, while in the presence of 10% molar sodium ascorbate, the yield was the maximum amount 92% (entry 4).

Then, other conditions such as temperature and use of various solvents (Table 3) were investigated. The yields of the reaction were better in solvents than solvent-free conditions (entries 1–10). Also, the polar solvents are carried out better the reaction compared to non-polar solvents (entries 1–5), the highest yield was obtained when the reaction was done in mixture of t-BuOH and H₂O with the ratio 2:1 at room temperature (entry 7). Increasing the temperature does not improve the yields of the reaction (entries 8, 9). Having these optimized reaction conditions in hand, the scope of reaction was extended to various azides and different terminal alkynes. According to the results shown in Table 4, all phenyl azides carrying either electron-donating or electron-withdrawing groups reacted successfully and gave the products in high yields within short reaction time. Benzyl azide compared with phenyl azides required shorter reaction time (entry 7). Moreover, the yield and reaction rate of phenyl azide with CO₂H substituent (entry 13) was lower than that of phenyl azide with other substituents. The both aromatic and aliphatic terminal acetylenes gave the corresponding triazoles in excellent yields and high purity.

To determine the applicability of catalyst recovery, at the end of the reaction, the Fe₃O₄-CF-Cu was separated from the reaction mixture by employing an external magnet. The separated catalyst was

Table 3. Screening of various solvents and temperature for the formation of compound 1.^a

Entry	Catalyst (mol%)	Solvent	T (°C)	Time (min)	Isolated yield ^b (%)
1	15	H ₂ O	rt	180	40
2	15	t-BuOH	rt	180	62
3	15	THF	rt	180	85
4	15	CH ₃ CN	rt	180	83
5	15	CH ₂ Cl ₂	rt	180	30
6	15	t-BuOH:H ₂ O (1:1)	rt	120	82
7	15	t-BuOH:H ₂ O (2:1)	rt	120	92
8	15	t-BuOH:H ₂ O (2:1)	50	120	92
9	15	t-BuOH:H ₂ O (2:1)	80	120	93
10	15	—	rt	120	Trace

^aReaction conditions: 4-nitro-phenylazide (1.5 mmol), phenylacetylene (1 mmol), sodium ascorbate (10 mol%), and Fe₃O₄-CF-Cu (15 mol%).^bIsolated yields.

Table 4. Synthesis of 1,2,3-triazoles 1–17 using $\text{Fe}_3\text{O}_4\text{-CF-Cu}$ MNPs as catalyst.^a

Compound	R	R ₁	Time (h)	Yields ^c (%)	m.p. (°C)	
					Found	Reported
1	4-NO ₂	Ph	2.0	92	254–255	254 ³⁴
2	4-Br	Ph	1.5	95	232–234	232 ³⁴
3	4-Cl	Ph	1.5	97	227–229	228 ³⁴
4	4-MeO	Ph	1.5	95	166–167	167 ³⁴
5	4-Me	Ph	1.0	98	174–175	174 ³⁴
6	2-NO ₂	Ph	3	90	143–145	142 ³⁴
7	C ₆ H ₅ CH ₂	Ph	0.5	98	130–131	132 ³⁴
8	4-O ₂ N	CH ₂ OH	1.5	89	201–202	201–202 ³⁵
9	4-Br	CH ₂ OH	1.0	93	134–135	134–137 ³⁵
10	4-Cl	CH ₂ OH	1.0	96	144–146	144–145 ³⁵
11	4-MeO	CH ₂ OH	1.0	91	127–128	127–129 ³⁵
12	4-Me	CH ₂ OH	1.0	96	125–127	124–125 ³⁵
13	4-CO ₂ H	CH ₂ OH	4	80	251–152	250–253 ³⁶
14	4-O ₂ N	Py	1.0	90	249–251	This work
15	4-Br	Py	1.0	96	180–181	This work
16	4-Cl	Py	1.0	93	201–203	This work
17	4-Me	Py	0.5	95	196–197	This work

^aReaction conditions: azide (1.5 mmol), terminal acetylene (2a–c; 1 mmol), sodium ascorbate (10 mol%), $\text{Fe}_3\text{O}_4\text{-CF-Cu}$ MNPs (15 mol%), at room temperature in *t*-BuOH:H₂O (2:1).

^bThe known products were identified by comparing of their melting points and new products were characterized by (FTIR and ¹H NMR).

^cIsolated yields.

washed with acetone to remove residual product, dried at 100°C under vacuum, and reused in a subsequent reaction in excellent yields. It showed the same activity as fresh catalyst (Figure 9).

