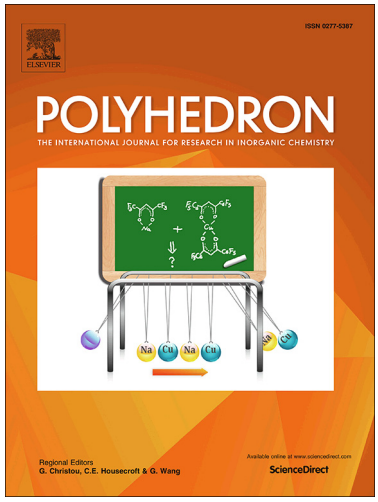


# Immobilization of Gd (III) complex on $Fe_3O_4$: A novel and recyclable catalyst for synthesis of tetrazole and S-S coupling

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# Immobilization of Gd (III) complex on $Fe_3O_4$: A novel and recyclable catalyst for synthesis of tetrazole and S-S coupling

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**Abstract**

In the present work, a novel catalysts prepared by the anchoring of Gd (III) complex with OH groups on the surface of $Fe_3O_4$ in which characterized by FT-IR, TGA, XRD, EDX, VSM, and ICP-OES techniques and tested in the synthesis of tetrazoles and S-S coupling. This designed methods indicated several advantages including easily recovered from the reaction mixture by magnetic field, several consecutive cycles without noticeable change in its catalytic activity, the use of green solvent, the use of aspartic acid as green ligand, chemical and physical stability of obtained catalyst, short time reaction and good to excellent isolated yields of all product. Also, up to date, Gd(III) complex don't used for the synthesis of tetrazoles and S-S coupling.

**Keywords** Recoverability, Gd, $Fe_3O_4$, Disulfide, Teterazole

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## 1. Introduction

The Heterogeneous catalysts have been known for decades and have become an effective strategy for efficient and environmentally friendly organic chemistry, and their efficiency has become increasingly effective [1, 2]. There are several types of heterogeneous catalysts, such as zeolites, mixed metal oxides, solid-supported catalysts, hydrotalcites, resins, polymers, etc [3]. Nanocatalysts, due to the small size (1-100 nm) and the presence of exposed metal atoms on the surface, are an important and emerging field in catalyst science and also minimizes the cost for each operation [4-6]. One of the most important and growing arena in heterogeneous catalysts is solid-supported catalysts [7]. Nanosupports such as $ZrO_2$, MgO, $Al_2O_3$, CaO, $Fe_3O_4$ and $SiO_2$, have attracted much attention due to their large surface area, versatile physical surface, good catalytic properties, inherent adsorptive properties and applications in catalysts [8-14]. In pursuit of green chemistry efforts, nanocatalysts are another field of exploration that avoids the use of flammable organic solvents, toxic reactions, hazardous reaction conditions and / or harsh conditions and extreme separation [15-17]. The use of green solvents, catalysts and alternative energy sources is essential for the development of a sustainable protocols [18-20]. Magnetite nanoparticles are one of the most widely used research and applied materials in various fields, including biotechnology, biomedicine, separation, catalytic, magnetic resonance imaging (MRI) and etc. Magnetite is an ideal supportable oxide, which is easily prepared, and has a very active surface for adsorption or immobilization of metals and ligands that can be separated by magnetic decantation after the reaction, thereby improving its efficiency, and its catalytic stability is maintained for several times [21]. In recent years, successfully supported magnetite catalysts using organic compounds as ligand or linker have been used for many important chemical reactions. Many scientists have used various metal-supported magnetite nanoparticles ($Fe_3O_4$-M) in many organic chemical reactions.

(Whether with or without the use of supported ligands) [22]. Supported nanomagnatite catalysts are emerging and comprehensive catalysts in the heterogeneous catalytic domain that are suitable for the development of suitable protocols. It opens the gats for a wide variety of research protocols that scientists work on, such as mannich type reactions, C–C, C–S, and C–O coupling reactions, coupling of thiophenols, alkylation, oxidation, reductions, click reactions, multicomponent synthesis, and asymmetric synthesis, among other named reactions. [22]. Supported nanomagnetite catalysts are an excellent and growing research field in catalytic science that has harmonies with the goals of green chemistry and the synthesis and development of organic chemistry. The most important aspect in the magnetic catalyst is the design and support of a specific ligand or metal as a catalyst in a particular organic reaction, which should be considered mechanically and the possibility of such a reaction on a laboratory scale with the potential of industrial application. Also, therecycling capability is one of the prominent features of the popularity and applications of nanomagnetite catalysts [22]. Selective oxidation of sulfides to sulfoxide and disulfides is one of the important methods for the synthesis of some chemical and biological drugs [23]. Sulfoxides play an important role in the activation of enzymes. Other roles of these compounds include anti-fungal, anti-hypertensive, antibacterial and anti-atherosclerotic effects, and other important biological functions. [24-25]. Disulfides, as oxidative products of thiol compounds, are beneficial in biological and chemical fields such as DNA dispersing properties, peptide stabilization in the three-dimensional structure of proteins, protective groups, and the effects of vulcanization of rubber [26,27]. To synthesize disulfides, the oxidation of thiols to disulfide is very common and desirable. Furthermore, there are reports of S-S coupling reactions with several supported metals heterogeneous catalysts such as MCM-41-Adenine-Zr [28], $Fe_3O_4$-AMPD-Cu [29], $Fe_3O_4$–adenine–Zn [30], Therefore, the search for the possibility synthesis of

these compounds under mild reaction conditions with recoverable effective heterogeneous catalyst is still in high demand. On the other hand, 1H-tetrazoles form an important category of heterocyclic compounds due to their application in pharmaceutical science and materials, including explosives and photography [31, 32]. These compounds can act as an isosteric replacement for carboxylic acids in drug design. [31]. Also, mentioned materials have biological activity such as antibacterial activity, antiviral, antifungal, analgesic, antiulcer, antiinflammatory, and antihypertensive activities [33-39]. The tetrazolium compounds have the ability to interact with metals and can be used as agents for the coordination of various metals ions [40]. These compounds are typically prepared by adding azide salts to organic nitriles or cyanides. [41-43]. Several syntheses of 1H-tetrazoles have been reported through the [3+2] cycloaddition of nitriles using $NaN_3$ or $TMSN_3$ in the presence of hetrogenious catalysts such as $FeCl_3$–$SiO_2$ [44], Zn/Al hydrotalcite [45], nano ZnO [46], montmorillonite K-10 [47], montmorillonite K10-Cu [48], CoY Zeolite[49], Nickel Zirconium phosphate nanoparticles [50], $CoFe_2O_4$@glycine-M (M= Pr, Tb and Yb) [51], MCM-41@AMPD@Zn [52], and Ni (II) on $Fe_3O_4$@tryptophan [53]. So far, there is no report on the use of gadolinium metal for the synthesis of disulfide coupling and 1H-tetrazoles. Gadolinium has been used as a catalyst in various reactions such as Lewis acid catalyst for acetylation of alcohols and phenols [54], catalyst for degradation of organophosphate pesticide [55], Hantzsch reaction [56], the synthesis of isoprene Rubber [57], polymerization of 1,3-Butadiene [58], heterogeneous recyclable Lewis acid catalyst for Michael additions [59], catalyst for acetylation of alcohols and amines [60]. Up to date, various catalysts reported in the the synthesis of N-containing heterocyclic compounds [61-63]. But, the use of Gd magnetic catalyst has not been shown in previous reports for the synthesis of N-containing heterocyclic compounds in the short reaction time and good to excellent yields. Based on mentioned introduction, we try to report of synthesis a novel catalyst

by anchoring Gd(III) complex on surface of $Fe_3O_4$ in order to one-pot synthesis of 1H-tetrazoles and S-S coupling. It was be found that obtained catalysts can be reused for several times without significant degradation in activity.

## 2. Experimental

### *2.1. Preparation of $Fe_3O_4$@L-aspartic-Gd*

$Fe_3O_4$ nanoparticles were prepared by a simple and versatile procedure following a previous reports [30]. In order to synthesis of chloro-functionalized $Fe_3O_4$, 1.0 g of $Fe_3O_4$ was added to a solution containing 1.5 mL of 3-chloropropyltrimethoxysilane (CPTMS) and toluene (30 mL) and stirred under reflux condition for 24 h. The obtain powder was separated be magnetic field, washed with hexane dried at 60 °C. Then, 1.5 mL of triethylamine was gradually added to a suspension containing 1g of chloro-functionalized $Fe_3O_4$ and 0.27 g of L-aspartic as ligand in which refluxed for 48 h and washed with ethanol/water to give $Fe_3O_4$@L-aspartic nanoparticles. Finally, 1 g of $Fe_3O_4$@L-aspartic nanoparticles and 0.86 g of $Gd(NO_3)_2$ was dispersed in ethanol and refluxed for 16 h to obtained $Fe_3O_4$@L-aspartic-Gd. In over step, obtained powder was separated with magnetic field and dried at 60 °C.

