Received: 5 January 2020 | Revised: 3 March 2020 | Accepted: 5 March 2020
DOI: 10.1002/aoc.5682

FULL PAPER

Applied Organometallic Chemistry WILEY

Green synthesis of the 1-substituted 1H-1, 2, 3, 4-tetrazoles over bifunctional catalyst based on copper intercalated into Mg/Al hydrotalcite modified magnetite nanoparticles

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An effective one-pot, convenient process for the synthesis of 1- substituted 1H-tetrazoles from triethyl orthoformate, amines, and sodium azide is described using copper (II) doped and immobilized on functionalized magnetic hydrotalcite (Fe_3O_4/HT-NH_2 Cu^{II}) as a novel recyclable catalyst. The application of this catalyst allows the synthesis of a variety of tetrazoles in good to excellent yields in water. The new catalyst was characterized using Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), thermogravimetric analysis (TGA), vibration sample magnetometry (VSM) and inductively coupled plasma analysis (ICP-OES). This new procedure offers several advantages such as short operational simplicity, practicability, and applicability to various substrates and the absence of any tedious workup or purification. The loading amount of Cu^{II} (doped and immobilized) on functionalized magnetic hydrotalcite was indicated to be 4.66 mmol g^{-1}, obtained from the ICP-OES analysis. Also, the excellent catalytic performance, thermal stability, and separation of the catalyst make it an excellent heterogeneous system and a useful alternative to other heterogeneous catalysts. Also, the catalyst could be magnetically separated and reused six times without significant loss of catalytic activity.

KEYWORDS
Fe_3O_4/HT-NH_2-Cu^{II} nanoparticles, hydrotalcite, one-pot, sodium azide, Tetrazole, triethyl orthoformate

1 | INTRODUCTION

Tetrazoles have received considerable interest in recent times because of their comprehensive utility. Among them, 1-substituted tetrazoles have attracted much attention and have been used in a variety of synthetic and medicinal chemistry applications as well as in material science, including propellants and explosives.[1–5] They are also regarded as biologically equivalent to the carboxylic acid groups.[6] Thus, the synthesis of this heterocyclic nucleus is of much current importance. In recent years several synthetic methods have been reported for the preparation of 1-substituted 1H tetrazoles.[7–11] One of the most efficient and conventional methods for the synthesis of 1-substituted 1H-tetrazoles is through [3 + 2] cycloaddition reaction between hydrazoic acid, primary amines, and triethyl orthoformate moieties.[12,13]

Some drawbacks suffer from this protocol, such as toxic procedure, acidic condition, and usage of a highly polar solvent. Recently, researchers attempt to avoid

https://doi.org/10.1002/aoc.5682

using hydrazoic acid as poisonous gas during the synthesis of tetrazoles. However, applying sodium azide in acidic media, leading to the elimination of hydrazoic acid, and by avoiding acidic conditions, the reaction required a substantial excess of sodium azide.

Several catalysts have been also reported for the preparation of tetrazoles using sodium azide, such as $FeCl_3$-SiO_2,[11] ZnS nanoparticles,[14] montmorillonite K-10 clay,[15] nano-TiO_2,[16] natrolite zeolite,[17] the Salen complex of Cu (II) supported on superparamagnetic Fe_3O_4@SiO_2 nanoparticles[18] Fe_3O_4@tryptophan@Ni[19] $CoFe_2O_4$@L-aspargine-Cu[20] $CoFe_2O_4$@Pr,[21] Fe_3O_4@R. *tinctorum*/Ag NP[22] Pd NPs/rGO-*T. Spicata*[23] and magnetic nanocatalysts of copper and manganese.[24–26] While many of the reported methods are worthwhile, some of them have lots of limitations and suffer from drawbacks such as low efficiency and high reaction temperatures, prolonged reaction time, the cost of the catalysts, and side reactions. Because of the limitations as mentioned above, introducing a green and highly efficient method using a new heterogeneous, magnetic reusable and nonhazardous nanocatalyst for the synthesis of tetrazoles is of importance. Today organic synthesis concerning the principle of green chemistry continues to be explored.

Among the attempts made in connection with this issue, also performing one-pot reactions (the combination of more than two or three different reactants in a single step through covalent bonds) using green and environmentally friendly catalysts and mild reaction conditions has been taken into consideration. For this purpose, to improve the long-term durability and activity of catalysts, hydrotalcite (HT) and magnetic hydrotalcite (MHT) have been widely studied as promising supporting materials for catalysts in organic reactions. Layered double hydroxides (LDHs) are a class of anionic clays with the structure based on brucite (Mg $(OH)_2$)-like layers in which some of the divalent cations have been replaced by trivalent cations yielding positively charged sheets. LDHs can be represented by a general formula, $[M^{2+}_{1-x}\ M^{3+}_{x}\ (OH)_2]^{x+}$ $(A^n)_{x/n}.mH_2O$ (where M^{2+} and M^{3+} are di, and trivalent metal ions and A^n indicates the interlayer anions such as CO_3^{2-} $^-$, Cl^-, SO_4^{2-}) with abundant surface hydroxyl groups. The first known compound in this class of materials is the double hydroxide of Mg with Al, known as hydrotalcite, which was found by Hochstetter in Sweden, with a chemical formula of $Mg_6Al_2(OH)_{16}CO_3.4H_2O$. The Mg-Al mixed oxides which are chemically active sites for use in catalytic reactions and also act as the anchoring sites for metal nanoparticles.[27–34]

On the other hand, the separation of hydrotalcite based catalysts from the reaction mixture is difficult to some extent,[27] replacement of conventional separation methods (centrifugation and filtration) with magnetic separation approaches is a fascinating technique. Thus, the incorporation of magnetic nanoparticles (MNPs) into the hydrotalcite structure[35,36] provides easy separation of catalysts from the reaction mixture using an external magnetic and also prevents MNP agglomeration.

In this research, we synthesized Fe_3O_4/HT-NH_2-Cu^{II} and developed a more efficient and convenient method for the one-pot condensation of primary amines, triethyl orthoformate, and sodium azide toward 1-substituted 1H-tetrazoles in the presence of this nanocatalyst as a new heterogeneous catalyst condition (Scheme 1).

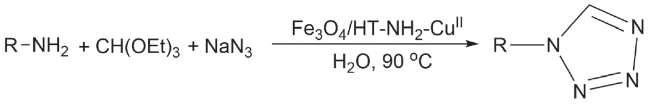
2 | EXPERIMENTAL

2.1 | General

All chemical reagents and solvents were purchased from Merck and Sigma-Aldrich chemical companies and were used as received without further purification. The purity determinations of the products were accomplished by TLC on silica gel polygram STL G/UV 254 plates or GC on a Shimadzu model GC-17A instrument. The FT-IR spectra were recorded on pressed KBr pellets using a Nicoet 800 FT-IR spectrometer at room temperature in the range between 4000 and 400 cm^{-1}. The NMR spectra were obtained on Brucker Avance 300 MHz instruments in DMSO-d6. All the yields refer to isolated products after purification by thin-layer chromatography or recrystallization.

