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Graphical Abstract

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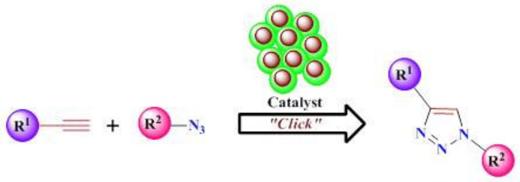

1,4-disubstituted 1,2,3-triazole
14 Examples

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PVP coated copper-iron oxide nanocomposite as an efficient catalyst for Click reactions

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ABSTRACT

A highly efficient Polyvinylpyrrolidone (PVP) coated copper-iron oxide magnetic nanoparticles as catalyst has been developed for the Huisgen 1,3-dipolar cycloaddition reactions between organic azides and terminal alkynes which is known to be the best example in click chemistry. The in situ generated Cu (I) species is the catalytically active species for click reaction. Wide ranges of 1,2,3 triazoles ave been synthesized in good yields by use of the catalyst at room temperature. This nanocatalyst can be recovered by applying external magnetic field which results in easy separation of catalyst without filtration and can be reused for three times without loss of its significant activity. This catalyst was characterized by FT-IR, XRD, XPS, FESEM and TEM.

Introduction

1,2,3-triazoles are five membered nitrogen containing heterocyclic compounds having aromatic character which are stable to light, moisture and oxygen. Various compounds consisting 1,2,3-triazole moiety shows biological activities such as antiviral,[1] fungicidal,[2] antibacterial,[3] antiallergic,[4] anticancer[5] and anti-HIV.[6] Sharpless[7] and Meldal[8] independently showed that copper (I) species can be used as catalyst for Husigen 1,3 cycloaddtion for terminal alkyne and organic azide under mild conditions towards 1,2,3 triazole synthesis. Cu(I) acts as an efficient and regioselective catalyst for this reaction yielding 1,4-disubstituted 1,2,3- triazoles. It is a classic example in click chemistry.[9,10] Click reactions have diverse applications in areas such as synthetic chemistry, supramolecular chemistry,[11] polymer and materials sciences,[12] bioconjugation[13] and combinatorial chemistry.[14] S. Kotha *et al.* have synthesised di-triazole based peptide as fluorescent chemosensor for Zn^{2+} ions using copper catalyzed Huisgen cycloaddition.[14d] .

Himo *et al.* have reported that copper metal alone can catalyse the click reaction owing to long reaction time and high catalyst loading.[15] Copper (I) containing oxide nanoparticles[16] and copper nanoclusters[17] have been used to catalyze Cu(I) azide-alkyne click reactions. Most of these procedures describe a homogeneous Cu(I) source –either by direct addition of a Cu(I) salt, or in situ reduction of Cu (II) by sodium ascorbate.[18] However, a profound impact on the development of new era of nanoparticles based materials as catalyst is a new challenge for researchers. In recent years, nanoparticles have become the centre of attention for its use as catalyst in organic reactions[19] as the nanoparticles provide high catalytic surface area which helps to enhance the rate of reaction. Orgueira *et al.* have used Cu(0) nanosize activated powder and amine hydrochloride salt as catalyst for click reaction.[20] Giorgio Molteni *et al* have reported mixed Cu/Cu-oxide nanoparticles as catalyst for click, 1,3-dipolar cycloaddition between azide and alkynes. [21]

In order to discover more reusable catalysts and to improve the efficiency of catalyst, solid supported catalysts have been developed for catalytic applications.[22,23,24,25] Solid support mostly entails soluble and insoluble polymers,[26,27] zeolites[28.29,30] or magnetic materials.[31,32,33] In addition to this, Cu(0) on charcoal, [34] Cu(0) nanoparticles[35,36,37,38] or CuO nanostructures[39] have also successfully exhibited activity for click reaction. Veerakumar *et al.* have synthesized 1,2,3-triazoles and thioethers by using highly dispersed silica-supported copper nanoparticles as catalyst.[40] In pursuit of a green catalyst, a development has been done in chemical synthesis which minimizes the pollution with respect to the increasing environmental issues.[16] Although, the use of heterogeneous catalyst system is being exploited to overcome the problem of separation of catalyst from the reaction.[41]

