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Short communication

Fe₃O₄@Hydrotalcite-NH₂-Co^{II} NPs: A novel and extremely effective heterogeneous magnetic nanocatalyst for synthesis of the 1-substituted 1H-1, 2, 3, 4-tetrazoles

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ARTICLEINFO	A B S T R A C T
Keywords: Tetrazole Sodium azide Triethyl orthoformate One-pot Fe ₃ O ₄ @HT@AEPH ₂ -Co ^{II} nanoparticles Hydrotalcite	In this study, we present a versatile and easy procedure for modifying a ferrite nanoparticles so step by step. A new nanocatalyst was prepared via Co^{II} immobilized onto an aminated ferrite nanoparticles (Fe ₃ O ₄ @H-T@AEPH ₂ -Co ^{II}). The catalyst was fully characterized by FT-IR, EDX, FE-SEM, TGA, XRD, and VSM analyses. In the preparation of 1-substituted-1-H-tetrazole, the corresponding nanocatalyst shown great catalytic activity. The reaction contains expeditious reusable catalyst (Fe ₃ O ₄ @AEPH ₂ -Co ^{II}) that promotes condensation between sodium azide, triethyl ortho-formate, and diversity of heterocyclic/aromatic amines. Also, an environmentally toxic solvent was eliminated. A significant improvement in the synthetic efficacy (95%, yield) was obtained by this new sustainable and eco-friendly protocol as well as high purity. The current procedure as a green protocol offers benefits including a simple operational procedure, an excellent yield of products, mild reaction conditions, minimum chemical wastes, short reaction time, and easy catalyst synthesis. Without any significant reduction in the catalytic performance, up to four recyclability cycles of the catalyst were obtained. The optimization results suggest that the best condition in the preparation of tetrazole derivatives is 0.005 g of the Fe ₃ O ₄ @HT@AEPH ₂ -Co ^{II}

substrate (i.e., electron-deficient and electron-rich).

1. Introduction

Among the known stable heterocycles, tetrazoles belong to a category of 5-membered heterocyclic compounds containing nitrogen, in which nitrogen content is maximum. It is believed that 2-phenyl-2H-tetrazole-5-carbonitrile to be the first compound having a tetrazole ring which was synthesized and characterized in 1885 [1].

In recent decades, considerable attention has been received to the chemistry of N-containing heterocycles (tetrazoles) because of their hopeful biological properties particularly antifungal [2], antimicrobial [3], antiulcer [4], antinociceptive [5], anti-HIV [6], antiallergic [7], anti-inflammatory [8], antiproliferative [9] and anticancer [10]. It is also presented that they are potential TNF alpha inhibitors [11], P2X7-antagonists [12], and inhibitors of anandamide cellular uptake [13]. Because of the application of tetrazole and derivatives thereof as lipophilic as spacers and metabolically established substitutes for a carboxylic acid in a drug study, their importance of them has augmented in medicinal chemistry [14]. There are tetrazole moieties in the structures

of several drugs approved by the Food and Drug Administration (FDA), which are important in medicine [15]. It has been reported that cell penetration and oral bioavailability are improved in a drug via the lipophilic character of moieties that are tetrazole [16]. In this regard, the potential therapeutic profile of tetrazole chemistry has occurred so much attention. In the class of nonpeptide angiotensin-II inhibitors, losartan, valsartan, and irbesartan are famous antihypertensive drugs possessing a biphenyl tetrazolyl part in their structure (Fig. 1). Likewise, there is also a tetrazole ring in the structure of TAK-456 as a wide range of antifungal drugs (Fig. 1).

Befitting coordinating properties are endowed by them. For example, nitrogen-containing heterocyclic ligands can form stable complexes by numerous metal ions. In organic synthesis, they can act as pioneers to many different of nitrogen heterocycles [17,18]. For the preparation of other complex heterocycles, the tetrazole ring is an important intermediate through various rearrangements [19]. Inherent acetylcholinesterase inhibition potency was detected in nitrogen-containing heterocyclic compounds. Therefore, they are among the most promising

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Fig. 1. Drugs in the market with a tetrazole moiety.

candidates for Alzheimer's disease treatment [20–22]. Therefore, there is a need to develop efficient protocols to synthase tetrazoles considering pharmacological applications of them. 1-substituted tetrazoles are interested due to their wide applications [23,24]. However, their application in medical practice is restricted due to the lack of convenient synthesis methods.