### *2.2. General procedure for the synthesis of disulfides*

A mixture of thiol (1 mmol) and $H_2O_2$ (37%) was stirred in solvent-free conditions at room temperature in presence of 0.006 g of $Fe_3O_4$@L-aspartic-Gd as catalyst. Progress of the reaction was monitored by TLC. After completion, the catalyst was separated by magnetic field and crystallized to obtain pure product.

*2.3. General procedure for the synthesis of 5-substituted tetrazoles*

A mixture of nitrile (1 mmol), sodium azide (1.2 mmol), $Fe_3O_4$@L-aspartic-Gd (0.05 g) in PEG (2 mL) at 100 °C was stirred in appropriate time. After the completion of reaction, HCl (4 N, 10 mL) was added to mixture. Then, the resultant organic layer was extracted with ethyl acetate and washed with distilled water to obtain corresponding tetrazoles. It was purifies over preparatory TLC.

*2.4. Selected spectral data*

**5-(4-Nitrophenyl)-1H-tetrazole** $^1$H NMR (400 MHz, DMSO, ppm): $\delta_H$= 8.22–8.28 (m, 2H), 8.35–8.42 (m, 2H).

**2-(1H-Tetrazol-5-yl)phenol** $^1$H NMR (400 MHz, DMSO, ppm): $\delta_H$= 8.1 (s, 1H), 7.51-753 (m, 1H), 7.21 (d, *J*= 6.2, 1H), 7.09–7.13(m, 1H), 11.22 (br, 1H).

**5-(4-Bromophenyl)-1H-tetrazole** $^1$H NMR (400 MHz, DMSO, ppm): $\delta_H$= 7.87–8 (m, 4H).

**5-(4-Hydroxy)-1H-tetrazole** $^1$H NMR (400 MHz, DMSO, ppm): $\delta_H$= 8.12-8.15 (m, 2H), 8.41–8.44 (m, 2H).

**1,2-Di(naphthalen-2-yl)disulfane** $^1$H NMR (400 MHz, DMSO): $\delta_H$= 7.52–7.57 (m, 4H), 7.66–7.76 (m, 2H), 7.91–7.95 (m, 4H), 7.96-8.03 (m, 2H), 8.04 (s, 2H) ppm.

**1,2-Bis(4-bromophenyl)disulfane** $^1$H NMR (400 MHz, $CDCl_3$): $\delta_H$= 7.45 (t, *J* = 8.2, Hz, 4H), 7.55 (t, *J* = 8.2 ,4H) ppm.

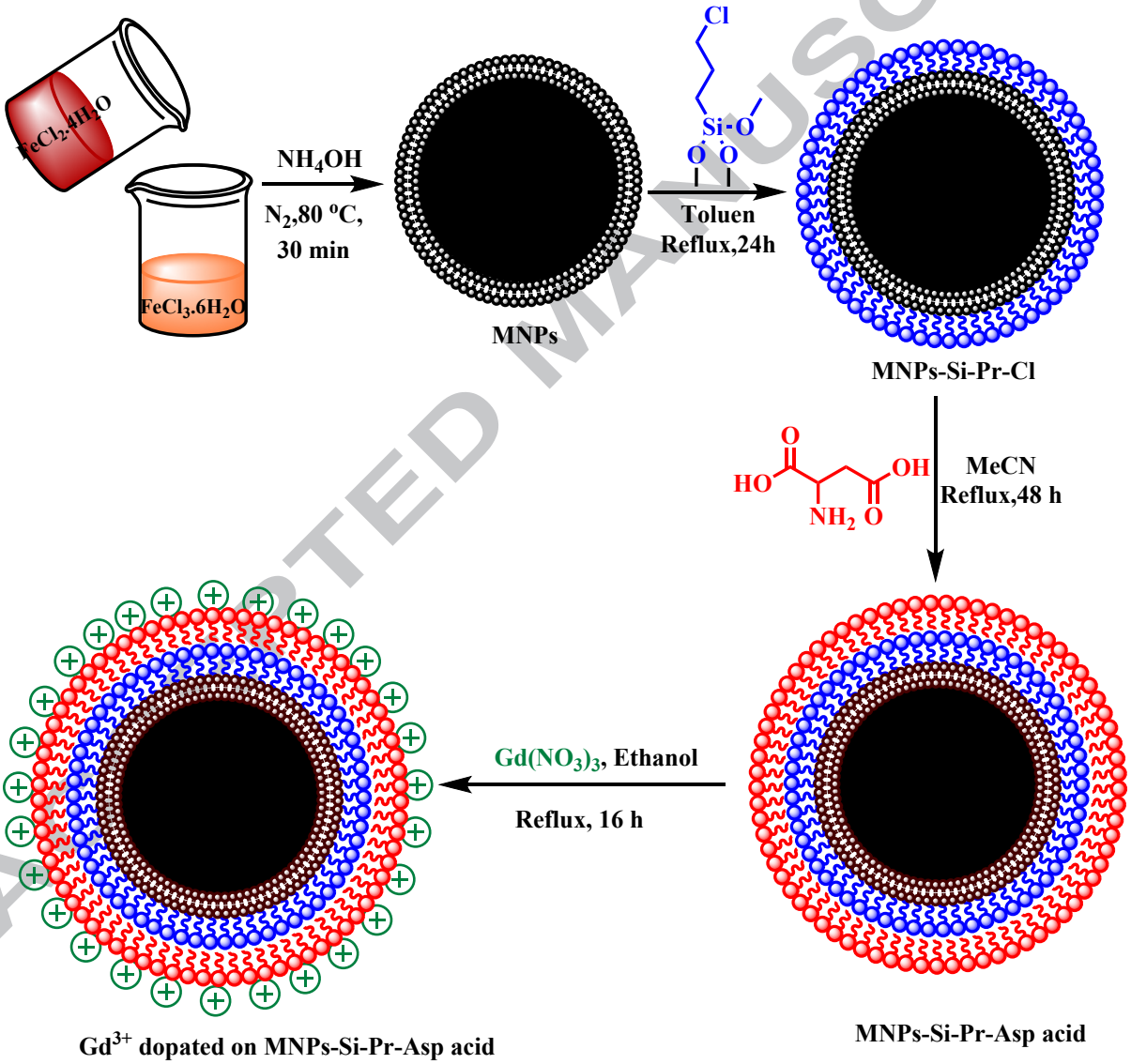
**1,2-Bis(4,6-dimethylpyrimidin-2-yl)disulfane** $^1$H NMR (400 MHz, $CDCl_3$, ppm): $\delta_H$= 2.53 (s, 12H), 6.89 (s, 2H) ppm.

**Dibenzyl disulfide** $^1$H NMR (400 MHz, DMSO, ppm): $\delta_H$= 4.02 (s, 2H), 4.2 (s, 2H), 7.36–7.37 (m, 4H), 7.38–7.45 (m, 6H).

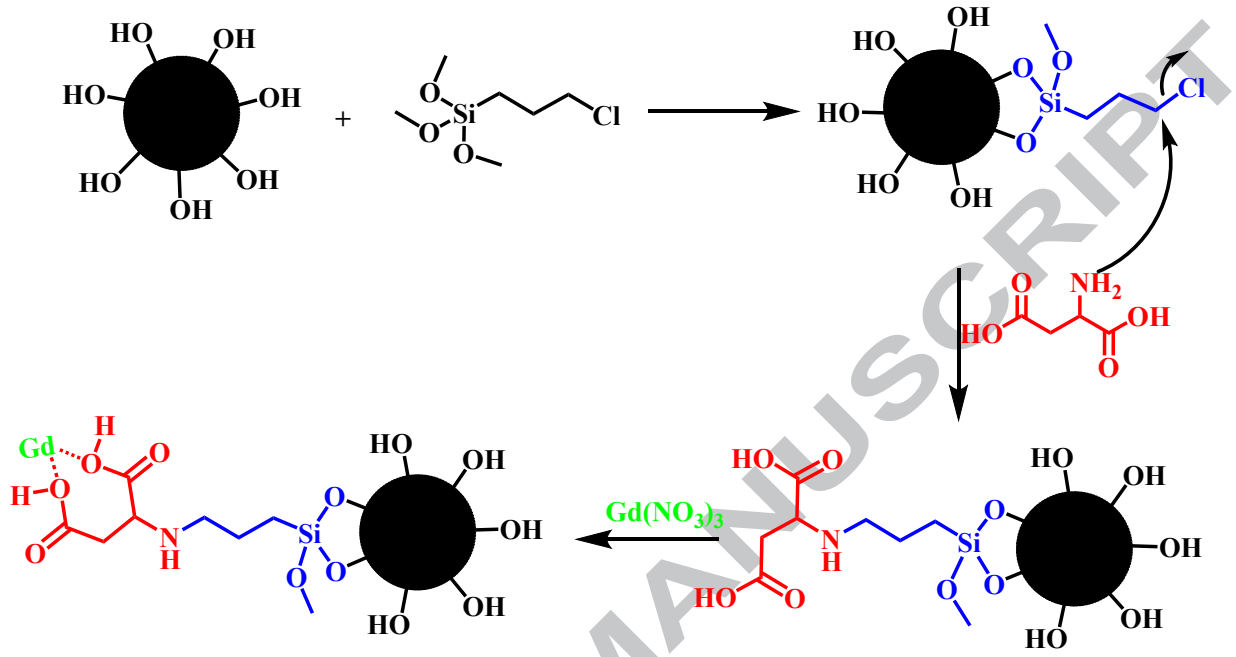
## 3. Results and discussion

### *3.1. Preparation of catalyst*

In this study, Gd complex immobilized on the surface of $Fe_3O_4$ and proposed the mechanism for synthesis of catalyst (Scheme 1 and 2).