Experimental

Chemicals and apparatus

All chemicals were available commercially and used without additional purification. The melting points of products were determined with an Electrothermal type 9100 melting point apparatus. ¹H NMR spectra were recorded on a Bruker 300 FT spectrometer, in DMSO-*d*₆ as the solvent using tetramethyl silane (TMS) as internal standard. FT-IR spectra were recorded with a Nicolet Avatar 370 FT-IR Thermo spectrometer. Elemental analyses were performed using a Thermo Finnegan Flash EA 1112 series instrument. Mass spectra were recorded with a CH7A Varianmat Bremem instrument at 70 eV electron impact ionization, in *m/z* (rel%). TEM was performed with a Leo 912 AB microscope with an accelerating voltage of 120 kV. SEM images were also recorded using Leo 1450 VP scanning electron microscope operating

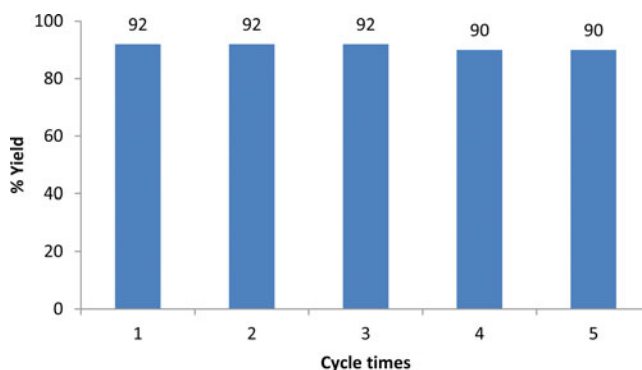


Figure 9. Recycling experiment for $\text{Fe}_3\text{O}_4\text{-CF-Cu}$ MNPs.

at an acceleration voltage 20 kV. EDS analysis was performed with a Leo 1450 VP. TGA analysis was carried out on a Shimadzu Thermogravimetric Analyzer (TG-50) in the temperature range of 25–900°C at a heating rate of 10°C min⁻¹ under air atmosphere. Ultrasonication was performed using a Soltec sonicator at a frequency of 40 kHz and a nominal power of 260 W. The magnetic property of catalyst was measured using a vibrating sample magnetometer (VSM, 7400 Lake Shore). The crystal structure of catalyst was analyzed by XRD using a XPEROLER-GNR diffractometer operated at 40 kV and 30 mA utilizing CuK α radiation ($\lambda = 0.154^\circ\text{A}$). The surface chemical compositions of catalysts were characterized by XPS (Thermo Scientific, ESCALAB 250Xi, Mg X-ray resource). Inductively coupled plasma mass spectrometry (ICP-MS) was carried out on a Arcos system-76004555-Germany.

Preparation of Fe₃O₄-CF MNPs

At first, CF powder (1.0 g) was ultrasonically dispersed in deionized water (100 mL) for 20 min at 70°C. Then to this mixture, iron salts including FeCl₃·6H₂O (2.01 g) and FeSO₄·7H₂O (1.08 g) were added and after dissolving them in mixture, aqueous ammonia (20 mL, 25%) was added dropwise under argon atmosphere. After completion of adding aqueous ammonia, the reaction mixture was stirred for another 60 min. During this process, iron oxide NPs coated with CF were precipitated, which were separated by an external magnet and washed with methanol, acetone and deionized water. The collected Fe₃O₄-CF MNPs were dried under vacuum at 60°C.

Preparation of Fe₃O₄-CF-Cu MNPs

Feather coated MNPs (1.0 g) were added in a solution of copper acetate (0.1 g) in ethanol (50 mL) and refluxed for 12 h under argon atmosphere. After completion of the reaction, the catalyst (Fe₃O₄-CF-Cu) was separated by an external magnet and washed several times with hot ethanol and dried under vacuum at 60°C for 6 h.

General procedure for the synthesis of 1,2,3-triazoles 1–17

Fe₃O₄-CF-Cu (15 mol%), was added to a solution of 4-nitrophenylazide (1.5 mmol) phenylacetylene (1.0 mmol) and sodium ascorbate (10 mol%) in t-BuOH:H₂O (2:1; 6 mL). The mixture was magnetically stirred at room temperature, for 2 h and the progress of the reaction was monitored by TLC. Upon the completion of the reaction, the reaction mixture was diluted with EtOAc and the catalyst was removed by an external magnet, washed with acetone and dried overnight to be ready for the next run. The organic layer was dried over anhydrous Na₂SO₄, followed by evaporation under reduced pressure to remove the solvent. The residue was purified by recrystallization from ethanol to afford 1-(4-nitrophenyl)-4-phenyl-1H-1,2,3-triazole (92%). The known products (**1–13**), were reported previously in the literature.^{34–36} Also, the analytical and spectral data (IR, ¹H and ¹³C NMR spectroscopy, mass spectrometry and elemental analysis for new products (**14–17**) are described below.