However, acid-catalyzed could be cycle added between isocyanides and hydrazoic acid in the preparation of 1-substituted tetrazoles [25,26]. In the presence of acetic acid, it also could be synthesized by cyclization between triethyl orthoformate, sodium azide, and primary amines [27]. Other methods include using various catalysts including natrolite zeolite [28], In(OTf)₃ [29], [Hbim]BF₄ [30], SSA [31], Yb (OTf)₃ [32]. Disadvantages include the usage of dangerous and costly reagent, prolonged reaction times, and use of the solvent with the high boiling point, high temperature, dull workup processes, the existence of highly hydrazic acid, and the problem in the recovery and separation of the catalyst, toxic waste generation. Therefore, it is important to create an ecofriendly and more effective procedure which reduce these disadvantages.

Designing and using appropriate center cores and catalytic species, novel approaches concern the maintainable growth of extremely selective nanostructured catalysts [33]. In the preparation of catalyst based on nano-magnetic, silica derivative has been used as a coating agent. This is due to many prominent features including great selectivity and good activity, effective recovery and good recyclability, excellent stability [34,35]. Therefore, it is needed to design and synthesize powerful and recyclable nano-magnetic catalysts. Heterogeneous catalysts in chemical processes are interested in the literature. It is due to their merits including good reusability and easy separation from the reaction mixture in comparison with homogeneous catalytic systems. It is important to pay attention to the low activity and selectivity of heterogeneous catalysts compared to homogeneous ones due to the low surface area. It is more important when the immobilization of the active catalytic kinds onto appropriate support is a case where the active sites in a supported system are not approached as in the equivalent homogeneous due to steric hindrance of the great support. Reducing support size by a combination of heterogeneous catalytic systems and nanotechnology can be a solution that multiplies the interactions of surface and reactants increasing the ratio of surface to volume. From the activity and selectivity point of view, nono chemical technology can be approached by both heterogeneous and homogeneous catalyst systems. However, due to the very small dimensions of nanomaterials, major restrictions are the facile recovery and separation of the catalyst. Magnetic nanoparticles are excellent alternatives. By using an external magnetic modest, they are effortlessly separated from the reaction medium. Besides, an excellent method of the separation of catalysts is the magnetization of common nano-solid supports. A novel type of heterogeneous reusable catalytic system is created by the combination of nanochemistry technology, and magnetic solid supports, and heterogeneous properties. These catalysts have the advantages of homogeneous



Scheme 1. Preparation of catalyst (Fe₃O₄@HT@AEPH₂-Co^{II}).

catalysts, like excellent selectivity and activity [35-37].

Nowadays, Organic synthesis is explored considering the principle of green. Therefore, it is important to use an eco-friendly catalyst and moderate reaction circumstances. Hydrotalcite (HTs) and magnetic hydrotalcite (MHTs) have been investigated extensively to enhance the long-term stability and activity of catalysts. In organic reactions, they are investigated as a hopeful material for the catalyst support. Hydrotalcite is a layer double hydroxide (LDH) with abundant surface hydroxyl groups, Mg-Al mixed oxides, and anionic $(\rm CO_3^{2-})$ interlayers. The general formula of a layer double hydroxide is $[\rm M^{2+}$ (1-x)\rm M^{3+}x(OH)_2]^{x+} $[\rm A^{n-}x'/n-mH_2O]^{x-}$. $\rm M^{2+}$ is di metal ion, $\rm M^{3+}$ is a trivalent metal ion, and $\rm A^{n-}$ is the interlayer anion. Plentiful surface hydroxyl groups are made of alternating cationic layers ((MgMg_6AlAl_22(OHMg_6Al_2(OH))_{16}^{2+} as the brucite-like). Mg-Al mixed oxide is chemically active sites to be used for the catalytic reaction. They as well as acts as an anchoring site for metal

nanoparticles [38–46].

It is difficult to separate the catalysts based on hydrotalcite from the reaction medium by conventional centrifugation and filtration separation methods [40]. Using of a magnetic separation approach is a suitable technique [47] that can be applied using a simple magnetic bar when magnetic nanoparticles are incorporated into the hydrotalcite structure [41,42]. It also prevents the agglomeration of MNPs, as well.

