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Author: Mohsen Esmaeilpour Jaber Javidi Fatemeh Nowroozi Dodeji Mehdi Mokhtari Abarghoui

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Facile synthesis of 1- and 5-substituted 1H-tetrazoles catalyzed by recyclable ligand complex of copper (II) supported on superparamagnetic Fe₃O₄@SiO₂ nanoparticles

Mohsen Esmaeilpour⁽¹⁾, Jaber Javidi⁽²⁾* Fatemeh Nowroozi Dodeji⁽²⁾, Mehdi Mokhtari Abarghoui⁽³⁾

 Chemistry Department, College of Science, Shiraz University, Shiraz, Iran
 Department of Pharmaceutics, School of Pharmacy, Shahid Beheshti University of Medical Sciences, Tehran, Iran

(3) Department of Chemistry, Isfahan University of Technology, Isfahan, Iran

*Corresponding author. Tel.: +98 7116137738, fax: +98 7112286008. E-mail address: Jaber Javidi@sbmu.ac.ir

Abstract

We report a new method for preparing functionalized superparamagnetic Fe_3O_4 @SiO₂ possessing high saturation magnetization. Magnetite particles were prepared by simple coprecipitation method in aqueous medium, and then Fe_3O_4 @SiO₂ nanosphere was synthesized by using nano Fe_3O_4 as the core, TEOS as the silica source and polyethylene glycol (PEG 1000) as the surfactant. Then, the silica-coated Fe_3O_4 nanoparticles were covered with ligand complex of Cu (II). The functionalized magnetic core–shell nanoparticles (MNPs) were investigated by fourier transform infrared spectroscopy, transmission electron microscopy, scanning electron microscopy, X-ray diffraction, thermogravimetric analysis, dynamic light scattering and N₂ adsorption/desorption. Also, its Cu content was determined by Inductively Coupled Plasma (ICP) analyzer. Then, the immobilized copper complex was used as an efficient catalyst for synthesis of 1- and 5-substituted 1H-tetrazoles from nitriles and amines in good to excellent yields. The results show that the supported catalyst could be conveniently recovered through the use of an external magnetic field and reused for subsequent reactions for at least 6 times with less deterioration in catalytic activity.

Keywords

1- and 5-substituted 1H-tetrazoles, Core-shell, Supported catalyst, Magnetic separation.

1. Introduction

The chemistry of heterocycles has acquired immense importance recently [1]. Tetrazoles which represent a significant class of heterocycles have attracted considerable interest in recent years because of their wide utility [2,3]. Among them,

1-substituted-1 H-tetrazoles and 5-substituted-1H-tetrazoles have received much attention and have been found in variety of synthetic and medicinal chemistry applications as well as in material science including propellants and explosives [4-6]. Particularly, this functional group show strong activities as antihypertensive drugs [7], sedatives [7], antiallergic [7], anti-imflammatory [8], antifungal [9], antibacterial [10], antimicrobial [11], hormonal [12], carboxylic acid isosteres [13], photography [14], herbicides [15] and diuretics activity [16]. Furthermore, tetrazoles have already been successfully used in various material sciences and synthetic organic chemistry as analytical reagents [17] and synthons [18].

Tetrazole rings can be prepared in several ways. The routes to 1-substituted tetrazoles include acid-catalyzed cycloaddition between isocyanides and trimethyl azide [19], acetic acid or trifluoroacetic acid catalyzed cyclization between primary amines, or their salts, with an orthocarboxylic acid ester and sodium azide [20], acid-catalyzed cycloaddition between hydrazoic acid and isocyanides [21], and cyclizations from an amine, triethyl orthoformate, and sodium azide using SSA [22], In(OTf)₃ [23], [HBIm]BF₄ [6], Yb(OTf)₃ [24], PCl₅ [25], and recently natrolite zeolite as a catalyst [26].

The most convenient rout for the preparation of 5-substituted 1H-tetrazoles is via [3+2] cycloaddition of azide to the corresponding nitriles. In earlier synthetic methods, the homogeneous catalysts were used, such as a stoichiometric amount of inorganic salts or metal complex as a catalyst, trimethylsilyl azide (TMSN₃) and tetrabutylammonium fluoride (TBAF) instead of metal salts under the solvent-free condition, or in micellar media and ionic liquid [27–29].

Also, different homogenous and heterogeneous catalysts such as $FeCl_3$ -SiO₂ [30], nano CuFe₂O₄ [31], ZrOCl₂ [32], nano ZnO/Co₃O₄ [33], γ -Fe₂O₃ [34], CdCl₂ [35], ZnO [36], Fe(OAc)₂ [28], Zn/Al hydrotalcite [37], Pd(OAc)₂/ZnBr [38], natural zeolite [39], and Zeolite and sulfated zirconia [40] have been reported for the promotion of reaction between nitrile and NaN₃ or TMS-N₃.

However, each one of these methods has more than one of these drawbacks: harsh reaction conditions, long reactions times, use of toxic and corrosive reagents, difficulty in separation and recovery of the catalyst, low yields, tedious work-ups, expensive moisture sensitive reaction conditions, and the presence of hydrazoic acid, which can be highly toxic and explosive along with volatile. Thus, the development of simple, convenient, and environmentally benign methods for the synthesis of tetrazoles remains required.

