Immobilization of La on THH-CO$_2$H@Fe$_3$O$_4$ nanocomposite for the synthesis of one-pot multicomponent reactions

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Abstract

The current research represents a facile and competent methodology in the development of a novel magnetic nanocatalyst. This composite was synthesized by immobilizing La on Fe$_3$O$_4$ nanoparticles pre-functionalized with tetrahydroharman-3-carboxylic acid ligand. The prepared nanomaterial was analyzed with FT-IR, SEM, EDX, XRD, and TGA techniques. The material was catalytically investigated towards the synthesis of 5-substituted 1$H$-tetrazoles, 1-substituted 1$H$-tetrazoles and tetrazolopyrimidine derivatives following different multicomponent pathways. The reactions were highly efficient affording high yields. The catalyst was retrieved magnetically and recycled in six consecutive runs without much reduction in activity.

1. Introduction

In the current age of catalysis science, designing of advanced materials has considerable importance and is challenging too. The probability of a catalytic organic transformation is significantly dependent on the arrangement and dispersion of active species [1, 2]. Among the different protocols for catalyst development, surface engineering over a heterogeneous support by functionalization with novel ligands followed by suitable disposing of active metal site is quite a popular, economic and safe process in terms of synthesis [3]. In connection with this perspective, designing of homogeneous catalysts lags behind in recent times due to their complicacy in handling and isolation towards reusability [4]. As a consequence, heterogenization of active homogeneous counterpart has come forth very rationally and it is the trend now-a-days to synthesize quasi-heterogeneous catalytic systems averting the direct use of hard chemicals in higher concentration thereby reducing the generation of toxic byproducts [5, 6]. This approach also justifies the sustainable viability towards global environment.

Now, among the different heterogeneous solid supports, silica, alumina, zirconia, mesoporous materials, carbon nanotubes, graphene oxide and magnetic nanoparticles are noticeably important [6–9]. Ferrite nanomaterials have been evolved due to their promising features like considerable mechanical and thermal stability, firm structure, high permeability and easy facile and hassle-free magnetic isolation from the system. Moreover, the nanometric dimension offers high surface area that facilitates the peripheral functionalizations with suitable organic scaffolds using the surface hydroxyl groups [10–12]. These organic linkers are further directed to anchor active species for catalysis.

Following up with our current research on the nanocatalytic organic reactions [13–17], we would like to introduce herein the lanthanum (La) anchored tetrahydroharman-3-carboxylic acid (THH-CO$_2$H) functionalized over Fe$_3$O$_4$ nanoparticles as a novel nanocomposite material [La/THH-CO$_2$H@Fe$_3$O$_4$] and explored its catalytic performance in the synthesis of tetrazoles following two, three and four component pathway respectively. The organic linker (THH-CO$_2$H) is a tryptophan derivative via Pictet-Spengler reaction.
The amino acid analog was selected as organic function as being an excellent complexing and stabilizing agent [19, 20].

Tetrazole derivatives are five-membered nitrogen rich heterocycles, find a plethora of applications in catalysis technology, as an excellent ligand in coordination chemistry, efficient stabilizing agents in metallopeptide chemistry, stable surrogates for carboxylic acids in active biomolecules. They are also used as plant growth regulators, shows very good potential as anti-inflammatory, anti-allergic, antihypertensive, antibiotic drug candidates [21–27].

Now, based on these applications, we are opting to demonstrate a competent methodology towards the preparation of diverse tetrazole derivatives following multicomponent coupling reactions catalyzed over our novel material (scheme 1). Additionally, the catalyst was easily retrieved by magnet and reused for several times.

2. Experimental

2.1. Materials and methods
The chemicals and solvents were procured from Merck and Sigma-Aldrich and used as such. XRD of the material was carried out using CoKα radiation (λ = 1.78897 Å, 40 kV, 25 mA). SEM and TEM analysis was done on FESEM-TESCAN MIRA3 and Zeiss-EM10C apparatus respectively. Magnetic properties were determined in a Vibrating Sample Magnetometer (VSM) MDKFD at room temperature. FT-IR spectra were recorded on a KBr disc in a VRTEX 70 model BRUKER FT-IR spectrophotometer. Thermal stability was measured by TGA over a Shimadzu DTG-60 instrument (50 °C–750 °C). ICP-OES analysis of was carried out to analyze the La content in the catalyst.