2.2 | Preparation of HT (I)

To a solution containing Mg $(NO_3)_2.6H_2O$ (10.25 g, 40 mmol) and Al $(NO_3)_3.9H_2O$ (7.50 g, 20 mmol) in 60 ml distilled water, a mixed solution (60 ml) containing NaOH (4 g, 100 mmol) and $NaHCO_3$ (2.1 g, 25 mmol) was added drop by drop under vigorous stirring at 60 °C. After 24 hr. The obtained white solid was filtered and washed with deionized water until the pH reached 7 to remove the alkali metal ions. The obtained Mg-Al hydrotalcite (I) (molar ratio Mg/Al = 2) was then dried at 80 °C for 12 hr.



SCHEME 1 Synthesis of tetrazoles derivatives catalyzed by Fe_3O_4/HT-NH_2-Cu^{II}

2.3 | Preparation of Fe_3O_4/HT (II)

In a three-necked 500 Ml, round-bottom flask equipped with an argon gas inlet tube and a dropping funnel, a mixture of $FeCl_3.6H_2O$ (2.1 g, 8 mmol) and $FeCl_2.4H_2O$ (1.05 g, 5.2 mmol) were dissolved in 100 ml deionized water. Then, the resulting mixture was mechanically stirred for 10 min at 80 °C under Ar atmosphere. Afterward, hydrotalcite (I) (4 g) and NaOH solution (100 ml, 5%) were simultaneously added into the solution under vigorous stirring. The resulting brown mixture was stirred at 80 °C for 24 hr. Finally, the mixture was permitted to cool to room temperature, and then Fe_3O_4/HT (II) was collected by an external magnet and washed with distilled water several times until the pH reached 7. Subsequently, Fe_3O_4/HT (II) was dried at 50 °C for 12 hr.

2.4 | Preparation of epichlorohydrin functionalized fe_3O_4/HT (Fe_3O_4/HT-E) (III)

Fe_3O_4/HT (II) (1.0 g) was incorporated with pure epichlorohydrin (6 ml) and dispersed by sonication for 30 min. After that, the mixture was refluxed for 72 hr. Successively, Fe_3O_4/HT-E (III) was magnetically collected, washed with ethanol (5 × 10 ml) until removing the additional amount of epichlorohydrin, and then dried at 60 °C under vacuum for 12 hr.

2.5 | Preparation of diethylenetriamine functionalized Fe_3O_4/HT-NH_2 (IV)

To a suspension of the obtained Fe_3O_4/HT-E (III) (1 g) in ethanol (10 ml) (by sonication for 30 min), diethylenetriamine (0.32 ml, 3 mmol) was added. The resultant mixture was refluxed for 48 hr. Then, Fe_3O_4/HT-NH_2 (IV) was separated magnetically, washed with ethanol (5 ×10 ml), and then dried at 60 °C for 12 hr.

2.6 | Preparation of Fe_3O_4/HT-NH_2-Cu^{II} nanoparticles (V)

To a solution of Cu $(OAc)_2$ (0.4 g, 2 mmol) in EtOH (15 ml), the obtained Fe_3O_4/HT-NH_2 (IV) (1 g) (by sonication for 30 min) was added and stirred at for 12 hr. Afterwards, the resulting suspension was collected using an external magnet and repeatedly washed with EtOH (4 ×10 ml) and dried at 80 °C for 8 hr.

2.7 | A typical procedure for the preparation of 1-substituted 1H-1,2,3,4-tetrazoles

A mixture of amine 5(a-l) (1 mmol), triethyl orthoformate 6 (1.4 mmol) and sodium azide (1.1 mmol) in the presence of 0.005 g Fe_3O_4/HT-NH_2-Cu^{II} was added to water (10 ml) as solvent and the reaction mixture was stirred at 90 °C until monitoring with TLC showed no further progress in the conversion. When the reaction mixture came to ambient temperature, nanocatalyst separated using an external magnet, washed with EtOH and acetone, and dried at room temperature for 24 hr for the next run use. The reaction mixture was then extracted with ethyl acetate (4 × 5 ml) the resulting solution dried over $MgSO_4$ and evaporated to get a solid product. The residue was concentrated and recrystallized from EtOAc–hexane mixture (1:9). The structural assignment of their products is based on ^{1}H-NMR, and IR spectra.

2.7.1 | Selected spectral data

1-phenyl-1H-tetrazole (Compound 1, Table 1): yellow solid; m.*p* = 65–67 °C, IR (KBr)/ $\mathcal{V}$ (cm^{-1}): 3060 (C-H, sp^2 stretch Ar), 1680 (C=N), 1590, 1465 (C=C); (3120, 3060, 2918, 1748, 1680, 1590, 1501, 1465, 1391, 1207, 1091, 1052, 995, 960, 911, 880, 760, 686, 507); ^{1}H NMR (CDCl3, 300 MHz) δ (ppm)*:* 7.53–7.75 (m, 5H, Ar), 9.11 (s, 1H tetrazole).

1-benzyl-1H-tetrazole (Compound 2, Table 1): White solid; m.*p* = 132–133 °C; IR (KBr)/ $\mathcal{V}$ (cm^{-1}): 3060 (C-H, sp^2 stretch Ar), 1643 (C=N), 1534, 1453 (C=C). (3271, 2928, 2859, 1590, 1457, 1408, 1360, 1299, 1245, 1200, 1132, 1003, 956, 881, 750, 633); ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 4.47–4.49 (s, 2H), 7.28–7.39 (m, 5H), 8.24 (s, 1H).

1,2-di (1-H-tetrazole-1-yl) benzene (Compound 3, Table 1): White solid; m.*p* = 169–173 °C, IR (KBr)/ $\mathcal{V}$ (cm^{-1}): 3060 (C-H, sp^2 stretch, Ar), 1618 (C=N) 1457, 1588 (C=C); (3316, 3060, 3004, 2935, 2859, 1618, 1588, 1457, 1408, 1360, 1299, 1245, 1200, 1132, 1003, 956, 881, 750, 633); ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm)*:* 7.12–7.63 (m, 4H), 8.24 (s, 1HTetrazole).

3 | RESULTS AND DISCUSSION

HT (I) was prepared through the co-precipitation method and synthesis of Fe_3O_4/HT (II), HT (I) was performed using an alkaline mixed salt-solution of ferrous and ferric ions. Thereafter, the surface of Fe_3O_4/HT (II) was modified by epichlorohydrin and then by diethylenetriamine

TABLE 1 Preparation of tetrazole derivatives using Fe_3O_4/HT-NH_2-Cu^{II} catalystEntry

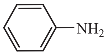
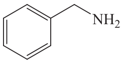
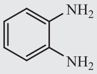
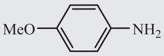
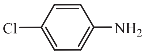
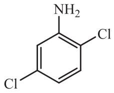
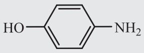
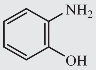
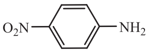
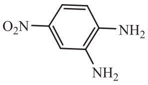
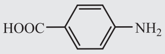
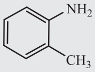
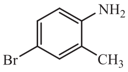
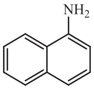
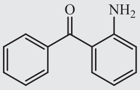
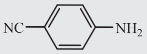
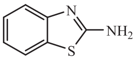
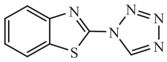
	Substrate	Product	Time(h)	Yield (%)
1			**1**	**94**
2			1	85
3			1.5	80
4			2.5	85
5			2	75
6			3	75
7			2.5	50
8			3	70
9		 2-(1*H*-tetrazol-1-yl)benzo[*d*]thiazole	2	65