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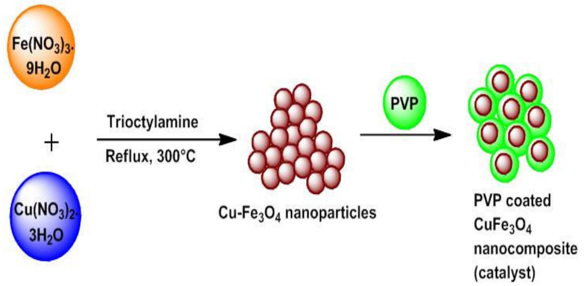
Recently, magnetic nanoparticles have emerged as viable and promising support for immobilization with applications in catalytic transformations such as robust, readily available and high surface area heterogeneous catalyst.[42,43] These particles can be separated easily from the reaction medium by applying external magnetic field thus, representing easy and environmentally benevolent means of catalyst recovery. Hudson *et al.* have reported the synthesis of magnetic bi-metallic copper-iron nanoparticles as heterogeneous catalyst for click reactions.[44a] P´erez *et al* reported Bimetallic nickel and copper on magnetite has been used as catalyst for multicomponent azide-alkyne cycloaddition.[44b] Moreover, magnetic nanoparticles coated with polymer as catalysts have gained much interest in organic reactions as they tend to minimize agglomeration. The nature of supporting materials on which nanoparticles are stabilized plays an important role in catalysis as it provides highly active catalyst surface, which increases the rate of reaction and helps to decrease the use of amount of catalyst in reaction.[19]

In this paper, we report the synthesis of new Polyvinylpyrrolidone (PVP) coated copper-iron oxide (Cu-Fe_3O_4) nanoparticles (NPs) as catalyst for click reactions. Our first attempt was to synthesize of PVP coated copper-iron oxide (Cu-Fe_3O_4) nanoparticles, where this catalyst can be magnetically recovered and reused. Further, PVP is used as stabilizing agent which prevents the agglomeration of nanoparticles. PVP is widely used due to its easy availability, low cost and biodegradable nature. Sarkar *et al.* have reported the synthesis of highly stable PVP coated copper NPs as catalyst for click reactions.[19] We report the development and synthesis of new PVP coated Cu-Fe_3O_4 nanocomposite as catalyst and scrupulously its application in click chemistry.

Synthesis of PVP coated copper-iron oxide nanocomposite

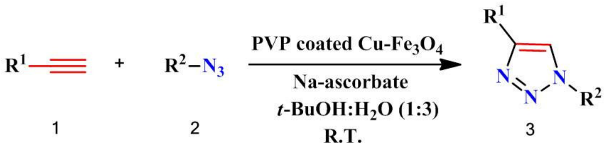
The copper-iron oxide nanoparticles were prepared from ferric nitrate nonahydrate and copper nitrate trihydrate using trioctylamine by reflux method (Scheme 1). Trioctylamine is playing a dual role of reducing as well as hydrolyzing agent.[45] The synthesized Cu-Fe_3O_4 nanoparticles were further coated with PVP as a supporting matrix. These PVP coated Cu-Fe_3O_4 nanocomposite was used as a catalyst for the click reactions.



Scheme 1: Synthesis of PVP coated copper-iron oxide nanocomposite

1,3-dipolar cycloaddition of azides and terminal alkynes catalyzed

In a typical copper catalysed cycloaddition reaction (Scheme 2), 1.0 equivalent of azide was mixed with 1.5 equivalent of alkyne with 0.05 mol % of catalyst and 0.1 equivalent of sodium ascorbate in *t*-butanol-water (1:3) medium. The reaction was carried out in shaker at room temperature. We observed good conversions and yields for a variety of azide-alkyne combinations (Table 1). The resulting products of 1,4-disubstituted 1,2,3-triazoles were purified and characterized by FT-IR, ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and mass spectrometry.



Scheme 2: 1,3-dipolar cycloaddition of azides and terminal alkynes catalyzed by PVP coated Cu-Fe_3O_4 nanocomposite.