Magnetic nanoparticles have been the focus of much research recently because they possess attractive properties that could potential used in catalysis, drug delivery, magnetic resonance imaging contrast enhancement, data storage, targeted drug, magnetic bioseparation, gene manipulation and immunoassay, enzyme immobilization and environmental remediation because of its excellent properties of

superparamagnetism, low toxicity, high magnetic susceptibility, biocompatibility, and high saturation magnetization [41-48]. However, pure magnetic particles are likely to form a large aggregation and alter magnetic properties. Therefore, an appropriate coating is important to avoid such limitations from occurring [49].

Recently, magnetic core–shell materials, which combine features of cores and various functional shells for different applications, have gained much attention and undergone intensive investigation for their unique magnetic responsively, low cytotoxicity [50,51], good stability [52], potential applications in medicinal [53,54], chemically modifiable surface [55,56], optical [57], environmental [58], biological [59] and chemical areas [60,61]. On the other hand to the issue observed in recovering and reusing most solid catalysts, core–shell nanostructure magnetic catalysts could be easily retrieved under the influence of a magnetic field and used in subsequent reactions. As a result of this property, using magnetic core–shell structure composites as catalysts has been recommended in literature [62,63]. Moreover, silica coating endows the magnetic nanoparticles with easily modifiable surface, which may be used to graft various desirable functional groups.

Nowadays, the functionalization of magnetic core–shell structure has attracted particular interest, mainly due to potential applications of those materials in catalysis, drug delivery, and adsorption [64-68].

Therefore, in this work, we report the preparation of $Fe_3O_4@SiO_2/ligand/Cu$ (II) as illustrated in Scheme 1 and its use as a magnetic nanocatalyst for facile construction of 5-substituted-1H-tetrazoles, and 1-substituted-1H-tetrazole ring systems in high yields.



Scheme1: Preparation process of Cu(II) complex functionalized Fe₃O₄@SiO₂ nanoparticle. **2. Experimental**

2.1. General procedure

Solvents were purified by conventional methods. All reagents were purchased from Aldrich. The ¹H and ¹³C NMR spectra were recorded on a Bruker Avance DPX 250 MHz spectrometer (using CDCl₃ or DMSO- d_6 with TMS as the standard). Fourier transform infrared (FT-IR) spectra were recorded on Shimadzu FT-IR 8300 spectrometer using pressed KBr pellets. X-ray powder diffraction (XRD) analysis was conducted on a Bruker AXS D8-advance X-ray diffractometer using Cu Ka radiation $(\lambda = 1.5418)$. Transmission electron microscopy (Philips EM208) with an accelerating voltage of 100 kV was used to examine morphology and size of the nanoparticles and field emission scanning electron microscopy (FE-SEM) images were obtained on HITACHI S-4160. Magnetic characterization was carried out on a vibrating sample magnetometer (BHV-55) at room temperature and dynamic light scattering (DLS) were recorded on a HORIBA-LB550. BET surface area and porosity of catalysts were determined from nitrogen physisorption measured on a Micromeritics ASAP 2000 instrument at 196°C. The amount of Cu nanoparticles supported on Fe₃O₄@SiO₂/ ligand was measured by ICP analyzer (Varian, Vista-pro) and atomic absorption spectroscopy. All products were identified by comparison of their spectral data and physical properties with those of the authentic sample and all yields refer to isolated products. The progress of the reaction was monitored by TLC and purification was achieved by silica gel column chromatography.

2.1.1. Preparation of Fe_3O_4 nanoparticles

Fe₃O₄ nanoparticles were prepared by chemical co-precipitation of Fe³⁺ and Fe²⁺ ions with a molar ratio of 2:1. Typically, a solution was prepared from FeCl₂.4H₂O (3.7 mmol, 736 mg) and FeCl₃.6H₂O (7.4 mmol, 2 g) in deionized H₂O (30 mL) under an Ar atmosphere and 400 mg of polyethylene glycol (PEG 1000) were added. The resultant solution was left to be stirred for 30 min in 80°C. Then 25% aqueous NH₃ was added drop wise with vigorous stirring to produce a black solid product when the reaction media reaches pH 10. The dropping rate was controlled with a constant dropper at 1 mL/min.

The resultant mixture was heated on water bath for 2 h at 60 $^{\circ}$ C and the black magnetite solid product was washed with deionized H₂O, filtered, dried and calcined at 600 $^{\circ}$ C for 6 h.

2.1.2. Preparation of Fe₃O₄@SiO₂ core-shell

The core–shell $Fe_3O_4@SiO_2$ nano spheres were prepared via hydrolysis of tetraethylorthosilicate (TEOS) in basic solution via Stober method [69] with minor modification. 40 mL of ethanol (98%), 10 mL of deionized water, and 1.5 mL

ammonia (25 wt %) were mechanically stirred for 10 min before addition of TEOS. Then, 0.10 g of freshly prepared iron oxide was added. After 30 min mixing, 2 ml of TEOS was added and the mechanical stirring was continued for 8 h. The obtained particles were sequentially washed with water and ethanol, and dried at 60°C for 6 h.

2.1.3. General procedure for the preparation of functionalized $Fe_3O_4@SiO_2$ nanoparticle with3-(triethoxysilyl)-propylamine($Fe_3O_4@SiO_2$ -NH₂)

 $Fe_3O_4@SiO_2 (0.5 g)$ was added to the solution of 3-(triethoxysilyl)-propylamine (1 mmol, 0.176 g) in ethanol (5 mL) and the resultant mixture was under reflux for 12 h under nitrogen atmosphere. After refluxing, the mixture was cooled to room temperature, filtered by an external magnet and the product was washed with ethanol and water to remove unreacted species and dried at 80°C for 6 h.