TABLE 1 (Continued)

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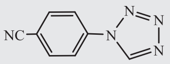
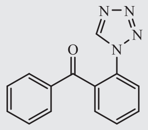
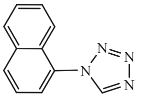
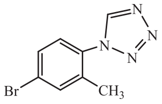
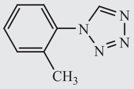
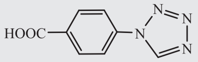
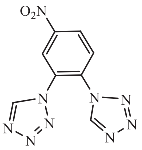
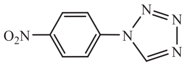
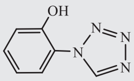
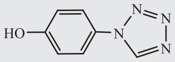
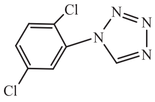
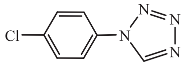
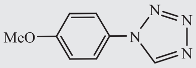
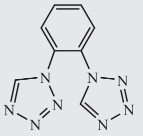
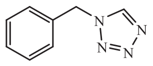
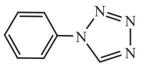
10	 4-(1*H*-tetrazol-1-yl)benzonitrile	 (2-(1*H*-tetrazol-1-yl)phenyl)(phenyl)methanone	1	55
11	 1-(naphthalen-1-yl)-1*H*-tetrazole	 1-(4-bromo-2-methylphenyl)-1*H*-tetrazole	1.5	90
12	 1-(*o*-tolyl)-1*H*-tetrazole	 4-(1*H*-tetrazol-1-yl)benzoic acid	2	45
13	 1,1'-(4-nitro-1,2-phenylene)bis(1*H*-tetrazole)	 1-(4-nitrophenyl)-1*H*-tetrazole	1.5	85
14	 2-(1*H*-tetrazol-1-yl)phenol	 4-(1*H*-tetrazol-1-yl)phenol	3	65
15	 1-(2,5-dichlorophenyl)-1*H*-tetrazole	 1-(4-chlorophenyl)-1*H*-tetrazole	3	50
16	 1-(4-methoxyphenyl)-1*H*-tetrazole	 1,2-di(1*H*-tetrazol-1-yl)benzene	2	85

(Continues)

TABLE 1 (Continued)

	Substrate	Product	Time(h)	Yield (%)
17	 1-benzyl-1*H*-tetrazole	 1-phenyl-1*H*-tetrazole	3	trace

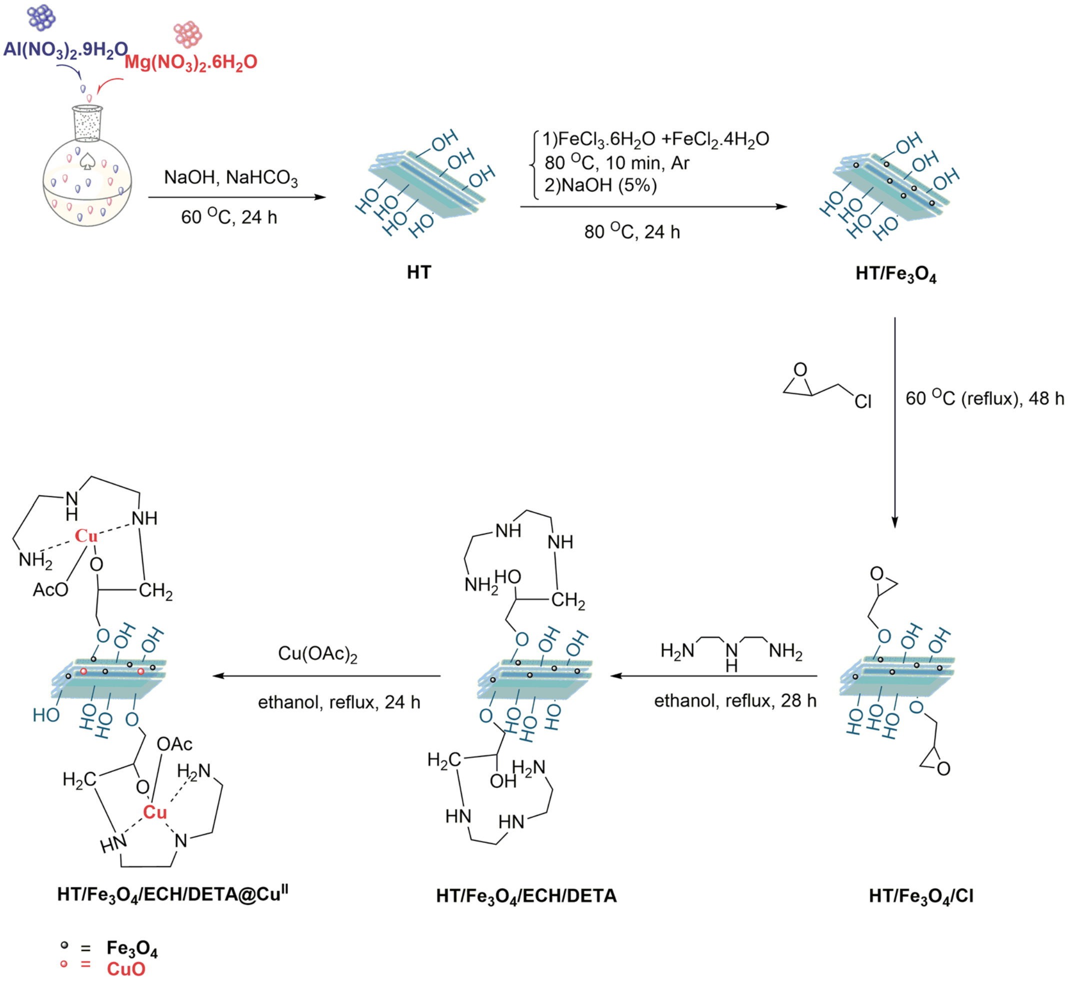
Reaction Conditions: amine (1 mmole), sodium azide (1.1 mmol), triethyl orthoformate (1.4 mmol), Fe_3O_4-HT-NH_2-Cu^{II}, H_2O (2 cc), 90 °C

to produce Fe_3O_4/HT-E (III), and Fe_3O_4/HT-E-NH_2 (IV) respectively. Then Cu (II) immobilized on Fe_3O_4/HT-NH_2(IV) in EtOH to obtain Fe_3O_4/HT-NH_2-Cu (II) (V) nanoparticles (Scheme 2).

The catalytic system was well characterized by using various techniques such as Fourier transform infrared spectroscopy (FT-IR), X-ray powder diffraction (XRD), transmission electron microscopy (TEM), field emission scanning electron microscopy (FE-SEM), energy-dispersive X-ray (EDX), thermogravimetric analysis (TGA), vibrating sample magnetometer (VSM) and inductively coupled plasma optical emission spectroscopy (ICP-OES).