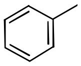
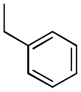
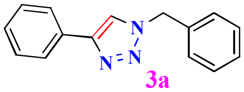
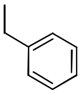
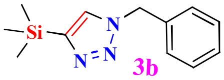
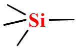
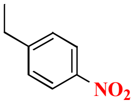
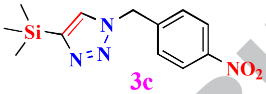
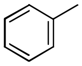
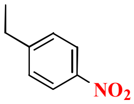
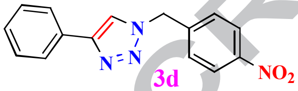
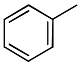
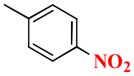
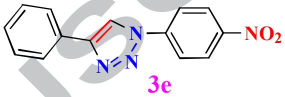
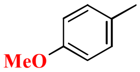
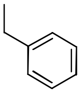
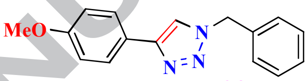
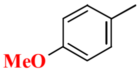
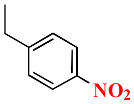
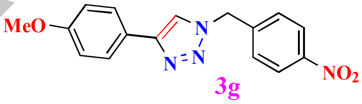
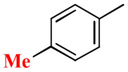
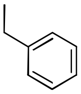
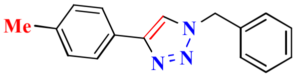
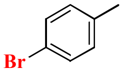
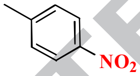
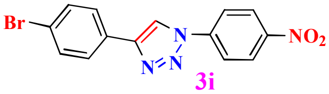
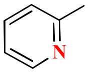
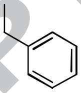
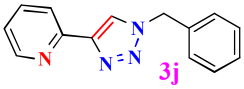
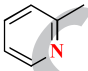
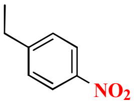
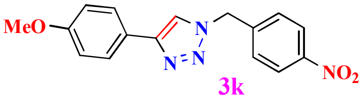
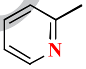
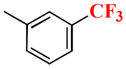
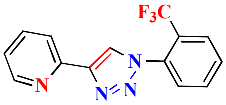
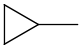
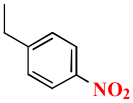
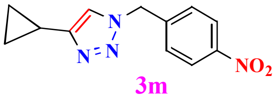
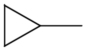
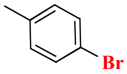
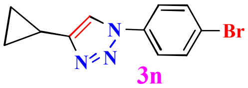
Normally click reactions are reported at elevated temperature, however by using the above nanocomposite, the click reaction proceeded under room temperature. This is particularly useful for the synthesis of energetic and biologically active triazoles where some groups are thermally sensitive. Energetic triazole is a relatively new field and we have synthesized various energetic triazoles like 3j, 3k, 3l by incorporating explosophores like NO_2, CF_3, cyclopropane. Incorporating trimethylsilyl (TMS) and bromide (Br) groups offer scope for further functionalization of triazoles (3b, 3c, 3i & 3n). We have explored the functional group compatibility of this process by incorporating groups such as electron withdrawing, electron donating and heterocycles. Electron donating substituents take comparatively less time to complete the reaction, than electron withdrawing groups (Entry 6 & 8).

In this click reaction, Cu (I) is considered the most active species in the mechanism and forms Cu (I) - acetylide complex with terminal alkynes which further reacts with azide to form 1,2,3- triazoles.[7] As reported by Sarkar[19a] *et al,* in nanoparticle state, copper may be present in zero as well as in +1 state because of its unsatisfied valences. Further, thermodynamic instability of Cu(I), it would have been oxidized to Cu(II) as most stable form.[20] To support our hypothesis, we performed an experiment in absence of sodium ascorbate (Entry 4) and observed that even after the reaction time is increased to two fold, the conversion factor was less when compared to the presence of sodium ascorbate. Hence it may be assumed that sodium ascorbate is acting as reducing agent, which reduces Cu(II) to Cu(I) and thus, enhancing the rate of reaction and yield of the product.