2.1.4. General procedure for the preparation of the ligand functionalized magnetite@silica nanoparticles ($Fe_3O_4@SiO_2/$ ligand)

The modification of $Fe_3O_4@SiO_2-NH_2$ with isatin was carried out via ligand formation between the amino group and the active carbonyl group of isatin as presented in Scheme 1. A suspension of isatin (1mmol, 0.147g) and $Fe_3O_4@SiO_2-NH_2$ (0.5 g) in ethanol (10 ml) was refluxed with continuous stirring under inert atmosphere for 16 h. Then the product was isolated by filtration and thoroughly washed several times with ethanol and distilled water, and then finally dried in a vacuum oven at 70°C

2.1.5. General procedure for Cu (II) complex functionalized magnetite@silica nanoparticles ($Fe_3O_4@SiO_2$ /ligand/Cu (II))

 $Fe_3O_4@SiO_2/$ ligand (0.5 g) was added to the solution of Cu (OAc)₂ (1 mmol,0.182 g) in ethanol (10 mL) and the resultant mixture was under reflux for 6 h. The catalyst was separated from the crude product using an external magnet and washed with ethanol and water. Then, it was dried in vacuum at 70°C for 6 h and kept under desiccator.

2.2. Typical procedure for the synthesis of 1-substituted-1H-tetrazoles

A mixture of amine (1 mmol), sodium azide (1 mmol), triethyl ortho-formate (1.2 mmol) and catalyst (0.01g, 0.4 mol% of Cu(II)) was taken in a round-bottomed flask and stirred at 100°C. The progress of the reaction was followed by thin-layer chromatography (TLC). After completion of the reaction, the reaction mixture was cooled to room temperature and diluted with ethyl acetate (2×20 mL). The catalyst was removed by using magnetic field and then the resulting solution was washed with

water, dried over anhydrous Na_2SO_4 and was evaporated. The residue was concentrated and recrystallized from EtOAc-hexane (1:10).

2.3. Typical procedure for the synthesis of 5-Substituted 1H-Tetrazoles

A mixture of nitrile (1 mmol), sodium azide (1.5 mmol), Cu complex catalyst (0.4 mol %) and DMF (3 mL) was taken in a round-bottomed flask and stirred at 110° C temperature. After completion of the reaction the catalyst was separated from the reaction mixture with an external magnet and reaction mixture was treated with ethyl acetate (2×20 mL) and 1 N HCl (20 mL). The resultant organic layer was separated and the aqueous layer was again extracted with ethyl acetate (2×15 mL). The combined organic layers were washed with water, concentrated, and the crude material was chromatographed on silica gel (Hexane-EtoAc, 1:1) to afford the pure product.

3. Results and discussion

Fig. 1 shows the FTIR spectra of Fe₃O₄ nanoparticles (MNPs), Fe₃O₄@SiO₂, Fe₃O₄@SiO₂-NH₂, Fe₃O₄@SiO₂/ligand and Fe₃O₄@SiO₂/Ligand/Cu (II) particles. The bands centered around 3400 cm⁻¹ and 1620 cm⁻¹ are, respectively, assigned to the O-H stretching and deforming vibrations of adsorbed water. The IR spectrum of pure Fe₃O₄ (Fig. 1(a)) shows the peak at 578 cm^{-1} corresponding to the Fe-O vibration. The adsorption peaks at 1080 and 805 cm^{-1} corresponds to the antisymmetric and symmetric stretching vibration of Si-O-Si bond in oxygen-silica tetrahedron, respectively (Fig1b). Evidently, it indicates that the silica has been successfully coated on the surface of superparamagnetic Fe₃O₄ NPs (Fig1b). Figure 1c shows the FT-IR spectrum of Fe₃O₄@SiO₂-NH₂ nanoparticles; the peaks at 581, 1000-1150, 1400-1410 and 1543 cm⁻¹ are attributed to Fe–O (stretching vibration), Si–O–Si (asymmetric stretching), C–N (stretching vibration) and N–H (bending), respectively. Also, the presence of several bands with medium intensity in 2810–2986 cm⁻¹ and 3050–3250 regions are allocated to C–H stretching of the propyl group and N–H stretching (Fig. 1c). In the FT-IR spectrum of the Fe₃O₄@SiO₂/ligand, a new band is observed at 1651 cm⁻¹ due to the C=N stretch of the newly formed azomethine group and another new band appears around 1497 cm⁻¹ because of the aromatic C=C stretch. These bands prove that isatin has been successfully grafted onto the $Fe_3O_4(a)SiO_2-NH_2$ nanoparticles (Fig. 1d). The C=O stretch of the amide group occurs at 1712 cm⁻¹ and O-H stretching band is found at 3400 cm⁻¹ (Fig. 1d). The free ligand exhibits a v(C=N)stretch at 1651 cm⁻¹ while in the complex, this band shifts to lower frequency and appears at 1628 cm^{-1} due to the coordination of the nitrogen with the metal (Fig1e). From the IR spectra presented in Fig. 1e, the absorption peaks at 580cm⁻¹ belonged to the stretching vibration mode of Fe-O bonds in Fe₃O₄, the absorption peak presented at 1000-1150cm⁻¹ due to stretching vibration of framework and terminal Si–O-Si groups. The presence of vibration bands in 3400 (O-H stretching), 2870-3080 (CH stretching), 1697 (C=O amide), 1628 (C=N), 1480-1600 (C=C aromatic ring



stretching) and 1478 (CH₂ bending) demonstrates the existence of ligand complex of Cu (II) on Fe₃O₄@SiO₂ nanoparticles in the spectrum (Fig.1e).