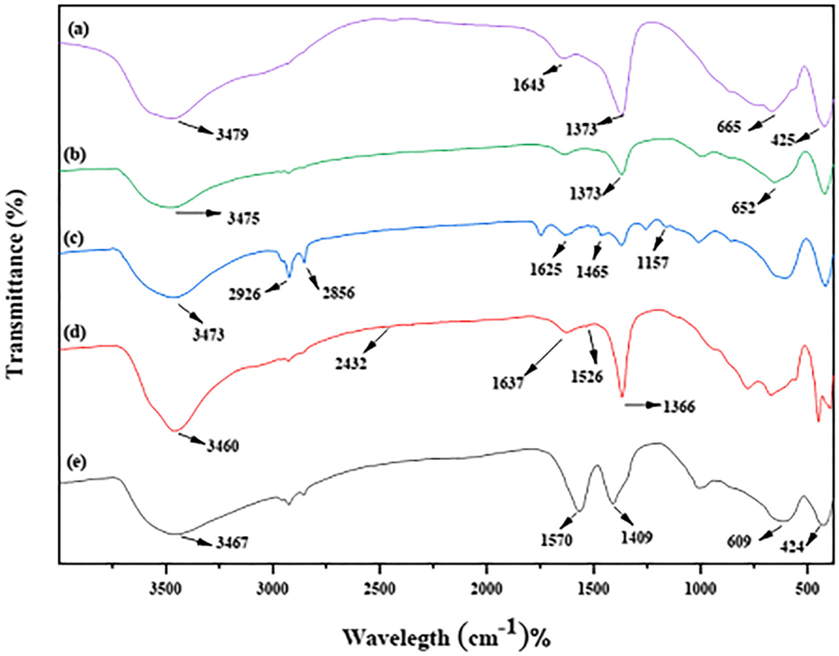
3.1 | FT-IR spectroscopy

Fourier transform infrared (FT-IR) spectroscopy evidences the modification of Fe_3O_4/HT NPs surface. Figure 1 illustrates the FT-IR spectra of HT (a), Fe_3O_4/



SCHEME 2 Preparation of catalyst (Fe_3O_4/HT-NH_2-Cu^{II})

FIGURE 1 FT-IR spectra of HT (a), Fe_3O_4/HT(b) and Fe_3O_4/HT-E (c) Fe_3O_4/HT-NH_2 (d), Fe_3O_4/HT-NH_2-$Cu^{(II)}$ (e)



HT (b), Fe_3O_4/HT-E (c), Fe_3O_4/HT-NH_2 (d) and Fe_3O_4/HT-NH_2- Cu^{II} (e). As shown in Figure 1a, the broadband at 3479 cm^{-1} was indicative of the OH symmetric stretching vibration of Mg–OH and Al–OH on the surface of the hydrotalcite structure. The vibration mode at 1634 cm^{-1} could be attributed to the bending vibrations of water molecules in a hydrotalcite structure. Also, the absorption bands appearing at 1373 and 665 cm^{-1} corresponded to the asymmetric stretching vibration of C–O (indicating the presence of CO_3^{2-}) and the angular bending mode of carbonate species, respectively. This shows that the carbonate anions are present between the layers of hydrotalcite. In Figure 1b, the FT-IR spectrum of Fe_3O_4/HT (II), the intensity of the adsorption band at 1366 cm^{-1}, became weaker because of the incorporation of Fe_3O_4 into the HT structure.

Four new absorption bands confirmed the existence of the grafted epoxy groups to the Fe_3O_4/HT framework at 2926, 2856 (related to the C–H stretching vibrations), 1465 cm^{-1} (related to the C–H bending vibration) and 1157 (related to the C–O-C stretching vibration). Furthermore in the FT-IR spectrum of Fe_3O_4/HT-NH_2 (Figure 1c), the appearance of a new band at 1526 cm^{-1} is assigned to the NH bending vibrations, could be authenticated the existence of the anchored diethylenetriamine groups to the hydrotalcite. Finally, the coordination of Cu $(OAc)_2$ can be verified by the stretching vibrations that appear at 1570 and 1409 cm^{-1} (corresponding to stretching modes of carboxylate groups) and 609 cm^{-1} (corresponding to stretching vibrations of Cu-N bond). Besides, this coordination can be authenticated by decreasing the intensity and frequency of the hydroxyl groups (Figure 1e).

3.2 | X-ray diffraction (XRD) analysis

The XRD patterns of HT (I) and Fe_3O_4/HT (II) have been presented in Figure 2. As seen in Figure 2a, the as-synthesized hydrotalcite nanoparticles exhibited characteristic diffraction peaks at around $2\theta = 11.9$, 22.61, 34.7, 38.8, 45.9, 60.31, and 61.51 which fitted well to the crystal planes of (003), (006), (012), (015), (018), (110), and (113) of the hydrotalcite.38furthermore, in Figure 2b, in comparison with the pattern of the as-synthesized hydrotalcite, additional peaks at $2\theta = 29.9$, 35.5, 43.4, 57.3, and 62.91 were found which can be assigned to the (220), (311), (400), (511), and (440) planes, proving the presence of the magnetic (Fe_3O_4) phase as a cubic lattice in the hydrotalcite structure. On the other hand, the intensity of diffraction peaks for the LDH@Fe_3O_4 is lower than that of pure LDH, guessed due to the smaller size of the particles.

3.3 | SEM-EDS images and SEM image with combined EDS-elemental mapping

The surface morphology of Fe_3O_4/HT-NH_2- Cu^{II} was shown in Figure 3. As given in Figure 3, the as-synthesized HT (I) shows irregular plate-like morphology, representing the character of layered materials. It is