Characterization of Catalyst

The FT-IR spectrum of Cu-Fe_3O_4 (Figure 1(a)) exhibit a broad band at ν_{max}/ cm^{-1} ~580 corresponding to the stretching vibration of the Fe–O bonds is seen which is assigned to spinel form of iron oxide (Fe_3O_4).[46] The peak at 578 cm^{-1} (Figure 1(b)) suggests the formation of the magnetite form of iron oxide. The band at ~2900 cm^{-1} is due to characteristic stretching vibration of C-H band. The band at 1650 cm^{-1} is attributed to C=C bond. The sharp peaks at 1290 and 1440 cm^{-1} of PVP coated Cu-Fe_3O_4 (Figure 1(b)) corresponds to C-N stretching and C-H bending vibrations of PVP respectively, which signifies that Cu-Fe_3O_4 nanoparticles are uniformly embedded in polymer matrix. A broad band at 3400 cm^{-1} is ascribed to the stretching mode of surface H_2O molecules [47].

Table 1: Huisgen 1,3-dipolar cycloaddition of orgnic azides and terminal alkynes carried out in Shaker[a]

Entry	R^1 1	R^2 2	Time [h]	Yield [%] [b]	Compound 3
1			3	55	 3a
2			5	83	 3b
3			3	67	 3c
4			3	84	 3d
5			7	41	 3e
6			3	84	 3f
7			6	100	 3g
8			1	92	 3h
9			7	44	 3i
10			7	85	 3j
11			7	80	 3k
12			8	100	 3l
13			1	73	 3m
14			4	91	 3n

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[a] Reaction conditions: 1.0 equivalent of azide, 1.5 equivalent of alkyne with 0.05 mol % of catalyst and 0.1 equivalent of sodium ascorbate in *t*-butanol-water (1:3) at room temperature.

[b] Yield of isolated and purified products.

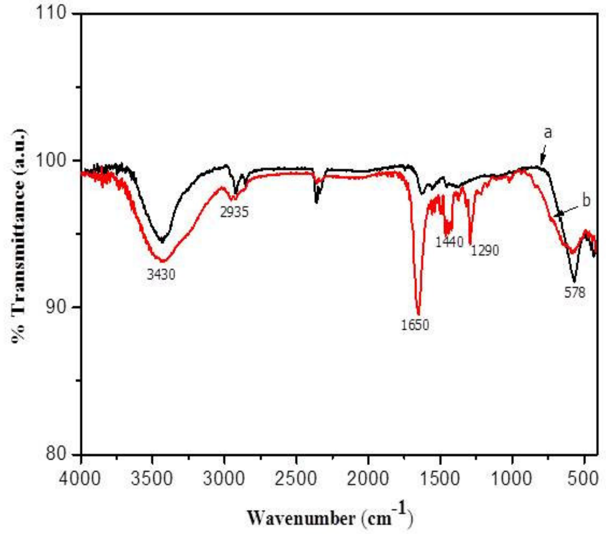


Figure 1: FT-IR spectrum of **(a)** Cu-Fe_3O_4 and **(b)** PVP coated Cu-Fe_3O_4

X-ray diffraction (XRD) measurements of the Cu-Fe_3O_4, PVP coated Cu-Fe_3O_4, pure PVP and used catalyst is depicted in Figure 2. XRD of Cu-Fe_3O_4 nanoparticles exhibit peaks at 2θ values 30.43, 35.78, 43.85, 57.31 and 62.93° correspond to the (220), (311), (400), (511) and (440) planes, respectively in accordance with the magnetite phase as per reported data (JCPDS 89-4319). In addition to this peaks at 43.85, 50.60 and 74.26° are also observed which corresponds to Cu nanoparticles (JCPDS 04-0836). The XRD pattern of pure PVP (Figure 2(c)) shows a broad peak at ~22.37° which confirms the amorphous nature of polymer. [48] Figure 2(b) illustrates the XRD pattern of PVP coated Cu-Fe_3O_4 in which a broad peak corresponding to pure PVP along with peaks assigned for Cu-Fe_3O_4 are also observed. In XRD of used catalyst (Figure 2(d)), the peak corresponding to PVP seems to be crystalline which has masked the other peaks, so it is difficult to locate the exact phase of copper and iron oxide.