2.2. Preparation of La/THH-CO2H@Fe3O4 nanocomposite
The core Fe3O4 nanoparticles were synthesized following the procedure as reported by Darabi et al [28]. Then, the modifications were followedover Fe3O4. 1.0 g of the MNPs powder was dispersed in 30 ml water and 1.5 g of tetrahydroharman-3-carboxylic acid ligand was added to it and refluxed for 24 h. The so prepared material (THH-CO2H@Fe3O4) was separated by a magnet, washed thoroughly with ethanol/water and then dried. For the next step, 1.0 g of THH-CO2H@Fe3O4 was again dispersed in 30 ml absolute EtOH and 1.08 g La(NO3)3.H2O was added to it under stirring followed by reflux for another 16 h. The final material was isolated by magnetic bar and dried in air.

2.3. Synthesis of 5-substituted-1H-tetrazoles (two components)
A mixture of nitrile (1.0 mmol) and sodium azide (1.5 mmol) was stirred in presence of La/THH-CO2H@Fe3O4 catalyst (0.1 g) at 120 °C in PEG 600 solvent. After completion (by TLC), the reaction was brought to ambient conditions and diluted with ethyl acetate (EtOAc, 3–20 ml). After magnetic removal of the catalyst, the filtrate was washed with HCl (1 N, 10 ml), dried with Na2SO4 and concentrated to obtain the crude solid. It was further recrystallised to have the pure product. All the known compounds that were authenticated by comparing the melting points with literature and spectroscopic analysis (As indicated in table 2).
Table 1. Optimization of reaction parameters towards the synthesis of 5-substituted-1H-tetrazoles over La/THH-CO₂H@Fe₃O₄.

| Yield (%) | Time h | Temp °C | Solvent   | Entry |
|-----------|--------|---------|-----------|-------|
| 70        | 12     | 100     | PEG-600   | 1     |
| 83        | 12     | 110     | PEG-600   | 2     |
| 95        | 3      | 120     | PEG-600   | 3     |
| 48        | 24     | 70      | Water     | 4     |
| 93        | 24     | 120     | DMF       | 6     |
| 55        | 24     | 70      | CH₂CN     | 7     |
Selected data of 5-(4-Nitrophenyl)-1H-tetrazole (table 2, Entry B): M.p.: 243–246 °C, FT-IR (KBr): 3508, 3101, 2919, 2854, 2755, 2474, 1656, 1608, 1521, 1439, 1346, 1156, 1101, 1024, 951, 854, 696, 645, 494 cm⁻¹ (see supplementary information figure S1 available online at stacks.iop.org/MRX/8/056101/mmedia).

2.4. Synthesis of 1-substituted-1H-tetrazoles (three components)
A mixture of amine (1.0 mmol), triethylorthoformate (1.2 mmol) and sodium azide (1.2 mmol) was stirred in presence of La/THH-CO₂H@Fe₃O₄ catalyst (0.1 g) at 120 °C in PEG 600 solvent. After completion (by TLC) solid products were obtained when added to chilled water. The catalyst was retrieved and all solid products were purified as described in section 2.3. (As indicated in table 4).

Selected spectral data of 1-(4-Methylphenyl)-1H-tetrazole (table 4, entry 5): M.p.: 97–101 °C. FT-IR (KBr): 3200-3600, 2863, 1695, 1591, 1360, 1488, 1415, 1350, 1319 1284, 1235, 1153, 1023, 972, 834 cm⁻¹ (see supplementary information figure S2).

2.5. Synthesis of fused pyrimidotetrazoles (four components)
A mixture of 2-cyano-guanidine (1 mmol, 0.084 g) and sodium azide (1.1 mmol, 0.072 g) was dissolved in PEG 600 in the presence of La/THH-CO₂H@Fe₃O₄ catalyst (0.1 g) at 120 °C for 5-amino tetrazole synthesis in
Table 3. Standardization of reaction conditions for the synthesis of 1-substituted 1\textit{H}-tetrazoles.

| Yield (%) | Time h | T °C | Solvent          | Entry |
|-----------|--------|------|------------------|-------|
| 91        | 2      | 120  | PEG-600          | 1     |
| 55        | 24     | 70   | Water            | 2     |
| 58        | 24     | 70   | C\textsubscript{6}H\textsubscript{5}OH | 3     |
| 68        | 12     | 70   | CH\textsubscript{3}CN | 4     |
| 85        | 12     | 120  | DMF              | 5     |
| 93        | 3      | 120  | Solvent-free     | 6     |
approximately 100% yield. Then, an aldehyde (1 mmol) and an acetoacetate ester (1 mmol) were added to the mixture. After completion (by TLC), the reaction mixture was cooled and all the solid products were obtained in pure form through process described in section 2.3.