Fig.1: FT-IR spectra a) Fe_3O_4 , b) Fe_3O_4 ($@SiO_2 c$) Fe_3O_4 ($@SiO_2$ -NH₂, d) Fe_3O_4 ($@SiO_2$ /ligand, e) Fe_3O_4 ($@SiO_2$ /ligand/Cu(II).

Fig. 2 shows the XRD patterns of Fe₃O₄, Fe₃O₄@SiO₂ and Fe₃O₄@SiO₂/ligand/Cu (II). As presented in Fig. 2, six characteristic diffraction peaks ($2\Theta = 30.1^{\circ}$, 35.4° , 43.1° , 53.4° , 57° and 62.6° correspond to (220), (311), (400), (422), (511) and (440) reflections of inverse spinel Fe₃O₄ NPs, respectively. it can be seen that the Fe₃O₄ obtained has highly crystalline cubic spinel structure which agrees with the standard Fe₃O₄ (cubic phase) XRD spectrum (PDF#88-0866). The characteristic diffraction peaks of Fe₃O₄@SiO₂ are at about 30.2, 35.5, 43.3 and 62.8, just like those of pure Fe₃O₄ (JCPDS:00-003-0862),indicating that the embedded Fe₃O₄ cores retain their magnetite crystalline structures after the silica coating, while the silica exists in an

amorphous state (Fig.2b). The same set of characteristic peaks were also observed for Fe₃O₄@SiO₂ and Fe₃O₄@SiO₂/ligand/Cu (II), indicating the stability of the crystalline phase of Fe₃O₄ nanoparticles during silica coating and surface functionalization (Fig2, Table1). From Fig. 2b, we can see the XRD pattern of Fe₃O₄@SiO₂ showing an obvious diffusion peak at $2\Theta = 15-25^{\circ}$, generally considered as the diffusion peak of amorphous silica. For Fe₃O₄@SiO₂/ligand/Cu (II) nanoparticles, the broad peak was transferred to lower angles due to the synergetic effect of amorphous silica. The broadening of each peak in XRD mean crystallite size was calculated by applying Scherrer's equation: D=K λ/β cos Θ , where K is a constant (K = 0.9 for Cu-K α), D is the average diameter in A°, β is the broadening of the diffraction line measured at half of its maximum intensity in radians, λ is the wavelength of the X-rays and Θ is the Bragg diffraction angle. The particle sizes of the magnetite calculated using the Scherrer equation were 14.1, 26.8.0, and 38.8 nm for Fe₃O₄@SiO₂, and Fe₃O₄@SiO₂/ligand/Cu (II), respectively (Table 1).



Fig. 2: XRD patterns of a) Fe₃O₄, b) Fe₃O₄@SiO₂ and c) Fe₃O₄@SiO₂/ligand/Cu (II).

Fig. 3 displays the TEM (a–c) and SEM (d–f) images of Fe_3O_4 , Fe_3O_4 @SiO₂ and Fe_3O_4 @SiO₂/ligand/Cu (II). As shown in Fig. 3a,d, The TEM and SEM images shows that Fe_3O_4 particles were spherical with a mean diameter of 15nm (Table1), were of uniform size, and showed good dispersity. Actually, in depths consider the TEM image indicated that large particles consisted of agglomeration of small particles. Subsequently, it shows spherical morphology after being coated with dense silica shell and mesoporous silica shell as shown as the FE-SEM images (Fig3e). According to the result calculated by Scherrer equation, it was found that the diameter of

Fe₃O₄@SiO₂ nanoparticles obtained was about 25 nm (Table1) due to the agglomeration of Fe₃O₄ inside nanospheres and surface growth of silica on the shell. The mesoporous silica shell on the surface of Fe₃O₄ is quite homogeneous and exhibits good monodispersity with an estimated thickness of 10 nm (Fig3b). As shown in Fig. 3c, a basically core–shell structure (dark colored core for Fe₃O₄@SiO₂ nanoparticles and light-colored shell for ligand) was obtained. The samples still remained monodisperse, and total average increase in diameter was approximately 40 nm (Table1). The morphology of Fe₃O₄@SiO₂/ligand/Cu (II) nanoparticles was also observed by FE-SEM (Fig. 3f). The nanoparticles are approximately spherical shapes with a smooth surface morphology. The diameter of the nanoparticles is found to be approximately 50 nm. The FE-SEM images indicate the successful coating of the magnetic Fe₃O₄ particles.

The hydrodynamic diameter of Fe₃O₄, Fe₃O₄@SiO₂ and Fe₃O₄@SiO₂/ligand/Cu (II) nanoparticles is determined by the DLS technique (Fig. 3). This size distribution is centered at a value of 14, 26 and 40 nm for Fe₃O₄, Fe₃O₄@SiO₂ and Fe₃O₄@SiO₂/ligand/Cu (II), respectively (Fig. 3 g-i). The theoretical curve of standard distribution from our studies was calculated by means of Microsoft Excel.



Fig. 3: TEM images of Fe₃O₄ (a), Fe₃O₄@SiO₂ (b), Fe₃O₄@SiO₂/Ligand/Cu (II) (c) and FE-SEM and DLS images Fe₃O₄ (d, g), Fe₃O₄@SiO₂ (e, h) and Fe₃O₄@SiO₂/Ligand/Cu (II) (f, i), respectively.