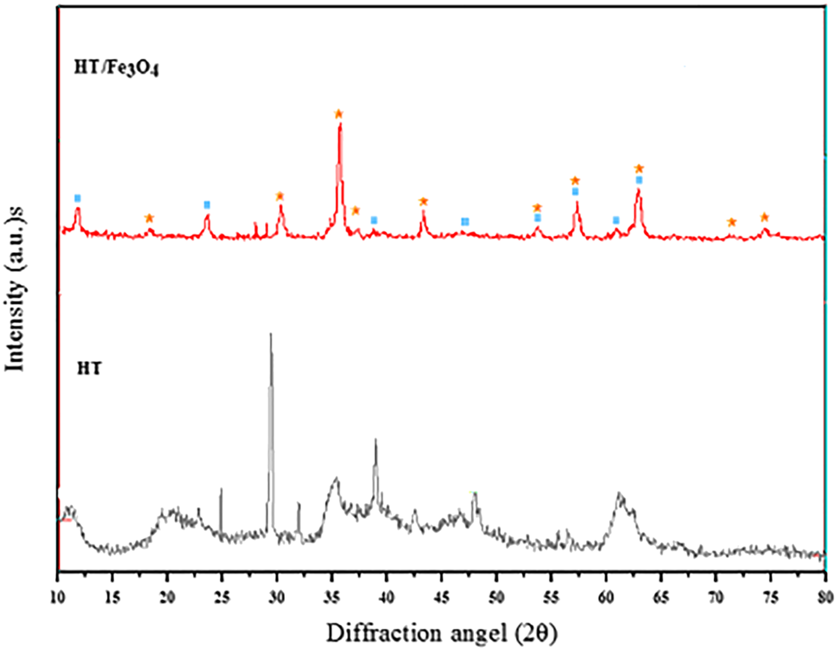


FIGURE 2 The XRD patterns of (a) HT (I), (b) Fe_3O_4/HT $^{(II)}$

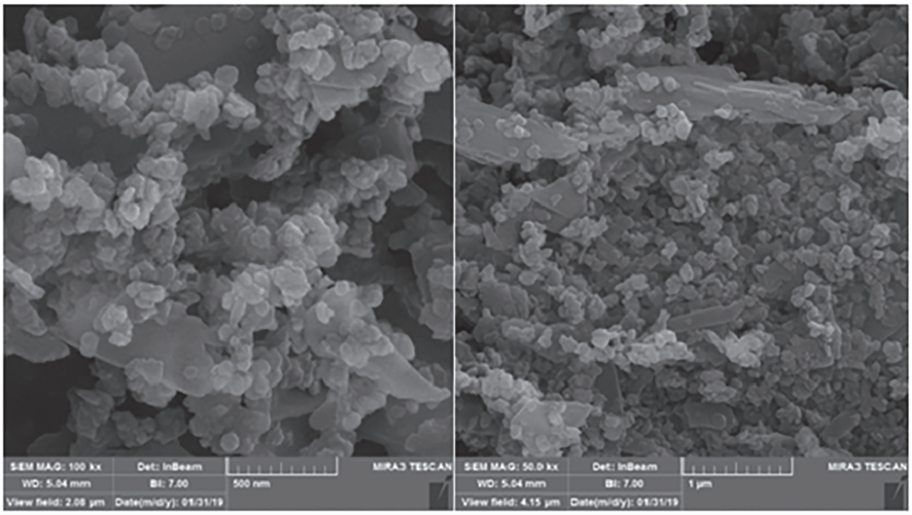


FIGURE 3 SEM image of Fe_3O_4/HT-NH_2-$Cu^{(II)}$

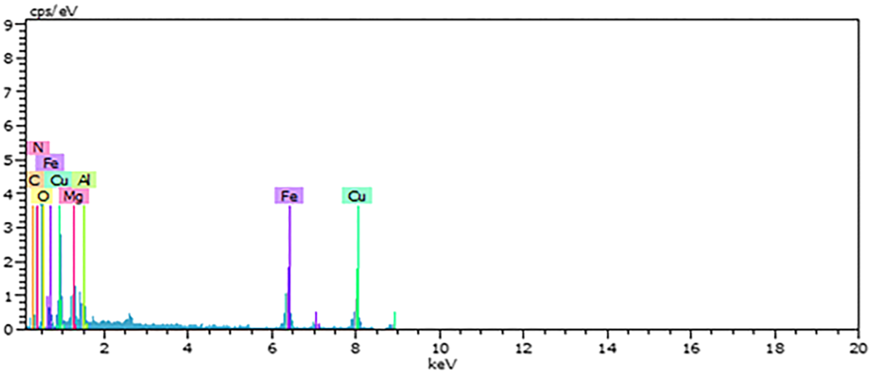


FIGURE 4 EDAX spectra of Fe_3O_4/HT-NH_2 -Cu^{II}

mentioned, that Fe_3O_4 NPs were dispersed on the surface of plate-like sheets of HT.

Moreover, the EDS analysis confirmed the presence of Al, Mg, O, C, N, Fe, and Cu elements in the nanocatalyst structure, as shown in Figure 4. And also, the substantial intensity of Cu^{II} indicated the successful coordination of Cu^{II} on the surface of Fe_3O_4/HT-NH_2 (Figure 5).

3.4 | Thermal gravimetric analysis (TGA)

To investigate the thermal stability of Fe_3O_4/HT-NH_2 -Cu^{II}, TGA analysis was carried under an air atmosphere at a heating rate of 10 °C min^{-1} from 25 to 900 °C (Figure 6).

TGA thermogram of Fe_3O_4/HT-NH_2-Cu^{II} (IV) is shown in Figure 6. The results showed weight loss steps. Evaporation of the absorbed physical and chemical water on the catalyst surface or between the layers happened at 35–260 °C (6. 5%). The Second step (260–400 °C, 11.34%) is due to the loss of the interlayer carbonate and hydroxyl groups.62 weight loss (9.66%) at 400–800 °C could be assigned to the removal of organic functional groups grafted on the surface of the catalyst.

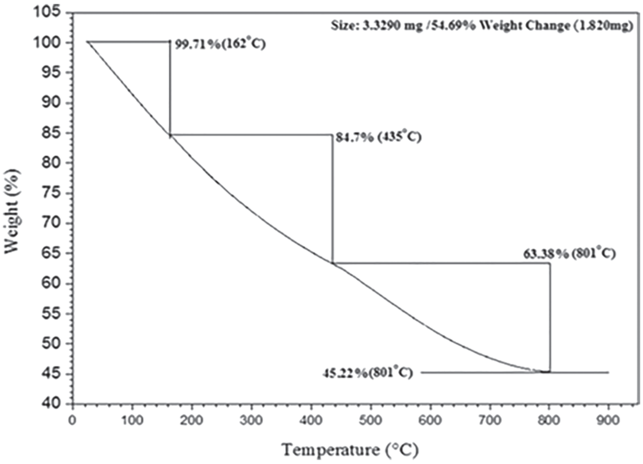


FIGURE 6 The TGA thermograms of Fe_3O_4/HT-NH_2-Cu^{II}

3.5 | Vibrating sample magnetometer (VSM) analysis

Magnetic characterization of Fe_3O_4/HT and Fe_3O_4/HT-NH_2-Cu^{II} was investigated using vibrating sample magnetometry at room temperature (Figure 7). As illustrated in Figure 7 the magnetization value of Fe_3O_4/HT-NH_2-Cu^{II} (9.961 emu g^{-1}) is lower than the magnetization