Selected spectral data of Methyl-7-(4-bromophenyl)-5-methyl-4,7-dihydrotetrazolo[1,5-a]pyrimidine-6-carboxylate (table 6, Entry 7): M.p.: 219-221 °C, FT-IR (KBr): 3255, 2949, 1690, 1648, 1574, 1488, 1432, 1350, 1278, 1227, 1153, 1012, 839, 813, 772 cm⁻¹ (see supplementary information figure S3).

### Table 4. Synthesis of 1-substituted 1H-tetrazoles under stabilized reaction conditions.

| Entry | R" | Product | Yield (%) | TON | TOF h⁻¹ | MP (°C) [References] |
|-------|----|---------|-----------|-----|---------|--------------------|
| 1     | C₆H₅− |         | 90        | 29.03 | 14.52   | (62–65) [32]       |
| 2     | p-NO₂-C₆H₅− |     | 35        | 11.29 | 5.65    | (200–203) [32]    |
| 3     | p-OMe-C₆H₅− |     | 94        | 30.32 | 15.31   | (113) [32]        |
| 4     | p-Cl–C₆H₅− |       | 82        | 26.45 | 13.23   | (152–154) [32]    |
| 5     | p-Me–C₆H₅− |       | 91        | 29.35 | 14.68   | (97–101) [32]     |
| 6     | o-Me–C₆H₅− |       | 88        | 28.39 | 14.19   | (126–129) [32]    |

3. Results and discussion

3.1. Analysis of catalyst characterization data

On complete synthesis of the La/THH-CO₂H@Fe₃O₄ nanocomposite (scheme 2), it was meticulously characterized using SEM, FT-IR, EDX, XRD, TGA and VSM analysis.

In order to justify the organo-ligand functionalization over Fe₃O₄ MNP and successful synthesis of the whole material, the FT-IR spectra of bare Fe₃O₄, THH-CO₂H@Fe₃O₄ and La/THH-CO₂H@Fe₃O₄ nanoparticles were co-plotted (figure 1). The O-H and characteristic Fe-O stretching vibrations are observed at 3400–3500 and 581 cm⁻¹ respectively, as shown in figure 1(a). This particular FT-IR pattern has been carried
Table 5. Optimization of reaction conditions for synthesis of tetrazolopyrimidine in the presence of catalyst.

![Chemical Reaction Image]

| Yield (%) | Time h | T °C | Solvent     | Entry |
|-----------|--------|------|-------------|-------|
| 90        | 5      | 100  | PEG-600     | 1     |
| 45        | 24     | Reflux | Water     | 2     |
| 80        | 24     | Reflux | C₂H₅OH   | 3     |
| 66        | 24     | 120  | DMF         | 4     |
| 10        | 24     | 70   | CH₃CN       | 6     |
Table 6. Synthesis of tetrazolopyrimidine derivatives under stabilized reaction conditions.

| Entry | R<sup>+</sup> | Product | Yield (%) | TON | TOF h<sup>−1</sup> | Measured MP (°C) [References] |
|-------|---------------|---------|-----------|-----|-----------------|-------------------------------|
| 1     | C<sub>6</sub>H<sub>5</sub>− | ![Image of product 1] | 90        | 29.03 | 5.81 | (202–205) [33] |
| 2     | C<sub>6</sub>H<sub>5</sub> | ![Image of product 2] | 92        | 29.68 | 5.94 | (190–192) [33] |
| 3     | p-NO<sub>2</sub>-C<sub>6</sub>H<sub>5</sub>− | ![Image of product 3] | 91        | 29.35 | 5.87 | (225–228) [34] |
| 4     | p-Me-C<sub>6</sub>H<sub>5</sub>− | ![Image of product 4] | 90        | 29.03 | 5.81 | (255–257) [34] |
| Entry | $R^x$ | Product | Yield (%) | TON | TOF h$^{-1}$ | Measured MP ($^\circ$C) [References] |
|-------|-------|---------|-----------|-----|-------------|-------------------------------------|
| 5     | $p$-F$-C_6H_5$ | ![Product 5](image) | 92 | 29.68 | 5.94 | (196–198) [33] |
| 6     | $m$-MeO$-C_6H_5$ | ![Product 6](image) | 86 | 27.74 | 5.55 | (197–200) [33] |
| 7     | $p$-Br$-C_6H_5$ | ![Product 7](image) | 90 | 29.03 | 5.81 | (219–221) [33] |
Table 6. (Continued.)