**Scheme 1**. Synthesis of catalysts.




**Scheme 2.** Proposed mechanism for synthesis of catalyst.

*3.2. Catalyst characterization*

FTIR spectra for the $Fe_3O_4$ nanoparticles, chloro-functionalized $Fe_3O_4$, $Fe_3O_4$@L-aspartic and $Fe_3O_4$@L-aspartic-Gd was shown in Fig. 1. All samples were shown the strong absorption at approximately 580 $cm^{-1}$ in which attributed to the presence of Fe–O stretching vibration. FTIR spectra of chloro-functionalized $Fe_3O_4$, $Fe_3O_4$@L-aspartic and $Fe_3O_4$@L-aspartic-Gd was shown the absorption peaks at approximately 2850–2975$cm^{-1}$ in which attributed to the presence of C–H stretching vibration. Absorption band at nearly 1385 $cm^{-1}$ (C–N stretching vibration) and absorption peak at approximately 1685$cm^{-1}$ (C=O stretching vibration) in the $Fe_3O_4$@L-aspartic and $Fe_3O_4$@L-aspartic-Gd were confirmed the grafting of L-aspartic on the surface of $Fe_3O_4$ nanoparticles.

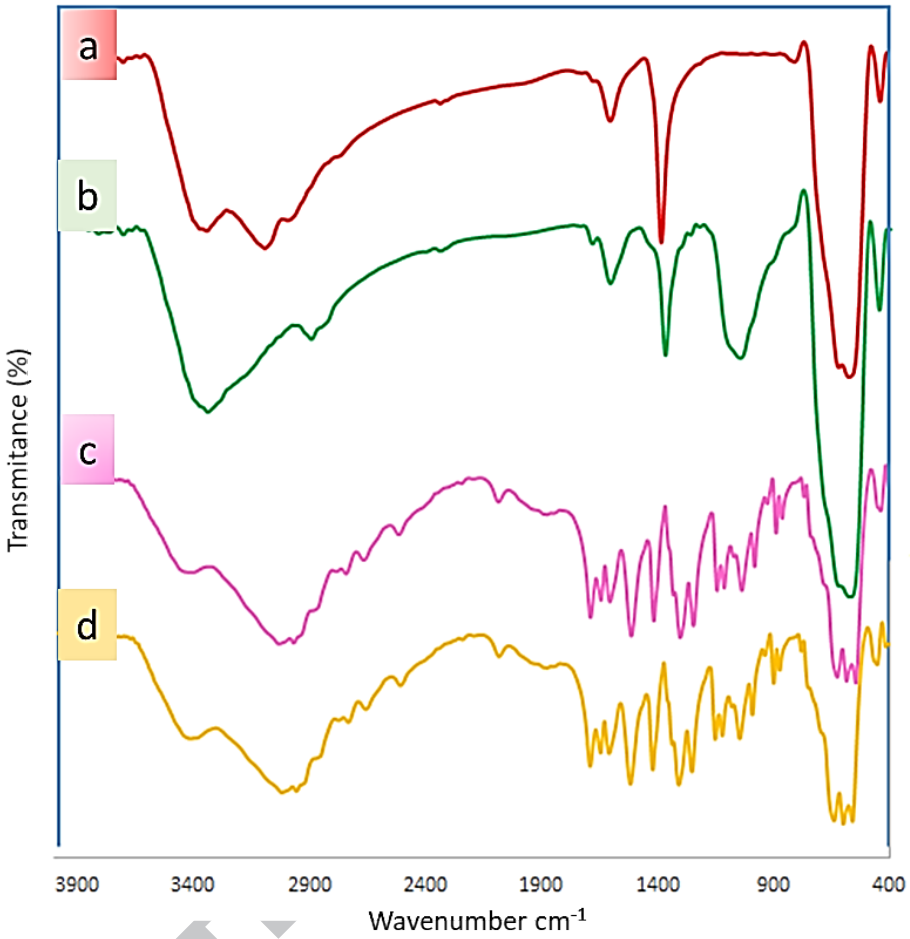



**Fig. 1** FTIR spectrum for bare $Fe_3O_4$ nanoparticles (a), chloro-functionalized $Fe_3O_4$ (b), $Fe_3O_4$@L-aspartic (c) and $Fe_3O_4$@L-aspartic-Gd (d).

The quantitative determination of the organic groups supported on the surface of $Fe_3O_4$ magnetic nanoparticles was investigated by thermo-gravimetric analysis (TGA) in Fig. 2. The small amount of weight loss below 200 °C was contributed to removal of physically adsorbed solvent on the surface of $Fe_3O_4$. Previously reports confirmed that the weight loss of about 2% between 200 and 600 °C was shown that related to decomposition of functional groups chemisorbed onto the surface

of magnetic nanoparticles [29]. As shown in Fig. 2, weight loss of about 11% between 200 and 600 °C was shown that related to decomposition of organic groups chemisorbed onto the surface of magnetic nanoparticles such 3-cholorthreemetoxysilan and L-aspartic.

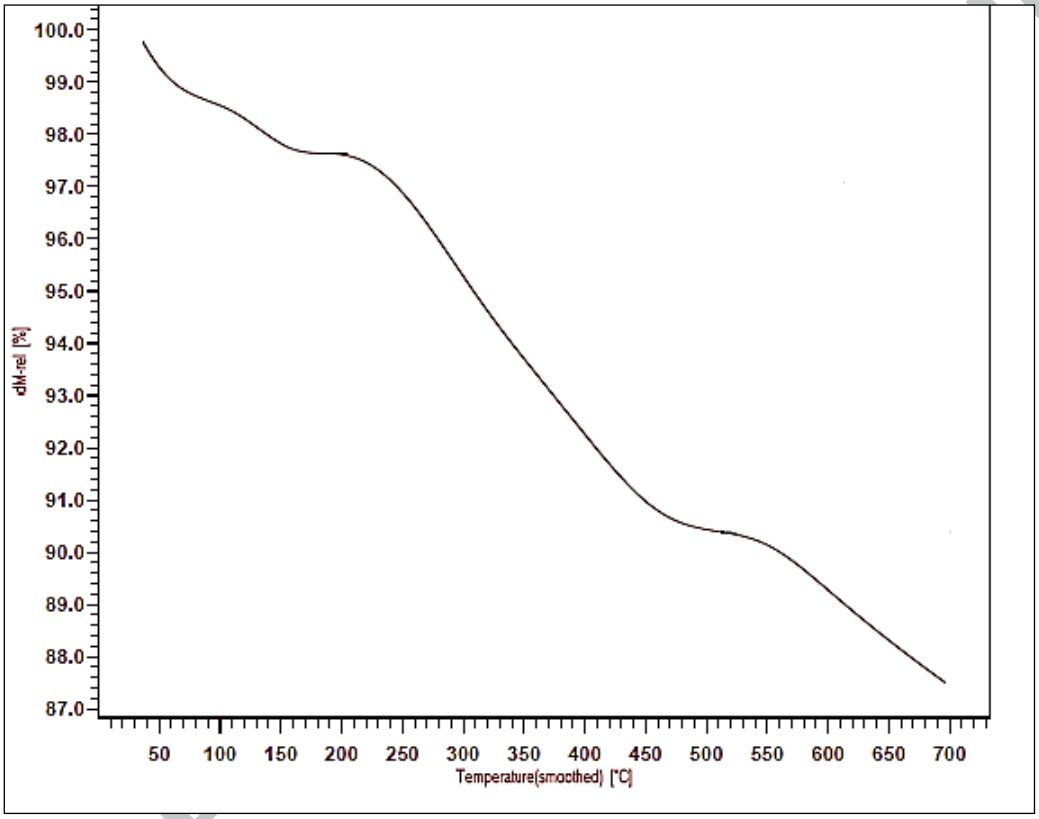



**Fig. 2** The TGA diagrams of $Fe_3O_4$@L-aspartic-Gd (d).

As shown in Fig. 3, surface morphology, the particle shape and fundamental physical properties of the $Fe_3O_4$@L-aspartic-Gd studied by Scanning Electron Microscopy (SEM) in which shown synthesized nanocatalyst have uniform nanometer-sized. Based on the synergistic effects theory, obtained morphology assisted to maximize the simultaneous

increasing of the catalyst efficiency and frequency of molecular interactions (higher yields) or decreasing activation energy of rate determining step (lower times).