 N_2 adsorption–desorption isotherms were conducted to investigate the porous structure and surface area of the bare Fe₃O₄ NPs, Fe₃O₄@SiO₂ and the Fe₃O₄@SiO₂/Ligand/Pd (II). The measured BET surface areas are 438.0, 430.3, and 353.6 m²/g for Fe₃O₄, Fe₃O₄@SiO₂, and Fe₃O₄@SiO₂/ligand/Cu (II) nanoparticles, respectively (Table 1).

Table.1: Selected properties of Fe₃O₄, Fe₃O₄@SiO₂, and Fe₃O₄@SiO₂/ligand/Cu (II) nanoparticles.

Sample	crystal structure	BET surface area $(m^2/g)^a$	Magnetite particle size (nm)	
			XRD ^b	TEM ^c
Fe ₃ O ₄	Cubic spinel	438.0	14.1	15
Fe ₃ O ₄ @SiO ₂	Cubic spinel	430.3	26.8	25
Fe ₃ O ₄ @SiO ₂ /ligand/Cu(II)	Cubic spinel	353.6	38.8	40

^aDetermined by N₂ adsorption using the Brunauer–Emmett–Teller method.

^bCalculated by the Scherrer equation based on powder X-ray diffraction patterns.

^cAverage particle size observed from the transmission electron microscopy images.

For investigation on the amount of the catalyst loading and stability of the materials, thermogravimetric analysis was used. Fig.4a shows the typical TGA curve of Fe₃O₄@SiO₂/ligand/Cu (II). The weight loss of 4.1% below 150°C for the sample is apparently owing to loss of adsorbed water or the water that formed from the condensation of hydroxyl groups. The weight loss between 150 and 780°C in Fig.4a was assigned to the decomposition of covalently bonded ligand (about 24.1%). Thus, the TGA curve confirmed the successful functionalization of magnetic nanoparticles Fe₃O₄@SiO₂ with complex ligand of Cu (II).

The magnetic properties of Fe_3O_4 (a) and the $Fe_3O_4@SiO_2/ligand/Cu$ (II) (b) were examined by vibrating sampling magnetometry (VSM) at room temperature (Fig. 4b). The saturation magnetization of Fe_3O_4 (a) and the $Fe_3O_4@SiO_2/ligand/Cu$ (II) were around 66.1 and 30.7 emu/g, respectively. Obviously, the saturation magnetization of Fe_3O_4 NPs gradually decreased with the increase of SiO_2 and ligand complex (Fig.4b). This figure shows almost zero coercivity, which proves the superparamagnetic properties of the synthesized magnetic nanoparticles. Superparamagnetic particles do not have permanent magnetic moments in the absence of an external field but can respond to an external magnetic field.



Fig.4: (a) Thermogravimetric analysis of $Fe_3O_4@SiO_2/ligand/Cu$ (II) nanoparticles. (b) Magnetization curves at 300 K for c) Fe_3O_4 and d) $Fe_3O_4@SiO_2/ligand/Cu$ (II) nanoparticles.

In summary therefore, the $Fe_3O_4@SiO_2/ligand/Cu$ (II) NPs were highly susceptible to an external magnetic field. This idea is also supported by Fig.5. In Fig.5a, the particles were well dispersed in DMF under normal conditions. These high saturation magnetization values suggest that the NPs can be effective carriers movable under a low/moderate strength magnetic field.



Fig.5: Photographs of the separation and redispersion processes of $Fe_3O_4@SiO_2/ligand/Cu(II)$: without external magnetic field (a), and with external magnetic field (b).

Determination of the Pd content was carried out by inductively coupled plasma (ICP) analysis on the digested catalyst in refluxing aq. HCl (37%). The obtained results revealed that 0.38 mmol per 1 g of Cu is immobilized on Fe₃O₄@SiO₂/ligand. In order to evaluate the optimum amount of catalyst required for synthesis of 1-substituted 1H-tetrazoles, the reaction was carried out in the presence varying amount of the catalysts and the results are presented in Table 2. The best result was achieved by carrying out the reaction with (0.4mol%, 1mmol, 1mmol, 1.2 mmol) ratio of

 $Fe_3O_4@SiO_2/ligand/Cu$ (II) catalyst, aniline, sodium azide and triethyl orthoformate under solvent-free conditions at 100°C (Table2, entry5). The results show clearly that catalyst is effective for this transformation and in the absence of it; the reaction did not take place even after higher reaction time (Table2, entry1). Use of a higher amount of catalyst did not improve the yield (Table2, entry6) while a decrease in the amount of catalyst decreases the yield (Table2, entries 2-4).

The effect of temperature was studied by carrying out the model reaction at different temperatures under solvent-free condition (room temperature, 60°C, 100°C and 110°C) and the best results were obtained at 100°C (Table2, entries5, 7-9). Then, the reactions were conducted in refluxing MeOH, EtOH, CH₃CN, DMSO and DMF as solvents and under solvent-less conditions (Table2, entries5,10-14). When the reaction was performed in solvent-free, the progress of the reaction was higher in comparison with solvent conditions. Therefore, the solvent-free condition was used for the synthesis of 1-substituted 1H-tetrazoles.