In this paper, an amino-functionalized Fe₃O₄@HT nanoparticle carrier is prepared. It was prepared with 2-aminoethyl dihydrogen phosphate (AEPH₂). It is a short-chained bifunctional organic molecule. It also has both an amino group and a phosphate group. For binding by Fe₃O₄@HT NPs, the phosphate group of AEPH₂ is useful. Co^{II} immobilized onto aminated Fe₃O₄@HT (Fe₃O₄@HT@AEPH₂-Co^{II}) was also studied. Because in the bonding of several metal ions, the amino group can perform as a point of anchor. In the preparation of 1-substituted 1Htetrazoles, a new magnetically reusable heterogeneous catalyst was

Table 1

Entry

Preparation of tetrazole derivatives using Fe₃O₄@HT@AEPH₂-Co^{II} catalyst.

Substrate	Product	Time (h)	Yield (%)
NH ₂		1	95
NH ₂ NH ₂	$ \sum_{\text{I-phenyl-} IH-\text{tetrazole} } N $	3	70
NH ₂	N N N N $N1,2-di(1H-tetrazol-1-yl)benzeneMeO N N N N N1-(4-methoxyphenyl)-1H-tetrazole$	2.5	85
OMe NH ₂		2.5	85
Cl NH ₂ Cl	Γ -(4-chlorophenyl)- Γ / Γ -tetrazole	3	45
CI ^{NH} 2	1-(2,5-dichlorophenyl)-1 <i>H</i> -tetrazole HO (N) (N) (N) (N) (N) (N) (N) (N)	3	90
OH NH ₂ OH	$\begin{array}{c} OH \\ N \\ $	3	82
NH ₂	2-(1 <i>H</i> -tetrazol-1-yl)phenol $O_2N \longrightarrow N \longrightarrow N$	3	95
NO ₂ NH ₂	$\frac{1-(4-nitrophenyi)-1H-tetrazole}{N = N}$	3	70
O NH ₂	I-(naphthalen-1-yl)-1 <i>H</i> -tetrazole	2.5	75
NH2	(2-(1H-tetrazol-1-yl)phenyl)(phenyl)methanone	3	60
$\left[\sum_{N}^{S} \right]_{NH_2}$	2-(1 <i>H</i> -tetrazol-1-yl)benzo[<i>d</i>]thiazole	2.5	30

(continued on next page)

Table 1 (continued)



Reaction Conditions: amine (1.0 mmole), sodium azide (1.0 mmol), triethyl orthoformate (1.2 mmol), Fe₃O₄@HT@AEPH₂-Co^{II}, H₂O, 90 °C

investigated. It was $Fe_3O_4@HT@AEPH_2-Co^{II}$ that was prepared using standard procedures according to the literature (Scheme 1).

2. Experimental section

2.1. General methods

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. 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-*d*₆. All the yields refer to isolated products after purification by thin-layer chromatography or recrystallization.

2.2. Synthesis of hydrotalcite (HT)

The aqueous solution with a volume of 60 mL was spilled in a 250 mL flask. It was contained Al(NO₃)₃·9H₂O (20 mmol, 7.50 g) and Mg (NO₃)₂·6H₂O (40 mmol, 10.25 g). Then, 60 mL of the mixed solution added to the solution dropwise. The vigorous stirring was also applied at 60 °C. It was contained NaHCO₃ (7.5 g) and NaOH (10.25 g). The prepared suspension was stirred at 60 °C for 24 h. The resulted white solid was filtered and then washed using deionized water. To remove the alkali metal ions the final pH was reached 7. The resulted Mg-Al hydrotalcite (I) was dried for 12 h at 100 °C. Its molar ratio was Mg/Al = 2.

2.3. Synthesis of Fe₃O₄@Hydrotalcite (Fe₃O₄@HT):

A mixture containing 1.05 g (5.2 mmol) of FeCl₂·4H₂O and 2.1 g (8 mmol) of FeCl₃·6H₂O was dissolved in deionized water with a volume of 100 mL. A three-necked 500 mL round-bottom flask was used. It was equipped with dropping funnel and argon gas inlet tube. Under the Ar atmosphere and at 80 °C, the mixture was stirred for 5 to 10 min. Then, 100 mL of NaOH solution (5%) and 4 g of hydrotalcite were concurrently added into the solution. 24 h stirring of the suspension was the next step at 80 °C. The resulted from brown powder (Fe₃O₄@HT) was separated

by an external magnetic field. Then, it was washed with 2 \times 100 mL distilled water. When the pH reached 7, for 12 h, Fe_3O_4@HT was dried at 50 $^\circ\text{C}.$