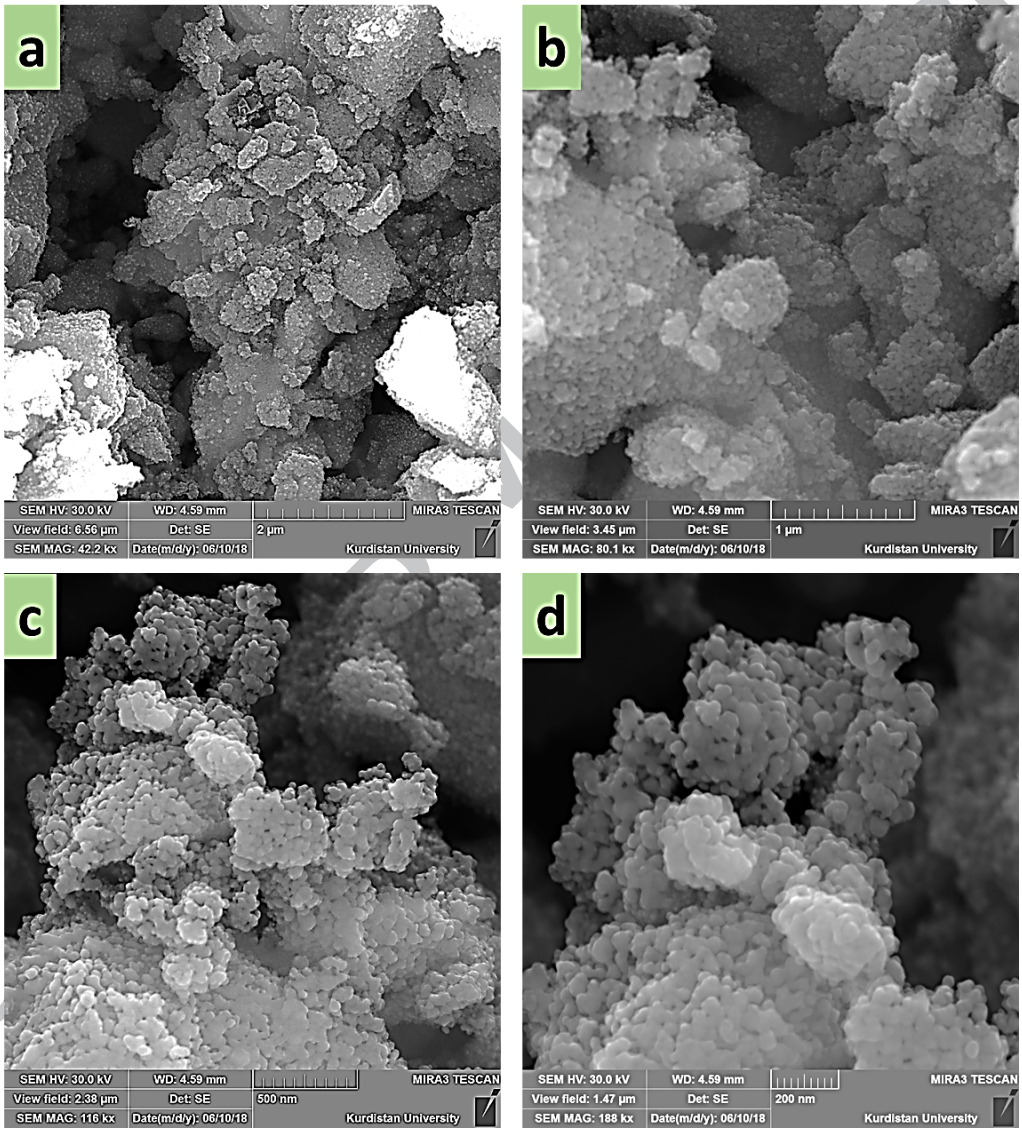



**Fig. 3** SEM images of $Fe_3O_4$@L-aspartic-Gd at 2 µm (a), 1 µm (b), 500 nm (c) and 200 nm (d).

The presence of the kinds of elements in $Fe_3O_4$@L-aspartic-Gd studied by the energy-dispersive X-ray spectroscopy (EDX) analysis in which confirmed the presence of Fe, O, N, C and Gd specie in the nanocatalyst according to the database of the EDX pattern in Fig. 4.

Also, the loading of Gd on the surface of the synthesized nanocatalyst was calculated by the ICP atomic emission spectroscopy technique. The exact amount of Gd loaded on modified magnetic nanoparticles was investigated by the ICP atomic emission spectroscopy technique in which found be 1.08mmol $g^{-1}$.

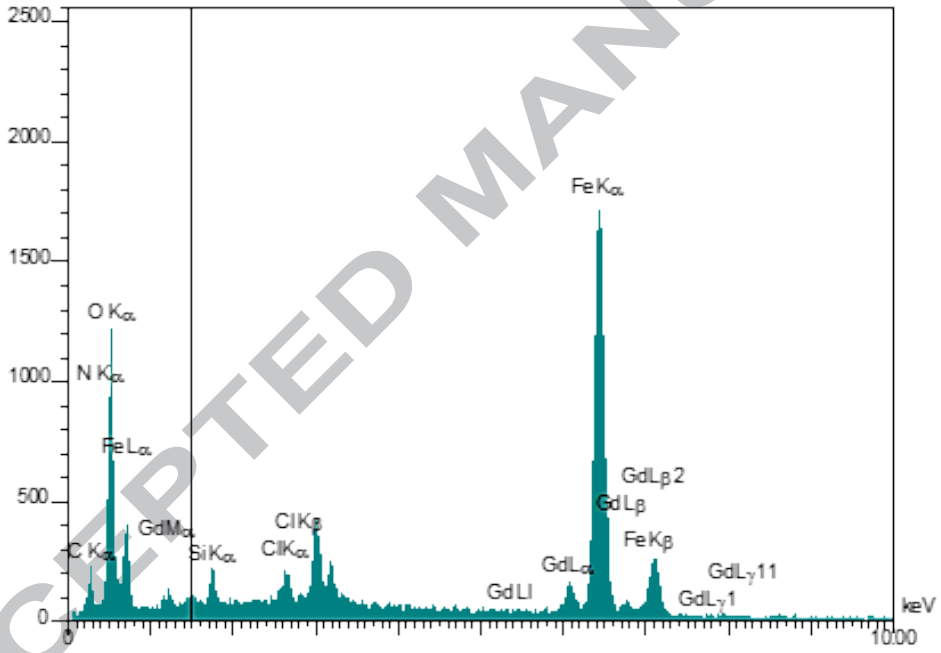



**Fig.4** EDX pattern of $Fe_3O_4$@L-aspartic-Gd.

The X-ray diffraction (XRD) pattern of $Fe_3O_4$@L-aspartic-Gd was investigated and a comparison has been depicted in Fig. 5. Six characteristic peaks for $Fe_3O_4$@L-aspartic-Gd crystal structure corresponding to (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), and (4 4 0) planes are clearly visible. The

$Fe_3O_4$ phase morphology has not been changed during the grafting of Gd complex on the magnetic nanoparticles as evident from the image [29].