Table.2: Optimization of different proportions of Fe ₃ O ₄ @SiO ₂ /ligand	/Cu (II) :	nanocatalyst
and also effect of solvents and temperature on formation of 1-substitut	ed 1H-te	etrazoles. ^a
		N

6	$NH_2 + HC(OEt)_2 + NaN_2 = Fe_3O$	4@SiO2/Schiff base/Ci	u(II) //	N
		Solvent, Temperature		
Entry	Solvent/catalyst amount (mol%)	Temp. (°C)	Time (h)	Yield ^b (%)
1	Solvent-free/None	120	10	8
2	Solvent-free/0.1	100	2	32
3	Solvent-free/0.2	100	2	66
4	Solvent-free/0.3	100	1	90
5	Solvent-free/0.4	100	0.75	93
6	Solvent-free/0.5	100	1	92
7	Solvent-free/0.4	r.t	4	17
8	Solvent-free/0.4	60	2	61
9	Solvent-free/0.4	110	1	92
10	MeOH/0.4	Reflux	2	65
11	EtOH/0.4	Reflux	2	58
12	CH ₃ CN/0.4	Reflux	2	54
13	DMSO/0.4	Reflux	2	73
14	DMF/04	Reflux	2	81

^a Conditions: aniline (1 mmol), triethyl orthoformate (1.2 mmol), and sodium azide (1 mmol).

^b Yields refer to isolated pure product.

A variety of amines such as substituted anilines, heteroaromatic amines, and an aliphatic amine were employed to investigate the scope and generality of this process. The results are recorded in Table3. Amines carrying different functional groups were subjected to the coupling reactions and in all cases the desired product was obtained in high yields. It was observed that under similar conditions, a wide range of anilines containing electron withdrawing as well as electron donating groups such as bromo, chloro, nitro, acetyl, methoxy, and methyl and an aliphatic butan-1-amine easily underwent condensation with triethyl orthoformate and sodium azide to give 1-substituted- 1H-1,2,3,4-tetrazoles in short reaction times with excellent isolated yields. (Table 3).

lable	.3: Preparation of 1-substitute	a TH-tetrazoles in the presence of	Fe ₃ O ₄ ($v_{\rm S1O_2/11}$	gand/Cu(II)."
Entry	Substrate	Product	Time (h)	Yield ^b (%)	Mp. (∘C) (Lit.) ^{c Ref} .
1	NH ₂		0.75	93	62-63 (63-64) ³
2	Br NH ₂	Br N N	1	91	170-171 (170) ⁷⁰
3	Cl—NH ₂		1.5	88	153-154 (153) ⁷⁰
4	O ₂ N-NH ₂	O_2N	2.5	83	201-2002 (200) ⁷⁰
5	H ₃ COC NH ₂	H ₃ COC	1.5	90	177 (175-177) ³
6	Me NH ₂		1	97	92 (92) ⁷¹
7	MeO NH ₂		1	97	114-115 (115) ³
8	N NH2		2	86	78-79 (77) ³
9	Me NH ₂		2	87	166 (166) ⁷⁰
10	CH ₂ NH ₂		2	89	130-132 (130) ⁷⁰
11	NH ₂		3	83	143 (142-144) ³

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^aConditions: amines (1 mmol), triethyl orthoformate (1.2 mmol), and sodium azide (1 mmol). ^bYields refer to isolated pure product. ^cMelting points reported in the parenthesis refer to the literature melting points.

Hence, we investigated the effects of different reaction parameters on the catalytic activity in order to optimize the protocol for formation of 5-substituted 1H-tetrazoles.

In the first, we chose the reaction benzonitrile (1mmol) with NaN₃ (1mmol) as model reaction; the results were summarized in Table 4. It was noted that in the absence of Fe₃O₄@SiO₂/ligand/Cu (II) nanocatalyst, there was no detectable amount of the desired product formed (Table4, entry 1). The results show clearly that catalyst is effective for this transformation. Various catalyst concentrations was also tested and use of a higher amount of catalyst did not improve the yield (Table4, entry6) while 0.4 mol% gave the best result (Table4, entry5). When the reaction temperature was increased to 110°C the yield was also increased while lowering the temperature to 80°C and room temperature led to decrease in reaction yields (Table4, entries 5,7,8). Then, the reactions were conducted in present variation solvent such as MeOH, EtOH, CH₃CN, DMSO, NMP, THF, water, toluene and DMF. A good yield of 92% was given in DMF in 4 h (Table4, entry5). We selected DMF as the solvent in the presence of 0.4 mol% of the catalysts at 110°C as the best conditions for this reaction.

	CN + NaN ₃ Fe ₃	O4@SiO2/Schiff base/Cu(II) Solvent, Temperature	- \	
Entry	Solvent/catalyst amount (mol%) Temp. (°C)	Time (h)	H Yield ^b (%)
1	DMF/None	120	12	Trace
2	DMF/0.1	110	6	17
3	DMF/0.2	110	6	67
4	DMF/0.3	110	6	88
5	DMF/0.4	110	4	92
6	DMF/0.5	110	4	91
7	DMF/0.4	r.t	12	Trace
8	DMF/0.4	80	8	53
9	DMF/0.4	120	4	92
10	Toluene/0.4	Reflux	6	38
11	Water/04	Reflux	12	Trace
12	THF/04	Reflux	12	Trace
13	NMP/04	Reflux	8	64
14	DMSO/04	Reflux	8	80
15	EtOH/0.4	Reflux	12	55
16	MeOH/0.4	Reflux	12	58

Table.4: Optimization of different proportions of Fe₃O₄@SiO₂/ligand/Cu(II) nanocatalyst and also effect of solvents and temperature on formation of 5-substituted 1H-tetrazoles.^a

^aConditions: benzonitrile (1 mmol) and NaN₃ (1 mmol).