| Entry |  R<sup>+</sup> | Product | Yield (%) | TON     | TOF h<sup>-1</sup> | Measured MP (°C) [References] |
|-------|----------------|---------|-----------|---------|-------------------|-------------------------------|
| 8     | 2,4-Cl<sub>−</sub>C<sub>6</sub>H<sub>3</sub>− | 91      | 29.35     | 5.87    | (200–203) [34]    |                               |
| Entry | R<sup>+</sup>                      | Product                                                                 | Yield (%) | TON  | TOF h<sup>-1</sup> | Measured MP (°C) [References] |
|-------|----------------------------------|-------------------------------------------------------------------------|-----------|------|-------------------|--------------------------------|
| 9     | 3,4,5-MeO-C<sub>6</sub>H<sub>5</sub>⁻ | ![](image1.png)                                                       | 91        | 29.35 | 5.87              | (252–256) [33]                |
| 10    | m-Cl-C<sub>6</sub>H<sub>5</sub>⁻    | ![](image2.png)                                                        | 90        | 29.03 | 5.81              | (214–216) [33]                |
Scheme 2. Synthesis of La/THH-CO$_2$H@Fe$_3$O$_4$ nanocomposite.

Figure 1. FT-IR spectrum of Fe$_3$O$_4$ (a), THH-CO$_2$H@Fe$_3$O$_4$ (b) and La/THH-CO$_2$H@Fe$_3$O$_4$ (c) nanocomposite.
over in the other spectrum too indicating that the basic core remained intact even after functionalization and metal depositions. The typical absorption peaks at 2840–2940 and 1620 cm\(^{-1}\) in figure 1(b) correspond to the aliphatic C–H and C=\(\text{N}\) stretching vibrations originating from tetrahydrozhen-3-carboxylic acid. The similar trend is continued in the La complexed nanocomposite in figure 1(c).

Thermal stability and apparent composition of the nanocomposite has been analyzed through thermogravimetric analysis (TGA) and the profile is documented in figure 2. It’s a typical reverse sigmoid curve. Initially, slight loss of mass occurs up to 100 °C due to the exclusion of physisorbed water or surface OH groups. A major break is encountered in the domain of 200 °C–250 °C resulting a 37.37% decrement in mass. This is because of the degradation of attached organo scaffolds on MNP surface, which in turn, justifies the strong bonding of THH-CO\(_2\)H over Fe\(_3\)O\(_4\). Subsequently 10.2% weight loss occurs as a result of the removal of chemisorbed solvent or water from the composite.

The structural morphology of La/THH-CO\(_2\)H@Fe\(_3\)O\(_4\) was ascertained following SEM analysis. Figure 3 represents that the nanocatalyst is of uniform spherical dimensions having particle size around 25 nm. The nanometric size and spherical shape definitely assist the material to enhance its catalytic proficiency and molecular interactions. The SEM analysis was accompanied by EDX analyses of the materials to determine the elemental compositions. As shown in figures 3(e) and (f) the profile justifies the elements as anticipated. The presence of C, N and O confirms the successful immobilization of THH-CO\(_2\)H ligand over ferrite surface.

The phase morphology and crystalline nature of the material were assessed by XRD study. Figure 4 depicts the sharp diffraction peaks are clear indication of high crystallinity of the material. The six characteristic peaks could be assigned to (220), (311), (400), (422), (511) and (440) reflection planes which resembles very much to the cubic spinel phase (JCPDS#01-075-0449) of Fe\(_3\)O\(_4\) NPs \cite{35, 36}. The XRD pattern also veriﬁes that the Fe\(_3\)O\(_4\) structural unit remained intact while surface modiﬁcations.

For iron based catalysts study of magnetism is obvious and thereby it was determined for the La/THH-CO\(_2\)H@Fe\(_3\)O\(_4\) and bare Fe\(_3\)O\(_4\) using a vibrating sample magnetometer (VSM). The typical magnetic hysteresis curves reveal their paramagnetic nature (figure 5). As can be observed, the saturation magnetization value (\(M_s\)) of Fe\(_3\)O\(_4\) (72 emu g\(^{-1}\)) is much higher than the modiﬁed material (45 emu g\(^{-1}\)) which can be anticipated due to surface functionalizations with non-magnetic materials \cite{37}.

### 3.2. Analysis of catalytic studies

Prior to the catalytic characterizations, it was the turn of catalytic explorations towards fine chemical syntheses. We concentrated on the synthesis of tetrazoles following different pathways over our developed catalyst. At the outset, we aimed at two component synthesis by coupling aryl nitriles and sodium azide towards 5-substituted 1\(H\)-tetrazoles. However, standardization of reaction conditions was the primary concern and thereby a coupling reaction between 4-nitrobenzonitrile and NaN\(_3\) was chosen as a model and a screening of solvent and temperature were investigated over it. The results have been shown in table 1. Amongst the various protic solvents like PEG 600, H\(_2\)O, EtOH and aprotic solvents like CH\(_3\)CN and DMF, PEG 600 resulted the best yield in shortest time (3 h) (table 1, entry 3). The solvent worked best at 120 °C. At lower temperature, however, the reaction was moderate in productivity (table 1, entries 1-2).
Subsequently, we continued with the optimized parameters to investigate the scope and generality over an array of aryl nitriles to couple with NaN₃. Both electron donating and attracting functionalized aryl nitriles reacted smoothly at the applied conditions affording outstanding productivity in short times. However, reaction with phthalonitrile was moderate in yield might be due to steric reason. All the known products were justified by matching their literature melting points (table 2).