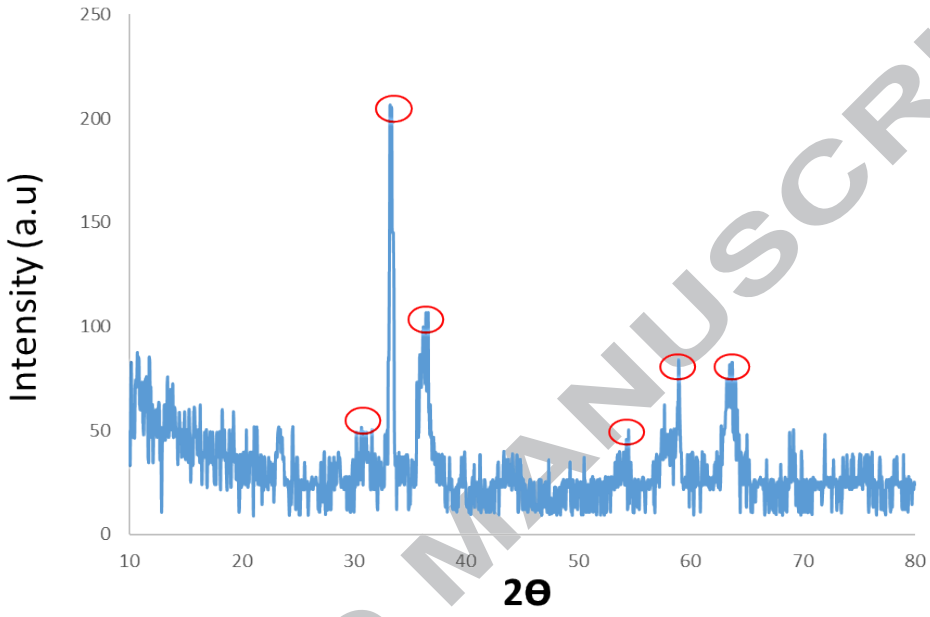
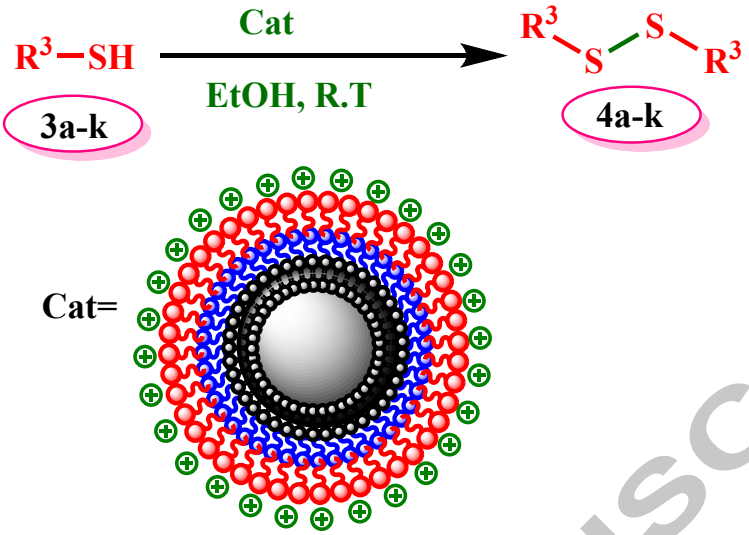



**Fig. 5** XRD pattern of $Fe_3O_4$@L-aspartic-Gd.

*3.3. Catalytic studies*

After synthesis and characterization, we focused our attention in the S-S coupling (Scheme 3) using the reaction of 4-methylthiophen (1 mmol) and $H_2O_2$ (37%) as model reaction in the presence of the $Fe_3O_4$@L-aspartic-Gd under the effect of various parameters like solvent, catalyst and $H_20_2$ concentration. The best conditions were obtained in EtOH at room temperature with in the presence of 0.006 g of catalyst and 0.5 mL $H_2O_2$. The results of this study were summarized in Table 1.




**Scheme 3.** General scheme for the synthesis of disulfide.

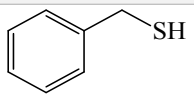
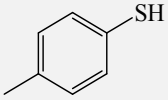
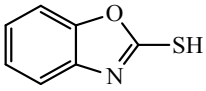
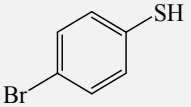
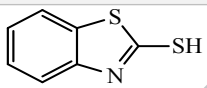
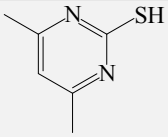
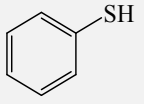
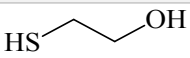
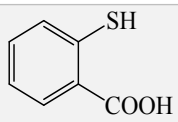
**Table 1**. Optimization of the reaction conditions for the synthesis of disulfide using $Fe_3O_4$@L-aspartic-Gd.

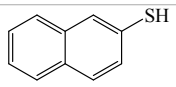
| Entry | Solvent | $H_2O_2$ (mL) | Catalyst (mg) | Time (min) | Yield (%)[a] |
|---|---|---|---|---|---|
| 1 | EtOH | 0.5 | 7 | 40 | 95 |
| 2 | EtOH | 0.5 | 6 | 40 | 95 |
| 3 | EtOH | 0.5 | 3 | 40 | 58 |
| 4 | EtOH | 0.4 | 5 | 40 | 84 |
| 5 | Solvent-Free | 0.4 | 5 | 40 | 76 |
| 6 | Ethyl acetate | 0.4 | 5 | 40 | 52 |
| 7 | Acetonitrile | 0.4 | 5 | 40 | 45 |
| 8 | Water | 0.4 | 5 | 40 | 28 |
| 9 | n-Hexane | 0.4 | 5 | 40 | 37 |

[a] Isolated yield.

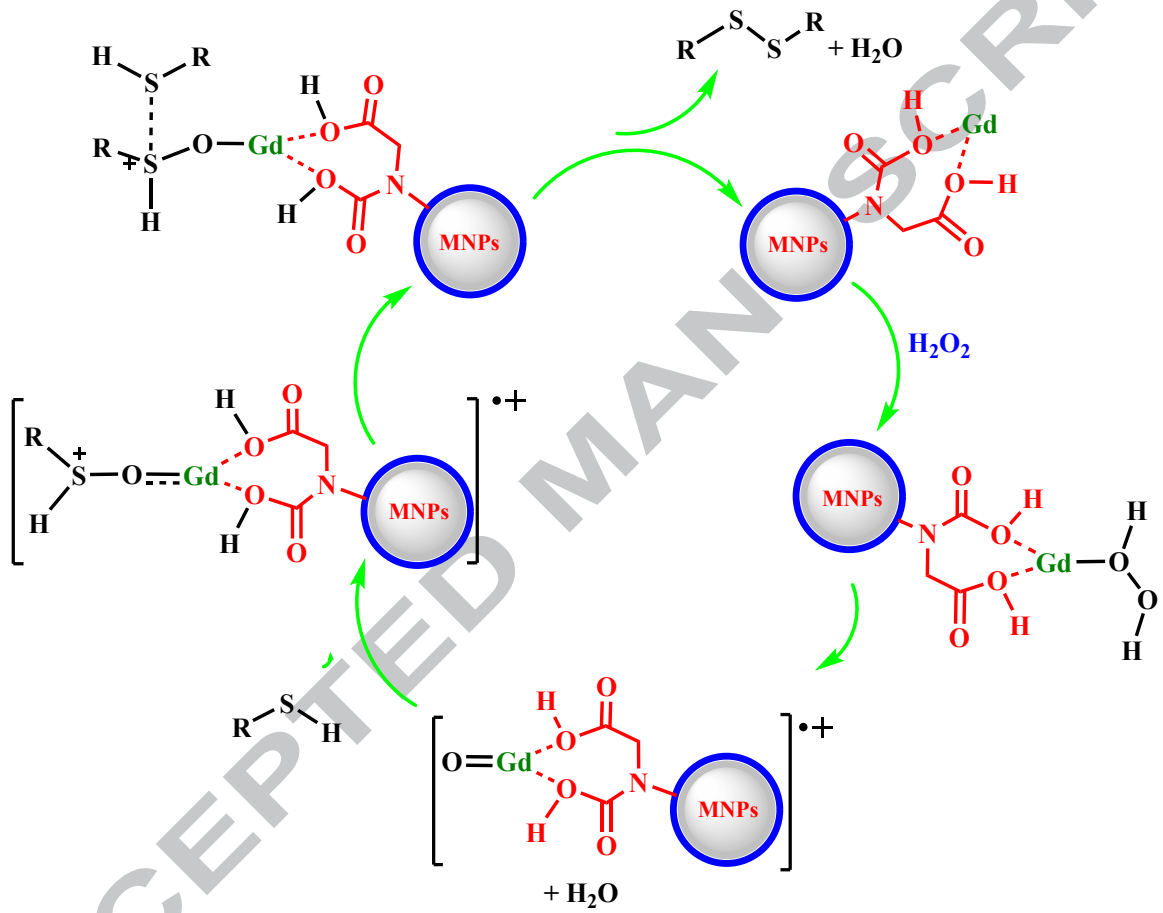
We confirmed the generality of this protocol in the synthesis of disulfide derivatives (with the optimal reaction conditions in hand) by a wide range of aromatic and aliphatic thiols bearing electron-donating and electron-withdrawing substituents with good compatibility (Table 2). Finally, a plausible reaction mechanism for the S-S coupling was designed in Scheme 4.