^bYields refer to isolated pure product.

The scope and generality of this reaction have been explored by the reaction of various nitrile compounds, with NaN₃ (Table5). Based on the optimal conditions obtained, various substrates such as benzonitrile and heteroaromatic benzonitrile were then examined. As shown in Table5 under similar conditions a wide range of nitrile compounds carrying different functional groups gave the desired products in good to excellent yield. Nitriles compound carrying electron-donating groups provided high yields of the desired products (Table5, entries 2-4,16,17). It is noticeable that, compared to electron-rich nitriles, nitriles bearing electron withdrawing groups

provided the corresponding products in shorter reaction time and comparatively higher reaction yields (Table5, entries 5-7, 9,11). Steric effect also shows its hindrance upon the rates and yields of the reactions. For example phthalonitrile reacted with azide within 5 h with the isolation of the desired product in 90% (Table5, entry 8).

را م	Substrate	Product	Time	Yield ^b	Mp. (°C) (Lit.) ^{c Ref} .
Entr			(h)	(%)	
1	CN CN		4	92	213-215 (215) ⁷⁰
2	Me		6	88	249 (248-249) ⁷¹
3	MeO-CN		8	89	232-234 (231-233) ⁷¹
4	HO-CN		6	91	233-234 (234-235) ²
5	Br-CN		3	92	266-267 (265-266) ³
6	Cl-CN		4	93	262 (261-263) ³
7	NC-CN		4	94	254-256 (256) ³
8	CN CN CN		5	90	210-211 (208-210) ⁷¹
9	O ₂ N-CN	O_2N	4	96	217-219 (219-220) ⁷¹

Table. 5: Preparation of 5-substituted 1H-tetrazoles in the presence of Fe_3O_4 @SiO₂/ligand/Cu(II).^a



^aReaction conditions: nitrile compounds (1 mmol), NaN₃ (1 mmol), Fe₃O₄@SiO₂/ligand/Cu(II) (0.4 mol%), DMF, 110 °C ^bIsolated vield.

^cMelting points reported in the parenthesis refer to the literature melting points.

Proposed mechanism for the formation of 1-substituted 1H-tetrazol (a) and 5substituted 1H-tetrazol (b) is shown in Scheme2. Initially of Fe₃O₄@SiO₂/Shiffbase/Cu (II) nanocatalyst reacts with azide to produce the [Fe₃O₄@SiO₂/Shiffbase/Cu(II)]-N₃ (I) catalytic species. The role of catalytic species (I) is activation of ethoxy groups and cleavage of C-O bonds. Generated carbenium ions can stable with resonance by neighboring hetero atom O/N or sequential nucleophilic displacements by amine and cyclization with azide (intermediates (II)-(IV)). Elimination of ethanol from (IV) leads to the final heterocycle.c(b)- Formation of [Fe₃O₄@SiO₂/Shiffbase/Cu(II)]-N₃ (I) is similar to (a). The [3+2] cycloaddition takes place between the C-N bond of nitrile and (I) to form the intermediate (II) (III). Precoordination of the nitrogen atom of the CN group of 2 with (I) to form complex (II) would enhance this cyclization step.



Scheme.2. Proposed mechanism for the formation of 1-substituted 1H-tetrazol (a) and 5-substituted 1H-tetrazol (b).

Several reports attributed to reaction of benzonitrile and NaN₃ with different catalyst have established. For comparison, several reports have been summarized in table6. It seems that the $Fe_3O_4@SiO_2/Shiffbase/Cu$ (II) nanocatalyst is active catalyst for this reaction. Short time and high yield high confirm this statement.

Entry	Catalyst	Conditions	Yield ^b (%)	Time (h)	Ref.
1	ZnS hollow spheres	DMF,120°C	86	36 h	[72]
2	FeCl ₃ –SiO ₂	DMF,120°C	79	12h	[30]
3	Nano CuFe ₂ O ₄	DMF,120°C	82	12h	[31]
4	Sulfated zirconia	DMF,110-120°C	90	24h	[40]
5	$BaWO_4$	DMF,120°C	75	24h	[73]
6	CaWO ₄	DMF,120°C	74	24h	[73]

Table.6: Comparison of various catalysts in synthesis of 5-substituted 1H-tetrazoles.^a

7	ZnWO ₄	DMF,120°C	75	24h	[73]
8	Zn/Al	DMF,120–130°C	84	12h	[37]
9	Fe ₃ O ₄ @SiO ₂ /ligand/Cu(II)	DMF,110°C	92	4h	This work

^aConditions: benzonitrile (1 mmol) and NaN₃ (1 mmol). ^bYields refer to isolated pure product.

Recycling of the catalyst is an important process from different aspects such as environmental concerns, costs of the catalyst and its toxicity. However, Pd salts are expensive; some of them are toxic, which makes the amounts of their leaching into the reaction mixture a serious worry. Therefore, we studied the recycling of the $Fe_3O_4@SiO_2/Salen Cu$ (II) catalyst for synthesis of 1- and 5-substituted 1H-tetrazoles under optimized conditions (Fig.6). The catalyst was recovered by a magnetic field and was washed with ethyl acetate (2×10 mL), dried and the catalyst reused for subsequent reactions for at least 6 times without observation of appreciable loss in its catalytic activity.