2.4. Fe₃O₄@HT@AEPH₂ synthesis

 $\rm Fe_3O_4@HT$ (1 g) was added to a mix of deionization water/ethanol (50 mL). Then, 1.69 g (12 mmol) of 2-aminoethyl dihydrogen phosphate was added to the mixture. It was dissolved in deionized water (20 mL). Stirring continuously of the solution at 25 °C for 48 h. Subsequently, deionized water and ethanol were used to wash the consequential nanoparticles (2-aminoethyl dihydrogen phosphate-functionalized Fe₃O₄@HT) repeatedly. Then, they were separated by an external magnetic field and dried.

2.5. Fe₃O₄@HT@AEPH₂-Co^{II} synthesis

0.99 g (4.2 mmol) of CoCl₂·6H₂O was added to a mixture of 1 g of Fe₃O₄@HT@AEPH₂ and 50 mL of ethanol. Vigorous stirring was used to reflux the mixture. It took 48 h to obtain Fe₃O₄@HT@AEPH₂-Co^{II}. An external magnet and ethanol were used to collect and repeatedly wash the product, respectively. Then, it was dried in a vacuum for 6 h at 25 °C.

2.6. General synthesis for the preparation of 1-substituted 1H-tetrazoles

In a round-bottomed flask, 0.005 g of Fe₃O₄@HT@AEPH₂-Co^{II}, 1.2 mmol of triethyl orthoformate, 1 mmol of sodium azide, and 1 mmol of amine were placed. The mixture was stirred at 90 °C. TLC was used to monitor the reaction. The mixture was cooled to 25 °C when the reaction was completed. Then, it was diluted with 3×20 mL of ethyl acetate. An external magnet was used to remove the catalyst. Then, it was dried over anhydrous Na₂SO₄. Using EtOAc–hexane with a ratio of 1:9, a crystallization step was carried out after concentration. Melting points, ¹H NMR, and FT-IR were utilized for the characterization of products. The synthesized compounds spectral data are reported.

2.6.1. Analytical data

1-phenyl-1H-tetrazole (Compound 1, Table 1): yellow solid; m.p = 65-67 °C, IR (KBr)/ \mathscr{V} (cm⁻¹): 3063 (C-H, sp² stretch Ar), 1681 (C = N), 1591, 1463 (C = C); (3122, 3063, 2918, 1747, 1681, 1591, 1500, 1463,



Scheme 2. Synthesis of tetrazoles derivatives catalyzed by Fe₃O₄@HT@AEPH₂-Co^{II.}



Fig. 2. FT-IR spectra of (a) HT, (b) $Fe_3O_4@HT$ (c) $Fe_3O_4@HT@AEPH_2$ and (d) $Fe_3O_4@HT@AEPH_2-Co^{II}$.

1391, 1205, 1090, 1051, 995, 962, 912, 881, 762, 684, 506); $^1{\rm H}$ NMR (CDCl_3, 300 MHz) δ (ppm): 7.52–7.76 (m, 5H, Ar), 9.11 (s, 1H tetrazole).

1-benzyl-1H-tetrazole (Compound 15, Table 1): White solid; m.p = 132–133 °C; IR (KBr)/ \mathscr{V} (cm⁻¹): 3061 (C-H, sp² stretch Ar), 1644 (C = N), 1535, 1454 (C = C). (3272, 2929, 2857, 1592, 1458, 1406, 1360, 1297, 1244, 1200, 1130, 1001, 955, 880, 752, 695); ¹H NMR (CDCl₃, 300 MHz) δ (ppm) 4.46–4.48 (s, 2H), 7.29–7.40 (m, 5H), 8.25 (s, 1H).

1,2-di (1-H-tetrazole-1-yl) benzene (Compound 2, Table 1): White solid; m.p = 169–173 °C, IR (KBr)/ \mathcal{V} (cm⁻¹): 3060 (C-H, sp² stretch, Ar), 1620 (C = N) 1455, 1589 (C = C); (3315, 3060, 3003, 2934, 2857, 1617, 1586, 1457, 1409, 1360, 1297, 1244, 1200, 1133, 1004, 955, 882, 750, 632); ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 7.11–7.62 (m, 4H), 8.22 (s, 1HTetrazole).