**Table 2.** Oxidative coupling of thiols into disulfides using $H_2O_2$ in the presence of $Fe_3O_4$@L-aspartic-Gd.

| **Entry** | Substrate | Product | Time (min) | Yield (%)[a] | TON | TOF ($h^{-1}$) | M. p (ºC) [Ref.] |
|---|---|---|---|---|---|---|---|
| **1** |  | **4a** | 35 | 98 | 151 | 4.31 | 68 [29] |
| **2** |  | **4b** | 40 | 95 | 147 | 3.67 | 40 [30] |
| **3** |  | **4c** | 30 | 94 | 145 | 4.83 | 93 [30] |
| **4** |  | **4d** | 85 | 84 | 130 | 1.53 | 90 [30] |
| **5** |  | **4e** | 40 | 92 | 142 | 3.55 | 174-176 [29] |
| **6** |  | **4f** | 145 | 90 | 139 | 0.96 | 165 [30] |
| **7** |  | **4g** | 45 | 88 | 136 | 3.02 | 102-105 [29] |
| **8** |  | **4h** | 50 | 92 | 142 | 2.84 | 58 [29] |
| **9** |  | **4i** | 30 | 92 | 142 | 4.73 | Oil [29] |
| **10** |  | **4j** | 90 | 90 | 139 | 1.54 | 282 [30] |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **11** |  | **4k** | 65 | 92 | 142 | 2.18 | 133 [30] |

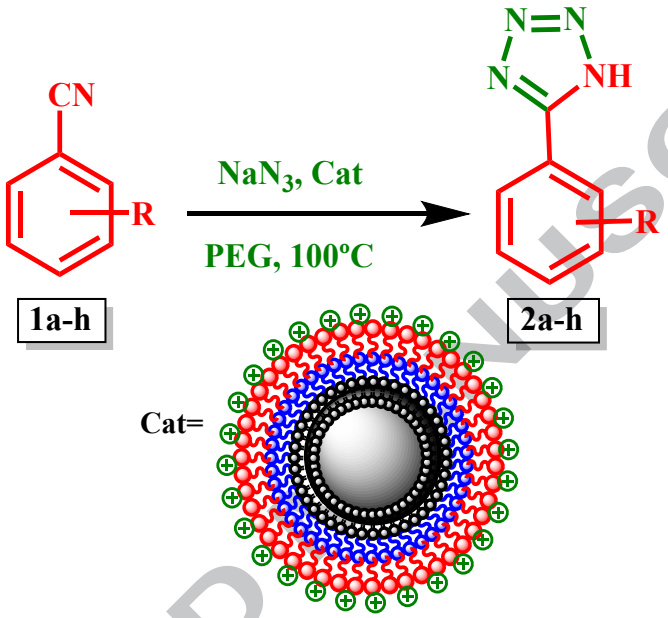
[a] Isolated yield.




**Scheme 4**. Proposed mechanism for oxidative coupling of thiols in presence of $Fe_3O_4$@L-aspartic-Gd.

After successefull oxidation of sulfides by using $Fe_3O_4$@L-aspartic-Gd, catalyst important application appeared in the synthesis of 5-substituted 1*H*-tetrazoles (Scheme 5). We initially investigated a model reaction of 4-chlorobenzonitrile (1 mmol) and sodium azide (1.2 mmol) to optimize the reaction conditions in the synthesis of corresponding tetrazole. Different factors like

solvent, temperature and amount of catalyst were examined on the outcome of reaction. It can be seen that the best performance was achieved in PEG at 100˚C in the presence of 0.05 g of $Fe_3O_4$@L-aspartic-Gd as a catalyst. The results found are summarized in Table 3.




**Scheme 5.** $Fe_3O_4$@L-aspartic-Gd catalyzed the one-pot synthesis of 5-substituted tetrazoles.

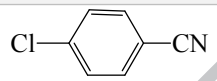
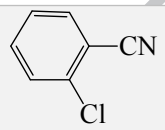
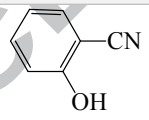
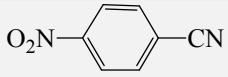
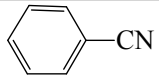
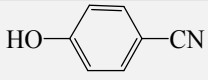
**Table 2.** Optimization of reaction conditions for synthesis of 5-substituted 1H-tetrazole derivatives in the presence of $Fe_3O_4$@L-aspartic-Gd.

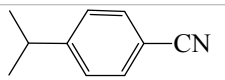
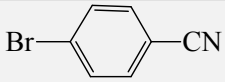
| Entry | Catalyst (mg) | Solvent | Time (min) | Temp (°C) | Yield (%)[a] |
|---|---|---|---|---|---|
| 1 | 50 | EtOH | 125 | 80 | 80 |
| 2 | 50 | DMSO | 125 | 120 | 75 |
| 3 | 50 | $H_2O$ | 125 | 100 | 53 |
| 4 | 50 | DMF | 125 | 120 | 75 |
| 5 | 50 | PEG | 125 | 80 | 70 |
| 6 | 50 | PEG | 125 | 100 | 90 |

| | | | | | |
|---|---|---|---|---|---|
| 7 | 70 | PEG | 125 | 100 | 93 |
| 8 | 60 | PEG | 125 | 100 | 90 |
| 9 | 40 | PEG | 125 | 100 | 77 |
| 10 | 50 | PEG | 125 | 120 | 92 |
| [a] Isolated yield. | | | | | |

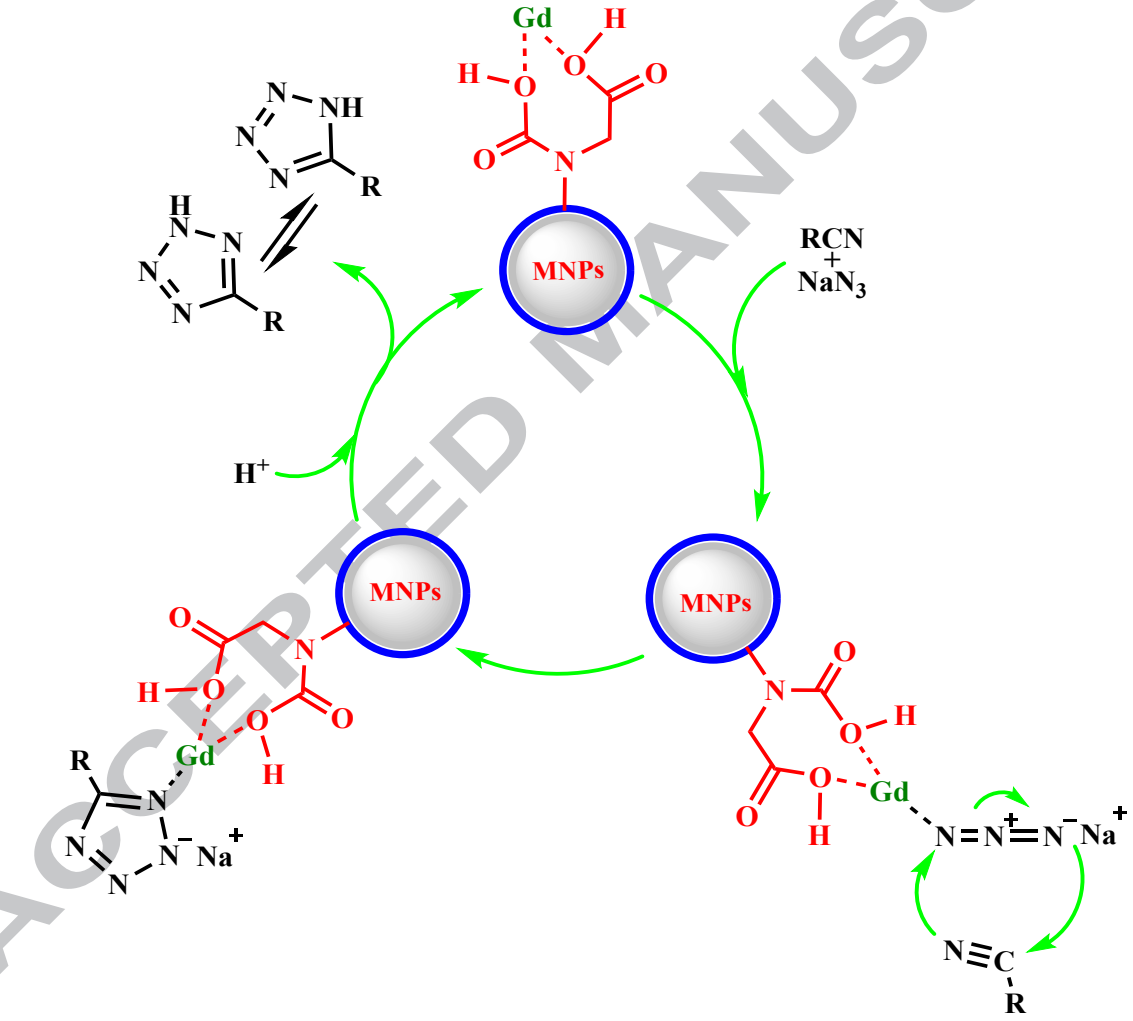
We confirmed the generality of this protocol in the synthesis of 5-substituted 1H-tetrazole derivatives by a wide range of aromatic and aliphatic nitriles under the optimal reaction conditions in hand and then a plausible reaction mechanism was designed for mentioned reaction in Scheme 6.