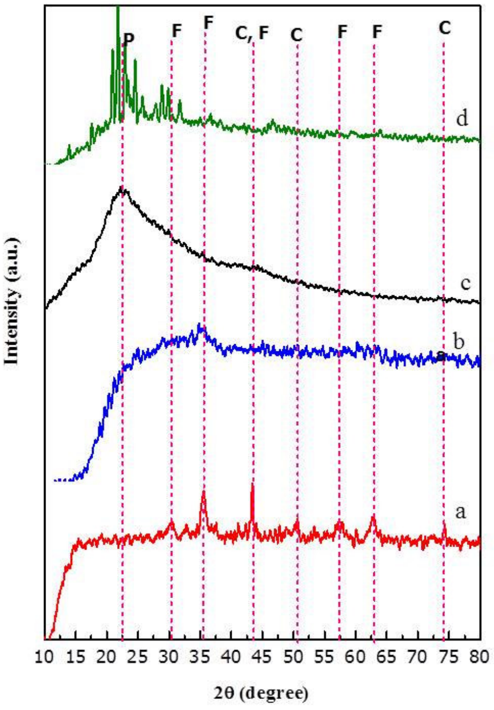


Figure 2. XRD patterns of: **(a)** Cu-Fe_3O_4 **(b)** Catalyst (before reaction) **(c)** Pure PVP and **(d)** Catalyst (after reaction). In this figure, P = polymer (PVP), F = Fe_3O_4, C = copper.

In order to know the exact oxidation state of copper in catalyst, as-synthesized Cu-Fe_3O_4, PVP coated Cu-Fe_3O_4 nanocomposite (catalyst) and used catalyst were characterized by X-ray photoelectron spectroscopic analysis (XPS) (Figure 3). XPS spectra of Cu-Fe_3O_4 (Figure 3 (a)) shows that the catalyst surface is composed of Cu(0) and Cu (II) species. The Cu 2p peaks at 953.7 eV was assigned to Cu(0)[49] and 934.2 eV with shakeup satellite peak at 942.3 eV were assigned to Cu (II)[16, 19b]. The XRD result of Cu-Fe_3O_4 does not show the existence of Cu (II), while XPS indicates the presence of Cu (II) ions on the nanoparticles surface, suggesting that Cu (II) is present only on the surface of the nanoparticles as a thin amorphous outer shell.

Figure 3 (b) shows the XPS spectra of catalyst (binding energies were observed at 934.4, 954.3 and satellite peak at 944.1 eV) and figure 3 (c) shows the XPS spectra of used catalyst (binding energies were observed at 934.9, 954.7 and satellite peak at 943.6 eV). This confirms that even after the reaction, the catalyst (copper) is present in Cu (0) and Cu (II) form and thus remains unaltered.

The field emission scanning electron microscopy (FESEM) images are shown in Figure 4. The SEM image shows that Cu-Fe_3O_4 nanoparticles are well incorporated in polymer matrix (Figure 4 (b)). There is no significant change observed in SEM image of catalyst even after the 3rd cycle (Figure 4 (b)). Energy dispersive X-ray (EDX) studies showed the composition of Cu-Fe_3O_4. It clearly indicates the presence of copper (Cu), iron (Fe) and oxygen (O) metals in the Cu-Fe_3O_4 nanoparticles, presented in Figure 5. No other peak related to any impurity has been detected in the EDX, which confirms that the as-synthesized Cu-Fe_3O_4 nanoparticles are composed only with copper, iron and oxygen.

The particle size of Cu-Fe_3O_4 nanoparticles was obtained by transmission electron microscopy (TEM) which was found to be ~10 nm. TEM image of nanocomposite (Figure 6) elucidates that these nanoparticles are well encrusted in polymer. The specific surface area of Cu-Fe_3O_4 nanoparticles and catalyst measured by BET method was 48.42 m^2/g and 0.88 m^2/g respectively. The turnover number (TON) of PVP coated Cu-Fe_3O_4 catalyst reached upto 8200 and turnover frequency (TOF) upto 2157 h^{-1}. Literature report on synthesized 1,4- disubstituted 1,2,3-triazoles using polymer-bound Cu-catalyst showed TON in the range of 200–375,[50] TON upto 8200 for nanoporous copper catalyst in click reaction[49] and TON 800 and TOF 505 h^{-1}.[51] Hence it can be said that this catalyst is superior as compared to some reported catalysts.