3. Results and discussion

3.1. Characterization

Thermogravimetric analysis (TGA), scanning electron microscopy (SEM), FT-IR, energy-dispersive X-ray spectroscopy (EDX), and powder X-ray diffraction (XRD) were utilized to investigate the structure and



Fig. 3. TGA curve of Fe₃O₄@HT@AEPH₂-Co^{II.}

morphology of the catalyst.

In this study, an environmentally benign heterogeneous catalyst was used to synthesize 1-substituted-1Htetrazole derivatives 4(a-o). H₂O was the solvent. Advantages include catalyst stability and recyclability, purity, and yield of products, reaction times, and useful methods. It has a wide range of applications. It is also compatible with various functional groups (electron-withdrawing/electron-donating) (Scheme 2).

3.1.1. FT-IR spectroscopy:

The catalyst structure was defined using FT-IR spectroscopy to confirm the existence of the bonded species. Fig. 2 represents the FT-IR spectra of HT, $Fe_3O_4@HT$, $Fe_3O_4@HT@AEPH_2$, and $Fe_3O_4@HT$. $T@AEPH_2$ - Co^{II} . For HT, the broadbands which were displayed in the range of 3130–3627 cm⁻¹ were assigned to OH group stretching and the absorption band which was around 1633 cm⁻¹ was caused by the flexural oscillation peaks of interlayer water molecules [48]. Also, the absorption peaks around 1369 cm⁻¹ were considered to be caused by the asymmetric stretching bond of intercalated NO_3^{2-} [49]. This indicates the presence of a small number of carbonate ions in the LDH phase. Al–OH stretching may be responsible for the bond at 667 and 733 cm⁻¹ [50]. The lattice vibration of metal–oxygen bonds (M–O) was responsible for the absorption peaks around 550–770 cm⁻¹ (Fig. 2a) [51].

In Fig. 2b, the principal bands were observed at $3250-3400 \text{ cm}^{-1}$ which is a broad absorption band attributed to stretching frequencies of hydroxyl groups and bound water on the surface of Fe₃O₄ NPs, 1010 and 864 cm⁻¹ which are asymmetric and symmetric stretching vibrations characteristic of Fe–O–H bond, and 580–620 cm⁻¹ which is attributed to the vibrational frequency of Fe–O bond [52–54].

In the FT-IR spectrum of $Fe_3O_4@AEPH_2$ (Fig. 2c) due to the stretching vibration of P = O, the characteristic band of $Fe_3O_4@AEPH_2$ appears at 1128 cm⁻¹. Two absorption bands at 1034 and 977 cm⁻¹ (asymmetric and symmetric stretching vibrations) confirm the presence of the P–O–Fe bond. Also, absorption bands at 1093, 984, and 570–605 cm⁻¹ are attributed to the asymmetric and symmetric stretching and bending vibrations of O–P–O bond, respectively. The broad characteristic band of Fe–O at around 580–620 cm⁻¹ covers the latter absorption



Fig. 4. SEM images of Fe₃O₄@HT@AEPH₂-Co^{II.}



Fig. 5. Energy dispersive X-ray analysis (EDAX) of Fe₃O₄@AEPH₂-Co^{II.}

band. Two absorption bands at 3564 and 3590 cm⁻¹ correspond to $-NH_2$ stretching frequencies. Two other absorption bands at 1617 and 1289 cm⁻¹ are also assigned to–NH bending vibration and –CN stretching vibration, respectively (Fig. 2c) [53].

The presence of an absorption band at 447 cm⁻¹ in the FT-IR spectrum of Fe₃O₄@AEPH₂-Co^{II}, confirms the coordination of Co^{II} on aminated Fe₃O₄ NPs. Structural vibrations of Fe₃O₄ NPs covers this absorption due to Co–N vibration (Fig. 2d). Upon coordination of Co^{II} on aminated Fe₃O₄ NPs, the intensities of –NH₂ stretching bands are decreased significantly [53].