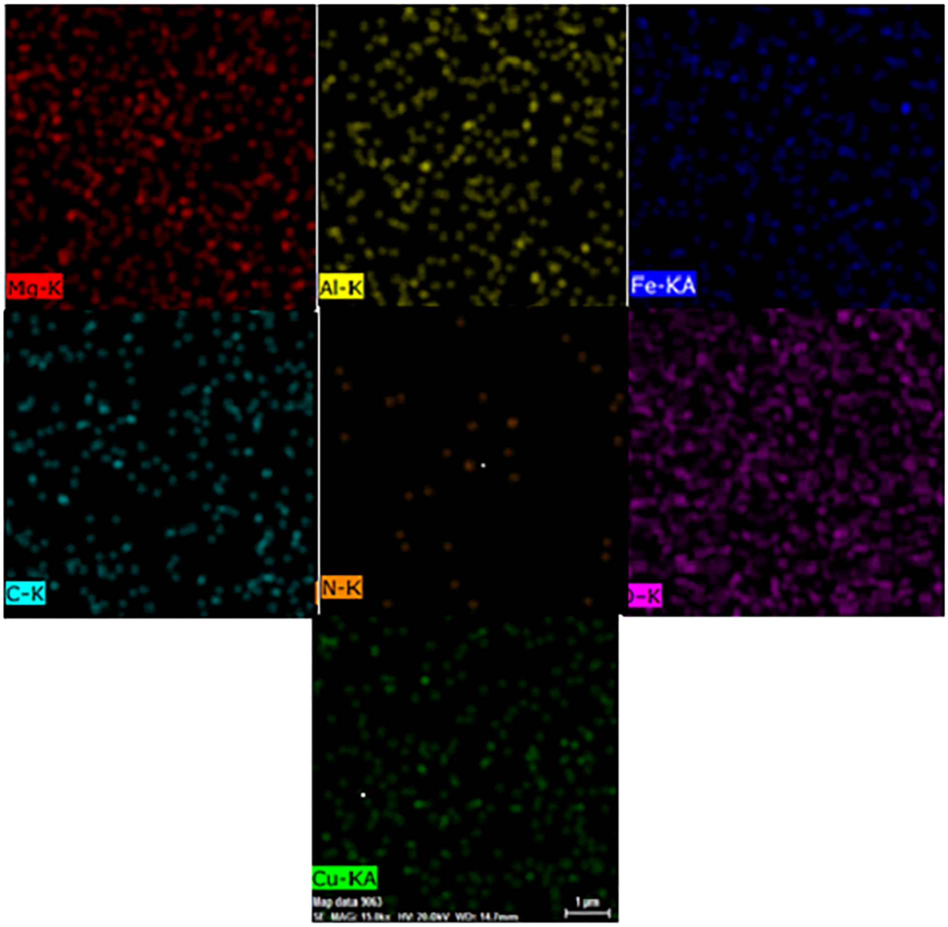


FIGURE 5 Elemental mapping of Mg, Al, Fe, C, N, O, and Cu

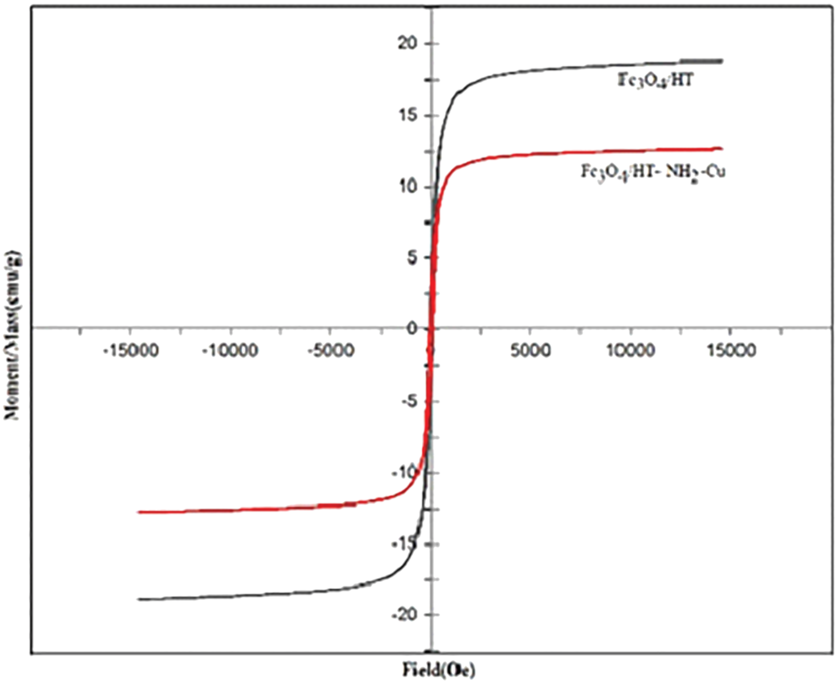


FIGURE 7 Magnetization curves of Fe_3O_4/HT and Fe_3O_4/HT-NH_2-Cu^{II}

value of Fe_3O_4/HT (18.837 emu g^{-1}) due to the immobilization of the Cu complex of diethylenetriamine on the surface of Fe_3O_4/HT. It is worth noting that both Fe_3O_4/HT and Fe_3O_4/HT-NH_2-Cu^{II} are superparamagnetic, which can be attributed to the presence of Fe_3O_4 NPs. On the other hand, the magnetic property of Fe_3O_4/HT-NH_2-Cu^{II} was enough for separated easy and rapid of nanocatalyst from the reaction mixture with a permanent magnet.

Also, the ICP analysis showed that 296.081 mg equal 4.66 mmol of copper was anchored on 1.000 g of the catalyst.

3.6 | Optimization of the catalyst

The subsequent purpose of the synthesis of tetrazole was to optimize the reaction conditions. Therefore, the catalytic efficiency was studied in the one-pot three-component synthesis of 1-substituted 1H-1, 2, 3, 4-tetrazoles as a model substrate in different reaction conditions (amount of the catalyst, temperature, and solvent nature and amount of the solvent).

3.7 | The effect of temperature

Typically the result of the effect temperature is shown in Figure 8 [sodium azide (1.1 mmol), aniline (1 mmol); triethyl orthoformate (1.4 mmol)], which is H_2O as a solvent. The yield is approximately 10% at 25 °C, even though the mixture was stirred for the lengthy reaction time. While the reaction temperature has been increased to 70 °C, the yield also enhanced, and when the temperature grew up to 90 °C, the excellent yield has been obtained.

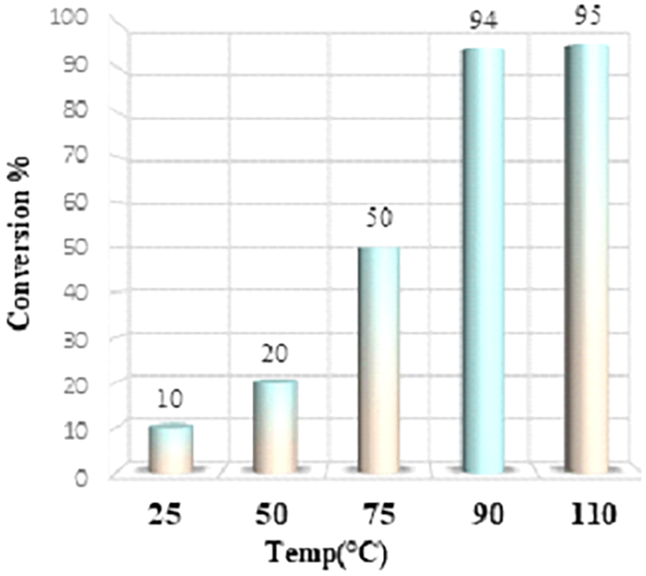


FIGURE 8 The effect of time in the synthesis of 1H-1,2,3,4-tetrazole by Fe_3O_4/HT-NH_2-Cu^{II}
Reaction conditions: sodium azide (1.1 mmol), aniline (1 mmol), triethyl orthoformate (1.4 mmol), 2 ml of H_2O, 0.005 g of Fe_3O_4/HT-NH_2-Cu^{II}

3.8 | The effect of the amount of catalyst

To check into the effect of the catalyst, systematic studies were carried out within the existence of various numbers of Fe_3O_4/HT-NH_2-Cu^{II} (Figure 9). First of all, a control experiment has been done in the lack of the Fe_3O_4/HT-NH_2-Cu^{II} catalyst to show the significant role of the catalyst. Therefore, the catalyst was eliminated from the solution, and the more substrate added to typically the filtrate where no extra tetrazole was produced below the similar conditions. Second, various amounts of the Fe_3O_4/HT-NH_2-Cu^{II} was used, and the best yield seemed to be obtained with 5 mg of catalyst.