^AReaction conditions: aniline (1 mmol), triethyl orthoformate (1.2 mmol), and sodium azide (1 mmol), Fe₃O₄@SiO₂/ligand/Cu(II) (0.4 mol%), solvent-free, 100°C.

^BReaction conditions: benzonitrile (1 mmol) and NaN₃ (1 mmol), Fe₃O₄@SiO₂/ligand/Cu (II) (0.4 mol%), DMF, 110°C.

To investigate the Cu leaching in these reactions, the filtrate of the reaction between of *p*-methoxy aniline, triethyl orthoformate, and sodium azide after completion was analyzed by ICP technique. The amount of Cu leaching after the first run was determined by ICP analysis to be only 0.4%, and after 6 repeated recycling was 3.2%.

4. Conclusion

In summary, Fe_3O_4 was successfully prepared by co-precipitation with $FeCl_2$ and $FeCl_3$ as reaction substrate, polystyrene (PS) as surfactant and aqueous NH₃ as precipitant. The core-shell $Fe_3O_4@SiO_2$ nanospheres were prepared by a modified

Stober method. Then, Fe_3O_4 @SiO₂ was coated with ligand complex of Cu (II). Then, we have developed a mild, convenient, and efficient protocol for the synthesis of 1and 5-substituted 1H-tetrazoles from nitriles and amines using magnetically separable Fe_3O_4 @SiO₂/ligand/Cu(II) nanoparticles as an efficient and recyclable catalyst. This method gives notable advantages such as easy separation of the catalyst by external magnetic field; excellent yields, short reaction times, non-toxic metal catalyst, and simplicity of operation make this method a facile tool for the synthesis of tetrazoles. Furthermore, the catalyst is magnetically separable and eliminates the requirement of catalyst filtration after completion of the reaction, which represents a major advantage for reactions from an economic and environmental point of view. In addition, nanocatalyst can be easily recycled by applying an external magnetic field while maintaining the catalytic activity without significant decrease even after running 6 times.

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Figure Captions:

Fig.1: FT-IR spectra a) Fe_3O_4 , b) Fe_3O_4 ($aSiO_2$ c) Fe_3O_4 ($aSiO_2$ -NH₂, d) Fe_3O_4 ($aSiO_2$ /ligand, e) Fe_3O_4 ($aSiO_2$ /ligand/Cu(II).

Fig. 2: XRD patterns of a) Fe₃O₄, b) Fe₃O₄@SiO₂ and c) Fe₃O₄@SiO₂/ligand/Cu(II).

Fig. 3: TEM images of Fe_3O_4 (a), $Fe_3O_4@SiO_2$ (b), $Fe_3O_4@SiO_2/Ligand/Cu(II)$ (c) and FE-SEM and DLS images Fe_3O_4 (d, g), $Fe_3O_4@SiO_2$ (e, h) and $Fe_3O_4@SiO_2/Ligand/Cu(II)$ (f, i), respectively.

Fig.4: (a) Thermogravimetric analysis of $Fe_3O_4@SiO_2/ligand/Cu(II)$ nanoparticles. (b) Magnetization curves at 300 K for c) Fe_3O_4 and d) $Fe_3O_4@SiO_2/ligand/Cu(II)$ nanoparticles.

Fig.5: Photographs of the separation and redispersion processes of $Fe_3O_4@SiO_2/ligand/Cu(II)$: without external magnetic field (a), and with external magnetic field (b).

Fig.6: Recyclability of $Fe_3O_4@SiO_2/ligand/Cu(II)$ (A) in the synthesis of 1-substituted-1H-1,2,3,4-tetrazoles (B) and in the synthesis of synthesis of 5-substituted 1H-tetrazoles.

Table Captions:

Table.1: Selected properties of Fe₃O₄, Fe₃O₄@SiO₂, and Fe₃O₄@SiO₂/ligand/Cu(II) nanoparticles.

Table.2: Optimization of different proportions of Fe₃O₄@SiO₂/ligand/Cu(II) nanocatalyst and also effect of solvents and temperature on formation of 1-substituted 1H-tetrazoles.^a

Table.3: Preparation of 1-substituted 1H-tetrazoles in the presence of $Fe_3O_4@SiO_2/ligand/Cu(II)$.^a

Table.4: Optimization of different proportions of Fe₃O₄@SiO₂/ligand/Cu(II) nanocatalyst and also effect of solvents and temperature on formation of 5-substituted 1H-tetrazoles.^a

Table. 5: Preparation of 5-substituted 1H-tetrazoles in the presence of Fe_3O_4 @SiO₂/ligand/Cu(II).^a

Table.6: Comparison of various catalysts in synthesis of 5-substituted 1H-tetrazoles.^a

Graphical abstract



A new magnetically separable catalyst consisting of complex of $Cu(\Pi)$ supported on superparamagnetic Fe₃O₄@SiO₂ nanoparticles was prepared. Then, the immobilized copper complex was used as an efficient catalyst for synthesis of 1- and 5-substituted 1H-tetrazoles from nitriles and amines in good to excellent yields.

Research highlight

- Preparation of the novel magnetic nanocatalysts •
- Ligand complex of $Cu(\Pi)$ functionalized magnetite@silica nanoparticles •
- Identification of catalyst by XRD, TEM, DLS, FE-SEM, FT-IR, BET, TGA and VSM
 - Catalyst recycling by external magnetic field •
- The synthesis of 1- and 5-substituted 1H-tetrazoles from nitriles and amines