In click reactions, Cu (I) is considered the most active species in the mechanism and forms Cu (I) - acetylide complex with terminal alkynes which further reacts with azide to form 1,2,3-triazoles.[7] As reported by Sarkar *et al*[19a], in nanoparticle state, copper may be present in zero as well as in +1 state because of its unsatisfied valences. Further, thermodynamic instability of Cu(I), it would have been oxidized to Cu(II) as most stable form.[20] To support our hypothesis, we performed an experiment in absence of sodium ascorbate (Entry 4) and observed that even after the reaction time is increased to two fold, the conversion factor was less when compared to the presence of sodium ascorbate. XPS results also support our hypothesis. Figure 3 (c) shows the XPS spectra of used catalyst where Cu 2p peak at 934.9 eV confirms the +2 oxidation state of copper. Hence, it may be assumed that sodium ascorbate is acting as reducing agent, which reduces Cu(II) to Cu(I) *in-situ* and in reversible manner. Thus, enhancing the rate of reaction and yield of the product.

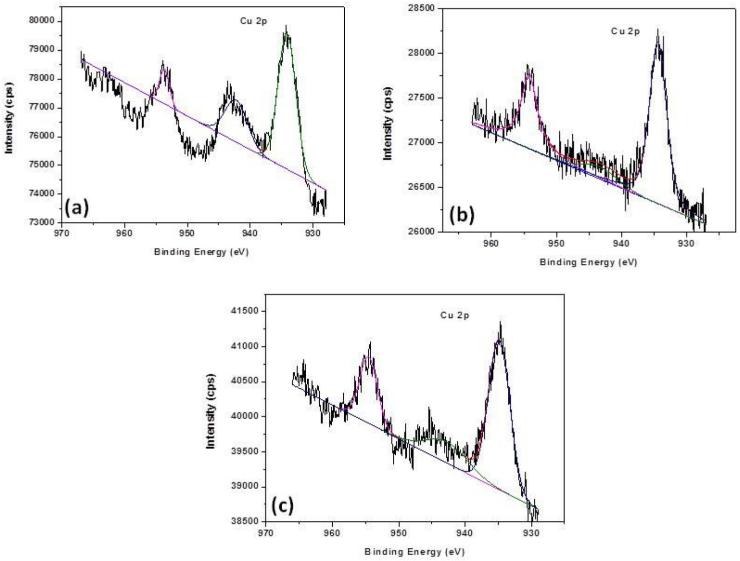


Figure 3. XPS spectra of: **(a)** Cu-Fe_3O_4 **(b)** Catalyst (before reaction) **(c)** Catalyst (after reaction).

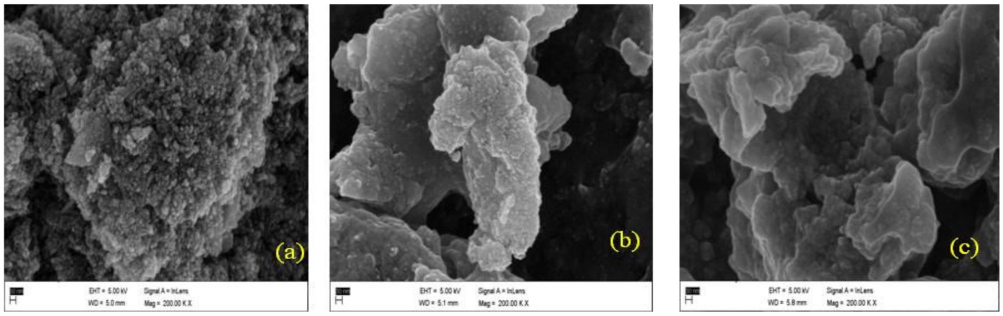
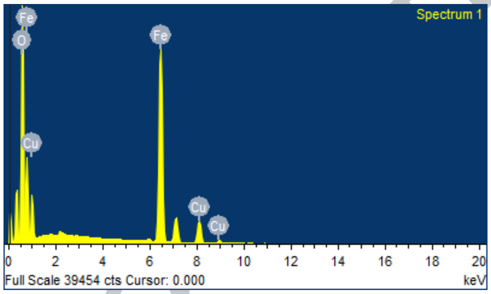


Figure 4: FESEM images of **(a)** Cu-Fe_3O_4 **(b)** PVP coated Cu-Fe_3O_4 (before reaction) **(c)** PVP coated Cu-Fe_3O_4 after 3rd cycle.