6-methyl-2-(((1-(4-nitrophenyl)-1H-1,2,3-triazol-4-yl)methyl)thio)pyrimidin-4(3H)-one (14): Yield 90%, mp 249–251°C. IR spectrum, ν , cm⁻¹: 3476 (N-H), 3125 (C-H triazole ring), 2923–2850 (C-H aliphatic), 1640 (C=O). ¹H NMR spectrum, δ , ppm: 2.22 s (3H, -CH₃), 4.55 s (2H, -CH₂), 6.04 s (1H, C=CH-C=O), 8.09 d ($J = 9$ Hz, 2H, Ar), 8.42 d ($J = 9$ Hz, 2H, Ar), 8.50 s (1H, C=CH-N), 12.47 brs (1H, -NH). ¹³C NMR spectrum, δ C, ppm: 24.9, 107.0, 120.5, 121.0, 122.6, 125.5, 126.0, 126.7, 141.2, 144.5, 145.5, 147.1, 147.1, 164.9. Found, %: C 48.88, H 3.99, N 24.02, S 9.20. Calculated, %: C 48.83, H 3.51, N 24.41, S 9.31; MS (m/z), 342 (M⁺).

2-(((1-(4-bromophenyl)-1H-1,2,3-triazol-4-yl)methyl)thio)-6-methylpyrimidin-4(3H)-one (15): Yield 96%, mp: 180–181°C. IR spectrum, ν , cm⁻¹: 3309 (N-H), 3145 (C-H triazole ring), 2994–2921 (C-H aliphatic), 1645 (C=O). ¹H NMR spectrum, δ , ppm: 2.19 s (3H, -CH₃), 4.56 s (2H, -CH₂), 6.02 s (1H, C=CH-C=O), 7.83 d ($J = 15$ Hz, 4H, Ar), 8.80 s (1H, C=CH-N), 12.41 brs (1H, -NH). ¹³C NMR spectrum, δ C, ppm: 24.7, 107.1, 121.7, 122.2, 122.4, 127.8, 133.1, 133.2, 136.2, 144.9, 165.1. Found, %: C 41.04, H 3.02, N 17.05, S 8.37. Calculated, %: C 44.46, H 3.20, N 18.52, S 8.48; MS (m/z), 378 (M⁺).

2-(((1-(4-chlorophenyl)-1H-1,2,3-triazol-4-yl)methyl)thio)-6-methylpyrimidin-4(3H)-one (16): Yield 93%, mp: 201–203°C. IR spectrum, ν , cm^{-1} : 3301 (N-H), 3141 (C-H triazole ring), 2994–2920 (C-H aliphatic), 1644 (C=O), 1501 (C=C Ar). ^1H NMR spectrum, δ , ppm: 2.19 s (3H, $-\text{CH}_3$), 4.53 s (2H, $-\text{CH}_2$), 6.03 s (1H, $\text{C}=\underline{\text{C}}-\text{C}=\text{O}$), 7.66 d ($J = 6$ Hz, 2H, Ar), 7.93 s (2H, Ar), 8.76 s (1H, $\text{C}=\underline{\text{C}}-\text{N}$), 12.41 brs (1H, $-\text{NH}$). ^{13}C NMR spectrum, δ C, ppm: 23.9, 106.5, 120.7, 121.6, 121.8, 126.9, 131.4, 131.5, 135.8, 144.0, 164.3. Found, %: C 49.95, H 3.26, N 19.45, S 9.93. Calculated, %: C 44.46, H 3.20, N 18.52, S 8.48.; MS (m/z), 333(M^+).

6-methyl-2-(((1-(p-tolyl)-1H-1,2,3-triazol-4-yl)methyl)thio)pyrimidin-4(3H)-one (17): Yield 95%, mp: 196–197°C. IR spectrum, ν , cm^{-1} : 3443 (N-H), 3137 (C-H triazole ring), 2916–2830 (C-H aliphatic), 1640 (C=O). ^1H NMR spectrum, δ , ppm: 2.24 s (3H, $-\text{CH}_3$), 4.52 s (2H, $-\text{CH}_2$), 6.04 s (1H, $\text{C}=\underline{\text{C}}-\text{C}=\text{O}$), 7.39 d ($J = 9$ Hz, 2H, Ar), 7.75 d ($J = 9$ Hz, 2H, Ar), 8.55 s (1H, $\text{C}=\underline{\text{C}}-\text{N}$), 12.5 brs (1H, $-\text{NH}$). ^{13}C NMR spectrum, δ C, ppm: 21.0, 24.8, 107.0, 120.2, 122.2, 130.6, 134.8, 138.7, 144.7, 144.7, 165.2. Found, %: C 56.94, H 4.09, N 21.65, S 9.90. Calculated, %: C 57.49, H 4.82, N 22.35, S 10.23.; MS (m/z), 313 (M^+).

Conclusions

In summary, novel copper(II) immobilized on CF coated Fe_3O_4 MNPs ($\text{Fe}_3\text{O}_4\text{-CF-Cu}$) were successfully prepared and fully characterized using FT-IR, TEM, SEM, EDS, XRD, ICP, TGA, XPS and VSM techniques. The new MNPs with average diameter of 20 nm performed well as catalyst in one-pot synthesis of 1,2,3-triazoles by reaction of various azides and three different terminal alkynes at room temperature in mixture of t-BuOH and water, giving high yields of the products within short reaction times. In addition, the catalyst can be easily recovered by a magnet and reused in the next runs without significant loss of catalytic activity. Further applications of this new catalyst for other reaction systems are currently under investigation.

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