3.1.2. Thermal gravimetric analysis (TGA)

Two weight losses were observed in the Fe₃O₄@HT@AEPH₂-Co^{II} TGA thermogram (Fig. 3). Hydrogen and by physically bonded water in the Fe₃O₄@HT@AEPH₂-Co^{II} structure is responsible for the weight loss by 15% at 27–250 °C. On the other hand, the organic segment decomposition anchored to the surface of the Fe₃O₄ NP is responsible for the weight loss by 20% at 250–450 °C. According to the thermogram, the AEPH₂ amount combined on Fe₃O₄ NPs is 20% (wt%). Therefore, Fe₃O₄@HT@AEPH₂-Co^{II} high thermal stability is confirmed by the removal of the pendent organic group at the elevated temperature that is

a conformation for the AEPH₂ covalent bonding on the Fe_3O_4 NPs' surface [53].

3.1.3. SEM-EDS images and SEM image combined EDS-elemental mapping:

 Fe_3O_4 @HT@AEPH₂-Co^{II} size and morphology was studied with field emission electron microscopy (FE-SEM). Fig. 4 presents the images. According to Fig. 5, the results of EDX analysis confirms C, P, O, Mg, Fe, Co, and Al presence. It was also confirmed that Co^{II} is supported on aminated Fe_3O_4 NPs.

The special structure of the synthesized $Fe_3O_4@AEPH_2-Co^{II}$ have been studied by elemental mapping evaluation of the nanoparticle affirmed the existence of P, O, Al, Ca, Fe, Mg, and Co in construction occurred (Fig. 6).

3.1.4. X-ray diffraction (XRD) analysis:

The crystalline structure of HT, $Fe_3O_4@HT$, and $Fe_3O_4@AEPH_2-Co^{II}$ was identified by XRD. The characteristic diffraction peaks of a wellcrystallized HT phase (JCPDS NO. 22–0452) was presented by MgAl-LDH at 20 of 11.69°, 35.05°, 61.04°, and 62.03°, corresponding to the reflections of planes (001), (100), (110), and (111), respectively. The successful synthesize of the HT was determined by the diffraction peaks



Fig. 6. Elemental mapping analysis of Fe₃O₄@AEPH₂-Co^{II.}



Fig. 7. XRD patterns of (a) HT, (b)Fe $_3O_4@HT$, (c)Fe $_3O_4@HT@AEPH_2-Co^{IL}$

(Fig. 7a) [47]. Fig. 7b presents that all the diffraction peaks can be indexed to (2, 2, 0), (3, 1, 1), (4, 0, 0), (4, 2, 2), (5, 1, 1) and (4, 4, 0) reflections which match well with the characteristic peaks of cubic structure (JCPDS 19–0629). We can conclude that the crystalline structure of Fe₃O₄ NPs is conserved after the surface modification with AEPH₂ and Co^{II} because the peak positions of Fe₃O₄ NPs (Fig. 7b) are unchanged during the production of Fe₃O₄@AEPH₂-Cu^{II} (Fig. 7c). Using the Debye–Scherrer equation $d = K \lambda/\beta \cos \theta$, the average crystallite sizes, d, of HT, Fe₃O₄@HT, and Fe₃O₄@AEPH₂-Cu^{II} calculated to be about 18.3, 30.3 and 45.6 nm, respectively [53].

3.1.5. Vibrating sample magnetometer (VSM) analysis

Fig. 8 presents the Fe_3O_4 @HT, and Fe_3O_4 @AEPH₂-Co^{II} M-H hysteresis curves. The superparamagnetic characteristic of Fe_3O_4 @AEPH₂-

 Co^{II} and Fe_3O_4 NPs is concluded from the room-temperature magnetization curves. The saturation magnetizations are 7.21 and 18.83 emu. g^{-1} for $Fe_3O_4@AEPH_2-Co^{II}$ and $Fe_3O_4@HT$, respectively. The surface-bound AEPH_2-Co^{II} presence was confirmed by a decrease in the $Fe_3O_4@AEPH_2-Co^{II}$ saturation magnetization.

3.2. Optimization of the reaction conditions

0.01, 0.008, 0.005, 0.003, and 0.001 g (Fig. 9) of the catalyst were investigated to obtain the optimum catalyst concentration. These different concentrations were investigated at 90 $^\circ C$ where H₂O was the solvent.