**Table** 4 Synthesis of 5-substituted 1H-tetrazole derivatives in the presence of $Fe_3O_4$@L-aspartic-Gd.

| **Entry** | Substrate | Product | Time (min) | Yield (%)[a] | TON | TOF ($h^{-1}$) | M. p (ºC) [Ref.] |
|---|---|---|---|---|---|---|---|
| **1** |  | **6a** | 125 | 90 | 16 | 0.13 | 261 [29] |
| **2** |  | **6b** | 135 | 92 | 17 | 0.126 | 183 [33] |
| **3** |  | **6c** | 45 | 91 | 17 | 0.38 | 225 [29] |
| **4** |  | **6d** | 35 | 97 | 18 | 0.51 | 218 [33] |
| **5** |  | **6e** | 90 | 91 | 17 | 0.19 | 215 [30] |
| **6** |  | **6f** | 40 | 93 | 17 | 0.43 | 250 [30] |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **7** |  | **6g** | 130 | 93 | 17 | 0.13 | 190 [33] |
| **8** |  | **6h** | 120 | 91 | 17 | 0.14 | 263 [30] |

[a] Isolated yield.




**Scheme 6**. Proposed mechanism for synthesis of 5-substituted tetrazoles in presence of $Fe_3O_4$@L-aspartic-Gd.

*3.4. Reusability of catalyst*

In the final step, the reusability of $Fe_3O_4$@L-aspartic-Gd catalyst was also investigated in the synthesis of 5-(4-nitroxyphenyl)-1H-tetrazole and dibenzyldisulfide in which shown no discernible change in reactivity and particle morphology (Fig. 6).

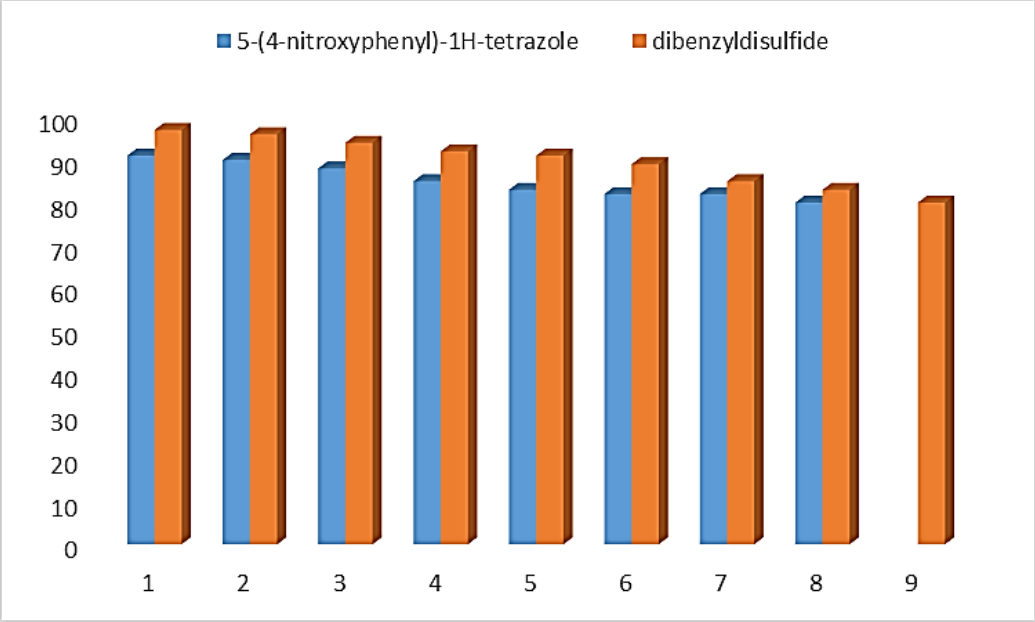



**Fig. 6** Reusability of $Fe_3O_4$@L-aspartic-Gd in the synthesis 5-(4-nitroxyphenyl)-1H-tetrazole and dibenzyldisulfide.

*3.5. Catalyst leaching study*

The Gd leaching in during reaction was studied by checking the amount of Gd after recycling of the catalyst in synthesis of 5-(4-nitroxyphenyl)-1H-tetrazole and dibenzyldisulfide by ICP-OEIS technique. It was be observed that only a trace of Gd has been leached from the initial load, 1.8 mmol/g, as confirmed by ICP-OES analysis. In justification to this, two reactions have been carried out under optimized reaction conditions. 4-nitrobenznitril (1 mmol), $NaN_3$ (1.2 mmol) in presence of $Fe_3O_4$@L-aspartic-Gd (0.05 g) for synthesis of 5-(4-nitroxyphenyl)-1H-tetrazole. The desired

product was obtained after 63 min (in the half time of the reaction) in 65% yield in this case. In the second reaction, 5-(4-nitroxyphenyl)-1H-tetrazole catalyst was isolated from the same reaction mixture in half time of the reaction and was continued without catalyst. Interestingly, in this case the yield of reaction (after 125 min) was 71 %. These results are a definite proof that the leaching of metal wasn't significant and the leached material was catalytically inactive.

*3.6. Comparison of catalyst*

In order to justify the efficiency of the catalytic protocol, the reaction data were compared with previously reported results. As shown in Table 5, our method offers significant advantages such as the recoverability and recyclability by simple filtration, low price, short reaction time and high reaction yield, non-toxicity, stability in comparison with the previously reported ones.

**Table 5.** Comparison of prepared catalysts in the synthesis of 5-phenyl-1H-tetrazole and dibenzyldisulfide with previously reported procedure.

| Entry | Substrate | Catalyst | Time (h) | Yield (%)[a] |
|---|---|---|---|---|
| 5 | Benzonitrile | $Fe_3O_4$/ZnS $HNS_s$ | 24 | 81 [61] |
| 3 | Benzonitrile | CoY zeolite | 14 | 90 [62] |
| 1 | Benzonitrile | $B(C_6F_5)_3$ | 8 | 94 [63] |
| 4 | Benzonitrile | $FeCl_3$–$SiO_2$ | 12 | 79 [64] |
| 6 | Benzonitrile | Mesoporous ZnS | 36 | 86 [65] |
| 7 | Benzonitrile | $Fe_3O_4$ | 12 | Trace [ this work ] |
| 8 | Benzonitrile | $Fe_3O_4$@L-aspartic | 12 | Trace [ this work ] |
| 9 | Benzonitrile | $Fe_3O_4$@L-aspartic-Gd | 1.5 | 91 [ this work ] |
| 11 | *p*-MePh-SH | SSA, KBr, wet SiO2 | 2 | 55 [66] |
| 12 | *p*-MePh-SH | VO-salen-MCM-41 | 2 | 95 [67] |
| 13 | *p*-MePh-SH | Ni-salen-MCM-41 | 2.6 | 95 [68] |
| 14 | *p*-MePh-SH | Cd-salen-MCM-41 | 2.5 | 98 [68] |

| | | | | |
|---|---|---|---|---|
| 15 | *p*-MePh-SH | $Fe_3O_4$ | 12 | Trace [ this work ] |
| 16 | *p*-MePh-SH | $Fe_3O_4$@L-aspartic | 12 | Trace [ this work ] |
| 17 | *p*-MePh-SH | $Fe_3O_4$@L-aspartic-Gd | 0.66 | 95[ this work ] |
| [a]Isolated yields. | | | | |

## 4. Conclusion

In this study, a novel catalyst was designed by anchored of Gd (III) complex on the surface of $Fe_3O_4$ in which shown high activity in the synthesis of tetrazole and S-S coupling. Also, the structure of this reusable and novel catalyst characterized by TGA, EDX, FT-IR, XRD, VSM, and ICP-OES. More importantly, the prepared catalysts shown attractive and significant features such as easy separation from reaction mixture by magnetic field, chemical and physical stability, high catalytic activity, easy work-ups, short time reaction and good to excellent isolated yields.

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**References**

[1] A. Corma, H. García, F. X. L. Xamena, Chem. Rev. 110 (2010) 4606.

[2] T. Tamoradi, M. Ghadermazi, A. Ghorbani-Choghamarani, New. J. Chem. 42 (2018) 5479.

[3] M. B. Gawande, R. K. Pandey, R. V. Jayaram, Catal. Sci. Technol. 2 (2012) 1113.

[4] D. Astruc, Nanoparticles and Catalysis, Wiley-VCH Verlag GmbH & Co. KGaA. 48 (2008) 1.

[5] S. Wittmann, A. Schatz, R. N. Grass, W. J. Stark, O. Reiser, Angew. Chem. Int. Ed. 49 (2010) 1867.

[6] A. Schatz, T. R. Long, R. N. Grass, W. J. Stark, P. R. Hanson, O. Reiser, Adv. Funct. Mater. 20 (2010) 4323.