We continued our exploration with three component coupling towards 1-substituted 1H-tetrazoles this time. Here also in a model reaction, the three substrates, viz., triethylorthoformate, sodium azide and 4-toluidine were allowed to couple together and different conditions like solvent and temperature variations
were imposed on it. The results have been documented in table 3. PEG 600 was established to be the best solvent among all to react at 120 °C in just 2 h resulting the best yields (table 3, entry 1).

Here again in the three component synthesis the standardized conditions were examined over a variety of aromatic amines towards 1-substituted 1H-tetrazoles, in order of generalization. The corresponding results have been presented in table 4. The reaction initially goes through the formation of imine intermediate by reaction between aromatic amines and triethylorthoformate, an aldehyde precursor, which afterwards undergoes [3 + 2] cycloaddition with azide to afford the corresponding 1-tetrazole product. Most of the aromatic amines offered impressive yields irrespective of the substitutions being electron donating or electron attracting, except the 4-nitroaniline (table 4, entry 2), which afforded poor result obviously due to the reduced electron density on amino group based on -R effect of the NO2 group at C-4. Here too the known products were verified by measuring melting points and compared with literature.

The endeavor was continued towards the preparation of fused pyrimidotetrazoles following a four component synthesis by coupling N-nitrologuanidine, sodium azide, aromatic aldehydes and β-ketoesters. The standardization of reaction conditions was necessary in his case too and thereby a specific reaction between N-nitrologuanidine, sodium azide, benzaldehyde and ethyl acetoacetate was selected as a probe. A screening of different solvents and temperatures were investigated upon said reaction and the results are being shown in table 5. Also PEG 600 was being the best solvent and reacted at 100 °C generating the corresponding product in 5 h only (table 5, entry 1). The reactions were much sluggish in other solvents producing moderate yields.

Figure 4. XRD pattern of La/THH-CO2H@Fe3O4 nanocatalyst.

Figure 5. VSM magnetization curve of (a) Fe3O4 and (b) La/THH-CO2H@Fe3O4 catalyst.
The scopes and limitations of the optimized conditioned were thereafter tested upon a series of substrates to generate a wide variety of fused pyrimidotetrazoles. Different aromatic aldehydes with wide range of substituted functional groups, being electron donating or electron withdrawing, were reacted under the established conditions and outstanding yields were obtained in all the cases (table 6, entry 1-10). Different esters were also equally compatible under the situations (table 6, entry 1-2). The results are shown in table 6.

3.3. Recyclability study of La/THH-CO₂H@Fe₃O₄

The reusability is the most important advantage of catalysis systems for commercial utilization. In this regard, the recovered La/THH-CO₂H@Fe₃O₄ was rinsed with hot ethanol, dried and recycled in the next runs for each reaction. The La/THH-CO₂H@Fe₃O₄ was used in the synthesis of 5-(4-Nitrophenyl)-1H-tetrazole, 1-(4-methylphenyl)-1H-tetrazole and Methyl-7-(phenyl)-5-methyl-4,7-dihydropyrimidine-6-carboxylate in six successive cycles (figure 6) with almost consistent reactivity.

3.4. Catalyst leaching study

The amounts of La leaching in synthesis of was studied by checking the La loading amount before and after recycling of the catalyst by ICP-OES technique. It was found that the amount of La in fresh catalyst and the recycled catalyst after 6 times recycling is 0.31 and 0.21 mmolg⁻¹, respectively which indicated the insignificant La leaching in the reaction.

4. Conclusion

To conclude, we demonstrated a simple and competent protocol for the synthesis of tetrazole derivatives using a novel reusable magnetic nanocatalyst. The La immobilized amino acid analog modified ferrite nanoparticle was synthesized following post-grafting approach and further characterized by different advanced physicochemical techniques. Catalytic performance of the synthesized nanostructure was tested in the synthesis of tetrazole derivatives in three different pathways following MCR strategy. All the products were obtained under mild conditions, in reaction short times and high yields. This is probably the first approach for La attached magnetic nanocatalyst in click chemistry towards the tetrazoles.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).
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