In the absence of a catalyst, the model reaction was completed in 6 h with a poor yield of 5% (see Fig. 9). Then, 0.01, 0.008, 0.005, 0.003, and



Fig. 8. M-H hysteresis curves of Fe₃O₄@HT (red curve), and Fe₃O₄@H-T@AEPH₂-Co^{II} (black curve). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

0.001 g of the catalyst were investigated in terms of yield and time. An increase by 70–95% was obtained in the yield by any subsequent increase in the catalyst concentration by 0.001 g. Fig. 4 suggests that the optimum yield is achieved using 0.005 g (0.00015 mol%) of the catalyst at 90 °C. When the catalyst content is less than 0.005 g (0.00015 mol%), the yield is in the range of 70–90%, and the reaction time is higher. When the catalyst content is more than 0.005 g, better yield didn't achieve. The catalyst surface saturation is the possible reason.

Various temperatures were also investigated to optimize the reaction temperature. The solvent was H₂O. The yield was better and the reaction time was shorter increasing the temperature from 25 °C to 90 °C. At 25 °C, the yield and time were 5% and 4.5 h. The yield is better increasing the temperature together with stirring (5–97%) (Fig. 10). But, no improvement was observed increasing the temperature up to 110 °C. Therefore, 90 °C was considered as the optimal temperature.

In the end, the influences of various solvents were investigated on the model reaction. Some organic solvents including ethanol, acetonitrile, H_2O , and DMSO were investigated. According to Fig. 11, the most effective solvent for the preparation of tetrazoles is H_2O .

Scheme 2 presents the general procedure of the experiment. The reaction of sodium azide and triethyl orthoformate was carried out with various amines using optimized reaction conditions. Short reaction times and high to excellent yields were achieved producing the corresponding 1-substituted 1H-tetrazoles. The reaction of several anilines with sodium azide and triethyl orthoformate was carried out in the presence of 0.005 g of Fe₃O₄@HT@AEPH₂-Co^{II}. Table 1 summarizes the

results.

Condensation of electron-withdrawing and electron-donating groups contained anilines was carried out. The groups include chloro, bromo, acetyl, and methyl. The reaction times were short and the isolated yields were excellent. The results are better in the case of the *para*-position anilines (see Table 1, entry 6) compared to the *ortho*-position anilines (see Table 1, entry 7). The steric hindrance on product formation is more for the *ortho*-position anilines. The spectral and physical data of all known compounds were compared



Fig. 10. The effect of diverse temperatures in the preparation of tetrazoles by $Fe_3O_4@AEPH_2-Co^{II}$. Conditions of reaction: aniline (1 mmol), triethyl orthoformate (1.2 mmol), sodium azide (1 mmol), in H₂O, 0.005 g of $Fe_3O_4@AEPH_2-Co^{II}$.



Fig. 11. The effect of diverse solvents in the preparation of tetrazoles by $Fe_3O_4@AEPH_2-Co^{II}$. Conditions of reaction: aniline (1 mmol), triethyl orthoformate (1.2 mmol), sodium azide (1 mmol), 0.005 g of $Fe_3O_4@AEPH_2-Co^{II}$.

Amount of Catalyst (g) Amount of Catalyst (mol%) Time (min) Vield (%)



Fig. 9. The effect of diverse catalysts in the preparation of tetrazoles by $Fe_3O_4@AEPH_2-Co^{II}$. Conditions of reaction: aniline (1 mmol), triethyl orthoformate (1.2 mmol), sodium azide (1 mmol), in H₂O, at 90 °C.



Scheme 3. The suggested mechanism for the synthesis of tetrazoles with Fe₃O₄/HT-NH₂-Co^{II.}

to the literature to be characterized.

3.3. Mechanism

Scheme 3 presents the possible $Fe_3O_4@HT@AEPH_2-Co^{II}$ catalyzed the mechanistic pathway for the tetrazole derivatives synthesis. There is a possible important role for the catalyst Co (II) in the cyclization procedures promotion. It is believed that the ethoxy group of triethyl *ortho*formate is activated by $Fe_3O_4@HT@AEPH_2-Co^{II}$. Besides, its elimination is facilitated using the catalyst. Cleaving the triethyl *ortho*-formate C–O bond is the mechanism to generate carbenium ion (I). The oxygen atom of other ethoxy groups and nucleophilic attack of the amine stabilized it. Then, the second ethoxy group producing carbenium ion (II) expulses. The neighboring N or O atom can stabilize it. Stabilizing takes place forming either the iminium (B) or oxonium (A) cation, respectively. Because of the greater basicity of nitrogen, an iminium cation formation is preferred. Then, the proposed imidoylazide intermediate (III) is formed by the azide anion sequential attack [34,35]. Cyclized tetrazoles