[7] N. T. S. Phan, C. S. Gill, J. V. Nguyen, Z. J. Zhang, C. W. Jones, Angew. Chem., Int. Ed. 45 (2006) 2209.

[8] A. Maleki, J. Rahimi, Z. Hajizadeh, M. Niksefat, J. Organomet. Chem. 881 (2019) 58.

[9] M. B. Gawande, S. N. Shelke, P. S. Branco, A. Rathi, R. K. Pandey, Appl. Organomet. Chem. 26 (2012) 395.

[10] M. B. Gawande, P. S. Branco, K. Parghi, J. J. Shrikhande, R. K. Pandey, C. A. A. Ghumman, N. Bundaleski, O. Teodoro, R. V. Jayaram, Catal. Sci. Technol. 1 (2011) 1653.

[11] I. H. A. El Maksod, E. Z. Hegazy, S. H. Kenawy, T. S. Saleh, Adv. Synth. Catal. 352 (2010) 1169.

[12] A. Fihri, M. Bouhrara, U. Patil, D. Cha, Y. Saih, V. Polshettiwar, ACS Catal. 2 (2012) 1425.

[13] M. B. Gawande, D. M. Nagrik, D. M. Ambhore, Lett. Org. Chem. 9 (2012) 12.

[14] A. G. Pelmenschikov, G. Morosi, A. Gamba, S. Coluccia, J. Phys. Chem. 99 (1995) 15018.

[15] V. Polshettiwar, R. S. Varma, Green Chem. 12 (2010 743.

[16] S. B. Kalidindi, B. R. Jagirdar, Chem. Plus. Chem. 5 (2012) 65.

[17] U. U. Indulkar, S. R. Kale, M. B. Gawande, R. V. Jayaram, Tetrahedron Lett. 53 (2012) 3857.

[18] M. B. Gawande, P. S. Branco, Green Chem. 13 (2011) 3355.

[19] R. B. N. Baig, R. S. Varma, Chem. Soc. Rev. 41 (2012) 1559.

[20] B. Vaddula, J. Leazer, R. S. Varma, Adv. Synth. Catal. 354 (2012) 986.

[21] V. Polshettiwar, R. Luque, A. Fihri, H. B. Zhu, M. Bouhrara, J. M. Bassett, Chem. Rev. 111 (2011) 3036.

[22] M. B. Gawande, P. S. Branco, R. S. Varma, Chem. Soc. Rev. 42 (2013) 3371.

[23] I. Fernández, N. Khiar, Chem. Rev. 103 (2003) 3651.

[24] T. Tamoradi, M. Ghadermazi, A. Ghorbani-Choghamarani, Catal. Lett. 148 (2018) 857.
[25] A. Shaabani, A. H. Rezayan Catal. Commun. 8 (2007) 1112.

[26] M. Nikoorazm, A. Ghorbani-Choghamarani, N. Noori, J. Prous. Mater. 22 (2015) 877.

[27] A. Ghorbani-Choghamarani, Z. Darvishnejad, M. Norouzi, Appl. Organomet. Chem. 29 (2015) 170.

[28] T. Tamoradi, A. Ghorbani-Choghamarani, M. Ghadermazi, Appl. Organometal. Chem. 32 (2018) 4340.

[29] M. Darabi, T. Tamoradi, M. Ghadermazi, A. Ghorbani-Choghamaran, Trans. Metal. Chem. 42 (2017) 703.
[30] T. Tamoradi, A. Ghorbani-Choghamarani, M. Ghadermazi, New. J. Chem. 41 (2017) 11714.
[31] A Maleki, A Sarvary, RSC Adv. 5 (2015) 60938.

[32] A Sarvary, A Maleki, Mol. Divers. 19 (2015) 189.

[33] T. Tamoradi, B. Mehraban-Esfandiari, M. Ghadermazi, A. Ghorbani–Choghamarani, Res. Chem. Intermed. 44 (2018) 1363.

[34] R. S. Upadhayaya, S. Jain, N. Sinha, N. Kishore, R. Chandra, S. K. Arora, Eur. J. Med. Chem. 39 (2004) 579.

[35] J. T. Witkowski, R. K. Robins, R. W. Sidwell, L. N. Simon, J. Med. Chem. 15 (1972) 1150.

[36] J. R. Maxwell, D. A. Wasdahl, A. C. Wolfson, V. I. Stenberg, J. Med. Chem. 27 (1984) 1565.

[37] P. F. Juby, T. W. Hudyma, M. Brown, J. Med. Chem. 11 (1968) 111.

[38] S. Hayao, H. J. Havera, W. G. Strycker, T. J. Leipzig, R. Rodriguez, J. Med. Chem. 10 (1967) 400.

[39] S. K. Figdor, M. S. Von Wittenau, J. Med. Chem. 10 (1967) 1158.

[40] L. M. T. Frija, R. Fausto, R. M. S. Loureiro, M. L. S. Cristiano, J. Mol. Catal. A: Chem. 305 (2009) 142.

[41] P. K. Kadaba, Synthesis. 71 (1973)17.

[42] S. J. Wittenberger, Org. Prep. Proc. Int. 26 (1994) 499.

[43] D. Habibi, M. Nasrollahzadeh, A. R. Faraji, Y. Bayat, Tetrahedron 66 (2010) 3866.

[44] M. Nasrollahzadeh, Y. Bayat, D. Habibi, S. Moshaee, Tetrahedron Lett. 50 (2009) 4435.

[45] M. L. Kantam, K. B. Shiva Kumar, K. Phani Raja, J. Mol. Catal. A: Chem. 247 (2006) 186.

[46] M. L. Kantam, K. B. Shiva Kumar, C. Sridhar, Adv. Synth. Catal. 347 (2005) 1212.

[47] O. Marvi, A. Alizadeh, S. Zarrabi, Bull. Korean Chem. Soc. 32 (2011) 4001.

[48] A. Najafi Chermahini, A. Teimouri, A. Moaddeli, Heteroatom Chem. 22 (2011) 168.

[49] V. Rama, K. Kanagaraj, K. Pitchumani, J. Org. Chem. 76 (2011) 9090.

[50] F. Abrishami, M. Ebrahimikia, F. Rafiee, Iran. J. Catal. 6 (2016) 245.

[51] T. Tamoradi, A. Ghorbani-Choghamarani, M. Ghadermazi, Solid State Sciences. 88 (2019) 81.

[52] S. Molaei, T. Tamoradi, M. Ghadermazi, A. Ghorbani-Choghamarani, Microporous and Mesoporous Materials, 272 (2018) 241.

[53] N. Moeini, T. Tamoradi, M. Ghadermazi, A. Ghorbani-Choghamarani, Appl. Organomet. Chem. 32 (2018) 4445.

[54] H. J. Yoon, S. M. Lee, J. H. Kim, H. J. Cho, J. W. Choi, S. H. Lee, Y. S. Lee, Tetrahedron Lett. 49 (2008) 3165.

[55] J. Vinoth Kumar, R. Karthik, S. M. Chen, K. Natarajan, C. Karuppiah, C. C. Yang, V. Muthuraj, ACS. Appl. Mater. Interfaces. 10 (2018) 15652.

[56] S. S. Mansoor, K. Aswin, K. Logaiya, S. P. N. Sudhan, ARAB. J. Chem. 10 (2017) 546.

[57] S. Kaita, K. Kaneko, A. C. Horiuchi, Y. Wakatsuki, Macromolecules. 37 (2004) 5860.

[58] S. Kaita, Z. Hou, M. Nishiura, J. Kurazumi, A. C. Horiuch, Y, Wakatsuki, Macromol. Rapid. Comm. 24 (2003) 179.

[59] R. Alleti, W. S. Oh, M. Perambuduru, C. V. Ramana, V. P. Reddy, Tetrahedron Lett. 49 (2008) 3466.

[60] W. SuáOh, V. Prakashá Reddy, Green Chem. 7 (2005) 203.

[61] A. Maleki, P. Ravaghi, M. Aghaei, H. Movahed, Res. Chem. Intermed 43 (2017) 5485.

[62] A. Maleki, J. Rahimi, O.M. Demchuk, A.Z. Wilczewska, R. Jasiński, Ultrason. Sonochem. 43 (2018) 262.

[63] A. Maleki, Polycycl. Aromat. Compd. 38 (2018) 402.

## Graphical Abstract

Initially, anchored Gd(III) onto the $Fe_3O_4$ was successfully performed and then prepared catalysts as a novel and reusable catalyst investigated for the one-pot synthesis of 5-substituted tetrazoles and S-S coupling. Then, FT-IR, SEM, TEM, EDX, ICP-OES, XRD, TGA and VSM were used for characterization of the obtained catalysts. Easy separation, chemical and hydrothermal stability, excellent reusability of the nanocatalyst, the use of inexpensive materials, and short reaction time are outstanding advantages of this method.