3.9 | The effect of solvent

We checked out this reaction in various solvent (Figure 10). The results showed that different solvents affect the efficiency of the reaction. Acetonitrile is given low yield (10%), while the use of solvents such as ethanol, DMF can improve yields compared to acetonitrile. Finally, when water is used, the results increased to 94% better than other solvents examined here. In the absence of a solvent, the results of the model reaction decreased to 35%.

Different amounts of solvent were investigated in this reaction. In the presence of diverse amounts of the solvent, the reaction models do. Also, the optimum amount of solvent is studied, and the results showed that 2 ml required for optimized reaction conditions (Figure 11).

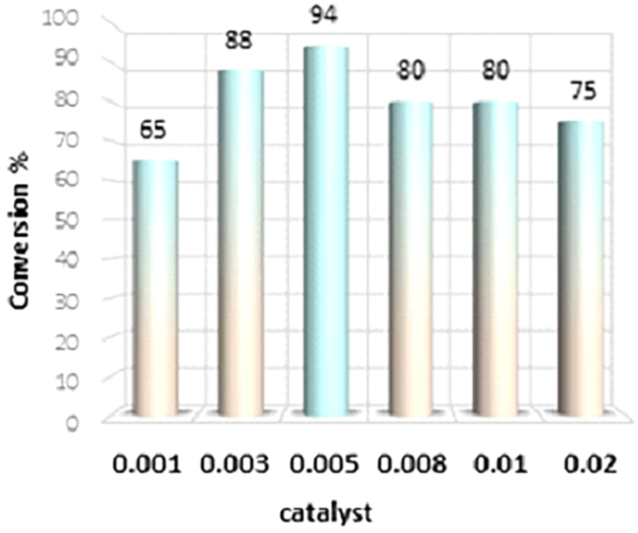


FIGURE 9 The effect of the amount of Fe_3O_4/HT-NH_2-Cu^{II} in the synthesis of 1H-1,2,3,4-tetrazole
Reaction conditions: sodium azide (1.1 mmol), aniline (1 mmol), triethyl orthoformate (1.4 mmol), 2 ml of H_2O

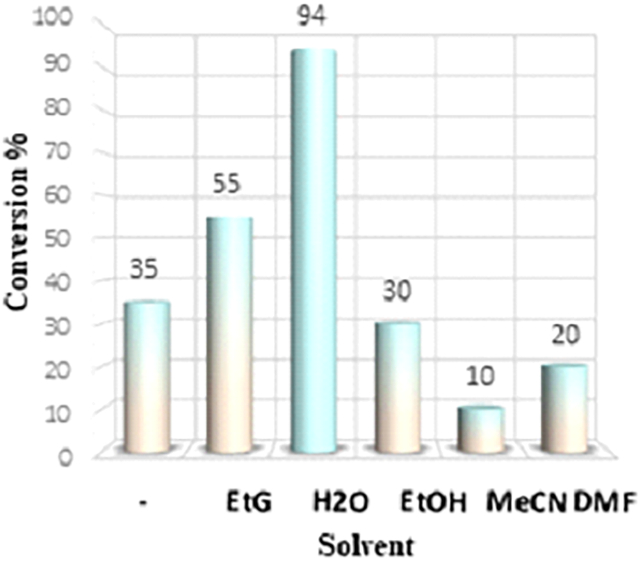


FIGURE 10 The effect of different solvents in the synthesis of 1H-1,2,3,4-tetrazole by Fe_3O_4/HT-NH_2-Cu^{II}
Reaction conditions: sodium azide (1.1 mmol), aniline (1 mmol), triethyl orthoformate (1.4 mmol), 0.005 g of Fe_3O_4/HT-NH_2-Cu^{II}, 90 °C

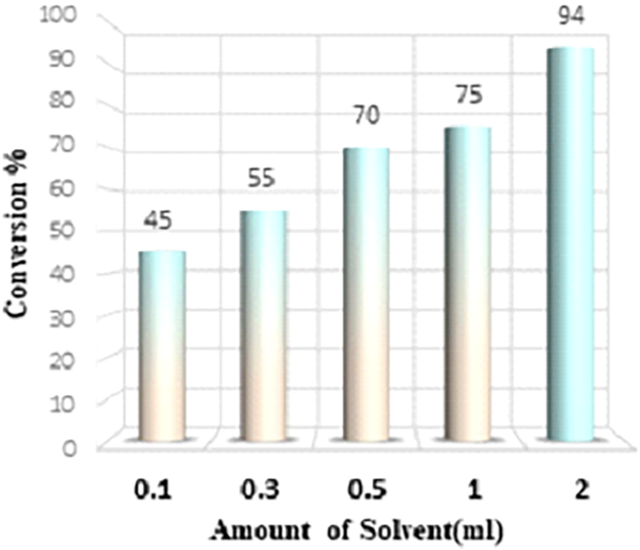
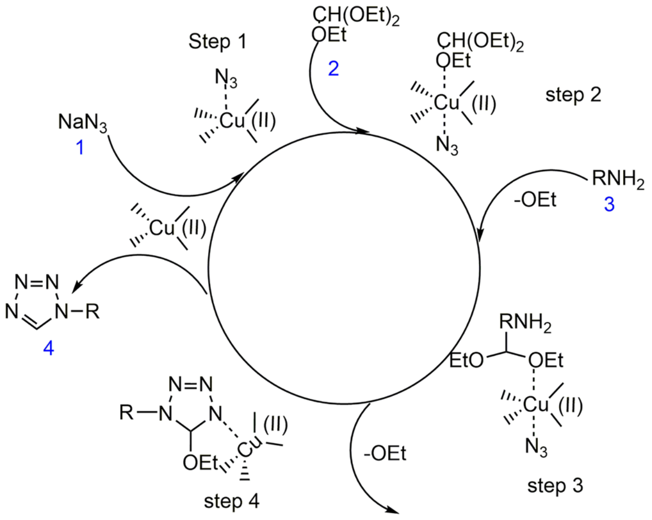


FIGURE 11 The effect of the amount of solvent in the synthesis of 1H-1,2,3,4-tetrazole by Fe_3O_4/HT-NH_2-Cu^{II}Reaction conditions: sodium azide (1.1 mmol), aniline (1 mmol), triethyl orthoformate (1.4 mmol), 0.005 g of Fe_3O_4/HT-NH_2-Cu^{II}, 90 °C

Some tetrazole derivative synthesized by the reaction of different aromatic amine, triethyl orthoformate, and sodium azide using Fe_3O_4/HT-NH_2-Cu^{II} nano-catalyst [aniline: 1 mmol; sodium azide: 1.1 mmol; triethyl orthoformate: 1.4 mmol; $T = 90\ ^\circ C$; H_2O as a solvent]. To extend the range of diverse substrates, arylamines with electron-releasing or electron-withdrawing group also examined to undergo a one-pot reaction of the three components of success for the synthesis of 1-substituted 1H-tetrazoles under H_2O as a solvent (Table 1).



SCHEME 3 Proposed mechanism for preparation of tetrazoles by Fe_3O_4/HT-NH_2-Cu^{II}

As can be observed in Table 2, this catalyst indicated good catalytic efficiency in short times in comparison to most of typically the reported works (Table 2).