Element	Weight%	Atomic%
O K	32.41	63.14
Fe K	54.92	30.65
Cu K	12.67	6.21
Total	100	

Figure 5: EDX of Cu-Fe_3O_4

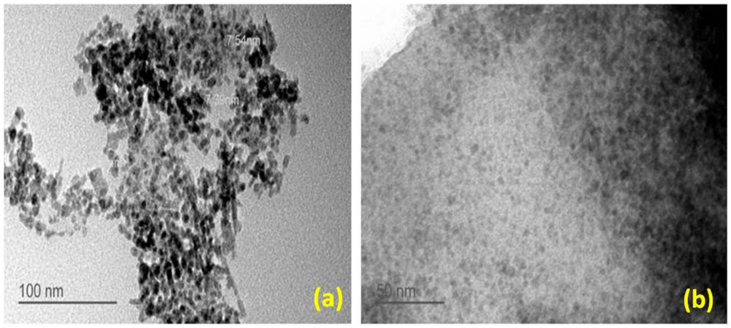
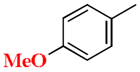
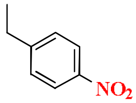
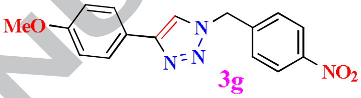
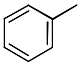
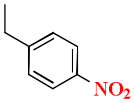
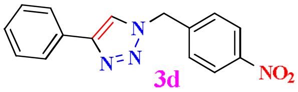


Figure 6: TEM images of **(a)** Cu-Fe_3O_4 and **(b)** PVP coated Cu-Fe_3O_4

Apart from conventional reaction condition, we have also attempted to synthesize the triazoles by ultrasonication method (Table 2). The same reactions (Entry 4 & 7) carried out on shaker were performed in sonicator (frequency 40 KHz). Ultrasonication decreased the reaction time as compared to reactions carried on shaker. This technique furnished good yields of 1,2,3- triazole products at short time.

Table 2: Huisgen 1,3-dipolar cycloaddition of orgnic azides and terminal alkynes carried out in ultrasonicator bath[a]

Entry	R^1 1	R^2 2	Time [min]	Yield [%] [b]	Compound 3
15			45	70	 3g
16			30	77	 3d

[a] Reaction conditions: 1.0 equivalent of azide, 1.5 equivalent of alkyne with 0.05 mol % of catalyst and 0.1 equivalent of sodium ascorbate in *t*-butanol-water (1:3) at room temperature.
[b] Yield of isolated and purified products.

Reusability study of the Catalyst

To ensure the reusability of the catalyst, we performed a set of experiments using PVP coated Cu-Fe_3O_4 nanocomposite for the click reaction between 4-ethynyltoluene and benzyl azide. After the completion of the first reaction, the catalyst was separated by applying external magnet. Then the catalyst was washed with methanol and dried in oven which showed magnetic property. Further a fresh reaction was performed using this catalyst under the same reaction condition. Likewise, the catalyst was recovered and reused for at least 3 times without losing its activity. The yield of the catalyst recovered was found to be decreased which may be due to loss of polymer because of its solubility in reaction mixture. But it is noteworthy that no significant change was observed in the catalytic activity of the catalyst. Results are summarized in Table 3.

Table 3: Reusability study of the PVP coated Cu-Fe_3O_4 nanocomposite as catalyst for Huisgen 1,3-dipolar cycloaddition reactions between benzyl azide and 4-ethynyltoluene.[a]

% Yield[b]		
1st run	2nd run	3rd run
81	69	52

[a] Reaction conditions: 1.0 equivalent of benzyl azide, 1.5 equivalent of 4-ethynyltoluene with 0.05 mol % of catalyst and 0.1 equivalent of sodium ascorbate in *t*-butanol-water (1:3) at room temperature.
[b] Yield of isolated catalyst.

Conclusions & Perspective

In conclusion, we have developed a simple and convenient route for the preparation of copper-iron oxide nanoparticles. We have successfully synthesized a new and effective PVP coated Cu-Fe_3O_4 nanocomposite which can expeditiously act as catalyst for 1,3-dipolar cycloadditions of azides and terminal alkynes. This catalyst can be separated magnetically and can be reused for at least 3 times. We have also explored another route for synthesis of 1,2,3-triazoles by ultrasonication method which was found to be very useful as a quick alternative to conventional reaction.

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