Fig. 12. Recyclability of Fe₃O₄@HT@AEPH₂-Co^{II} in the preparation of tetrazole. Conditions of reaction: aniline (1 mmol), triethyl orthoformate (1.2 mmol), sodium azide (1 mmol), at 90 °C, H₂O as a solvent, 0.005 g of Fe₃O₄@AEPH₂-Co^{II}.

Table 2

Comparison of results by Fe₃O₄@HT@AEPH₂-Co^{II} with various catalysts.

Entry	Catalyst	Reaction conditions	Time (h)	Yield (%)	Ref.
1	Natrolite zeolite	Solvent free – 120 °C	4	80–94	[28]
2	Cu NPs/bentonite	Solvent free – 120 °C	3	83–95	[56]
3	NHTf ₂	Glycerol – r.t.	3	84–95	[57]
4	ZnS nanoparticle	Solvent free – 130 °C	3–7	56–78	[58]
5	ZnS nanoparticle	US, DMF, r.t.	0.5	70–92	[59]
6	Ag ₂ O	AcOH – 100 °C	0.5	85–93	[60]
7	Fe ₃ O ₄ @silica sulfonic acid	Solvent free – 100 °C	0.5 – 3	78–97	[61]
8	Fe ₃ O ₄ @HT@AEPH ₂ - Co ^{II}	$H_2O=90\ ^\circ C$	1	95	This work

Reaction conditions: aniline (1 mmol), sodium azide (1 mmol), triethyl orthoformate (1.2 mmol)

4(a–o) is formed when the fourth nitrogen atom comes within the bonding distance after bending away of the three nitrogens from the linear arrangement [55].

3.4. The catalyst reusability

An outstanding characteristic of the proposed catalyst is its reusability. Under optimal circumstances, the catalyst recovery possibility was studied for the triethyl orthoformate, aniline, and sodium azide reactions. An external magnet was used to recover the catalyst. Then, ethyl acetate was used to wash the recovered catalyst. As presented in Fig. 12, with no significant catalytic activity deterioration, 5 times of reusing were obtained.

3.5. Comparison of the proposed catalyst with other catalysts

In the model reaction, the proposed catalyst activity was measured and a comparative study was carried out to compare the proposed catalyst with heterogeneous catalysts. The reaction took a prolongedtime period and the yields were not satisfactory investigating the model reaction with catalysts natrolite zeolite, Cu NPs/bentonite, NHTf₂, and ZnS nanoparticle (see Table 2, entries 1–4). Using Ag₂O and Fe₃O₄@silica sulfonic acid as catalysts, relatively good performance for the preparation of 1-phenyl-1H-tetrazole was obtained (see Table 2, entries 6 and 7). For the present synthetic protocol, the benefit of this catalyst over other catalysts is the usage of green solvent and less time than some other catalysts.

4. Conclusion

Fe₃O₄@HT@AEPH₂-Co^{II} was introduced as a reusable and efficient catalyst in the preparation of 1-substituted 1H-tetrazoles from a sodium azide, triethyl orthoformate, and amine. Organic synthesis could be enhanced improving the catalytic investigation on new approaches toward magnetic nanoparticles. A high surface area is provided by the magnetic nanocatalyst to interact with compounds. Due to the simple Fe₃O₄@HT@AEPH₂-Co^{II}, was introduced as a reusable and efficient catalyst in the preparation of 1-substituted 1H-tetrazoles from a sodium azide, triethyl orthoformate, and amine. Organic synthesis could be enhanced improving the catalytic investigation on new approaches toward magnetic nanoparticles. A high surface area is provided by the magnetic nanocatalyst to interact with compounds. Due to the simple recyclability of the catalyst, a new way could be provided for continuous processes. Chief advantages of the proposed catalyst include solvent-free conditions, good yields, nontoxicity, a very easy operation, recyclability, and short reaction times. By an external magnet, recovery of the catalyst

can be easily carried out from the reaction medium. On the other hand, with no significant catalytic activity deterioration, the catalyst could be reused 6 times.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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