A plausible mechanism for the synthesis of diverse 1-substituted 1H-tetrazoles of aromatic amine reaction, triethyl orthoformate, and sodium azide in the presence of Fe_3O_4/HT-NH_2-Cu^{II} catalyst under H_2O as a solvent shown in Scheme 3. The suggested mechanism may be due to Lewis acidity Cu catalysts, which can catalyze the transformation of the dissociation of the triethyl orthoformate and facile establishment of the intermediate to perform the cyclization reaction to produce the corresponding product.

3.10 | The catalyst reusability and stability

Reusability and recovery of catalyst are significant mainly because of the environmental and even economic aspects, so typically the reusability of the Fe_3O_4/HT-NH_2-Cu^{II} catalyst was also studied [reaction circumstances: aniline:

TABLE 2 Comparison of results by Fe_3O_4/HT-NH_2-Cu^{II} with various catalysts

Entry	Catalyst	Reaction conditions	Time (h)	Yield (%)	Ref.
1	Natrolite zeolite	Solvent free - 120 °C	4	80–94	[17]
2	Cu NPs/bentonite	Solvent free - 120 °C	3	83–95	[37]
3	$NHTf_2$	Glycerol – r.t.	3	84–95	[38]
4	ZnS nanoparticle	Solvent free - 130 °C	3–7	56–78	[14]
5	ZnS nanoparticle	US, DMF, r.t.	0.5	70–92	[39]
6	Ag_2O	AcOH - 100 °C	0.5	85–93	[40]
7	Fe_3O_4@silica sulfonic acid	Solvent free - 100 °C	0.5–3	78–97	[41]
8	Fe_3O_4/HT-NH_2-Cu^{II}	H_2O – 90 °C	1–3	50–90	This work

Reaction conditions: NaN_3, RNH_2, CH $(OEt)_3$

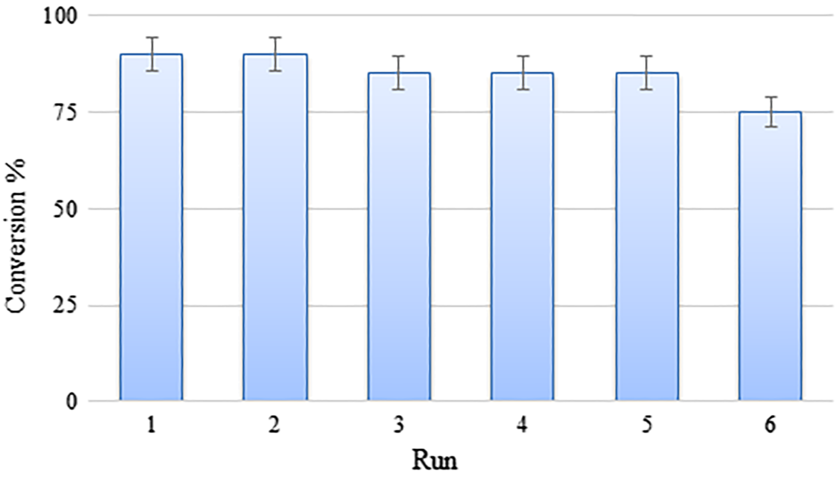


FIGURE 12 Recyclability of Fe_3O_4/HT-NH_2-Cu^{II} in the synthesis of 1H-1,2,3,4-tetrazole

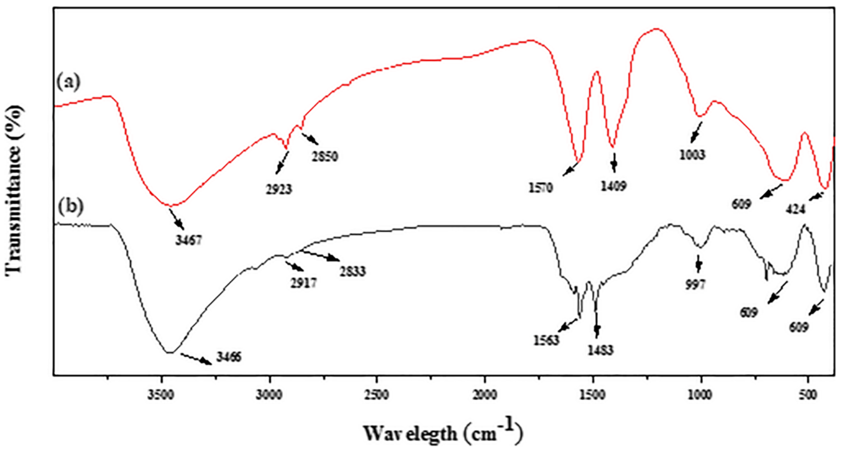


FIGURE 13 FT-IR of Fe_3O_4/HT-NH_2-Cu^{II} in the synthesis of 1H-1,2,3,4-tetrazole a) First run, b) recovered catalyst (fifth run)

1 mmol; sodium azide: 1.1 mmol; triethyl orthoformate: 1.4 mmol; H_2O as a solvent, 90 °C]. As a result, the catalyst was separated by an external magnet after the first run, washed using ethanol, and dried at 120 °C under vacuum oven, after which used for the subsequent successive runs under similar circumstances (Figure 12). No notable decrease of activity was observed, demonstrating that the fact the applied catalyst is able and has great stability through the one-pot preparation of the 1-substituted 1H-1, 2, 3, 4-tetrazoles. Fe and Cu weren't detected in the reaction solutions based on ICP-AES evaluation via the hot filtration approach. After the solid-free filtrates were subsequently stirred continuously under optimized reaction conditions for its substrates as mentioned above, the results of 1-substituted 1H-1, 2, 3, 4-tetrazoles were significantly less than 5 percent after 12 hr.

Until at least five runs, the Fe_3O_4/HT-NH_2-Cu^{II} exhibited high catalytic activity (Figure 13). For more study, the characterization of Fe_3O_4/HT-NH_2-Cu^{II} after the fourth run was investigated. The Fourier transform infrared spectrum of the recovered catalyst (black) has good accordance with the similar fresh catalyst (red), with the presence of the basic peaks, and the outcomes confirmed that the catalyst afterward, the fourth run did not demonstrate a significant change in the structure.

4 | CONCLUSIONS

In conclusion, numerous tetrazole derivatives were produced by using the Fe_3O_4/HT-NH_2-Cu^{II} catalyst in diverse stages. This kind of catalyst was found to be suitable and sufficient for the quick synthesis of different tetrazoles in H_2O as solvent conditions at 90 °C. The other investigation showed high catalytic performance with efficient recycling. Moreover, an appropriate reaction condition was optimized via considering the effect of different parameters, such as the amount of catalyst, the reaction time, numerous solvents, and the amount of solvent to achieve the highest conversion of substrates.

ACKNOWLEDGEMENTS

We gratefully acknowledge the support of this work by the University of Birjand.

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How to cite this article: Salimi M, Zamanpour A. Green synthesis of the 1-substituted 1H-1, 2, 3, 4-tetrazoles over bifunctional catalyst based on copper intercalated into Mg/Al hydrotalcite modified magnetite nanoparticles. *Appl Organometal Chem*. 2020;e5682. https://doi.org/10.1002/aoc.5682