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# Investigation of Fe<sub>3</sub>O<sub>4</sub>@boehmite NPs as efficient and magnetically recoverable nanocatalyst in the homoselective synthesis of tetrazoles†

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Magnetic boehmite nanoparticles (Fe<sub>3</sub>O<sub>4</sub>@boehmite NPs) were synthesized from a hybrid of boehmite and Fe<sub>3</sub>O<sub>4</sub> nanoparticles. At first, boehmite nanoparticles (aluminum oxide hydroxide) were prepared via a simple procedure in water using commercially available materials such as sodium hydroxide and aluminum nitrate. Then, these nanoparticles were magnetized using Fe<sub>3</sub>O<sub>4</sub> NPs in a basic solution of FeCl<sub>2</sub>·4H<sub>2</sub>O and FeCl<sub>3</sub>·6H<sub>2</sub>O. Fe<sub>3</sub>O<sub>4</sub>@boehmite NPs have advantages of both boehmite nanoparticles and Fe<sub>3</sub>O<sub>4</sub> magnetic materials. Magnetic boehmite nanoparticles have been characterized by various techniques such as TEM, SEM, EDS, WDX, ICP, FT-IR, Raman, XRD and VSM. SEM and TEM images confirmed that particles size are less than 50 nm in diameter with a cubic orthorhombic structure. Then, Fe<sub>3</sub>O<sub>4</sub>@boehmite NPs were applied as a homoselective, highly efficient, cheap, biocompatibility, heterogeneous and magnetically recoverable nanocatalyst in the synthesis of 5-substituted 1*H*-tetrazole derivatives. Fe<sub>3</sub>O<sub>4</sub>@boehmite NPs can be recycled for several runs in the synthesis of tetrazoles. Also, all tetrazoles were isolated in high yields, which reveals high activity of Fe<sub>3</sub>O<sub>4</sub>@boehmite NPs in the synthesis of tetrazole derivatives. Fe<sub>3</sub>O<sub>4</sub>@boehmite NPs shows a good homoselectivity in synthesis of 5-substituted 1*H*-tetrazole derivatives.

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## 1 Introduction

In homogeneous catalyst systems, good catalytic activity is usually observed, due to the solubility of the catalyst in the reaction mixture and thus the easy access of the reactants to the catalyst sites. Therefore homogeneous catalysts perform better practicality than heterogeneous catalysts.<sup>1–3</sup> However, in the homogeneous catalyst systems, purification of the products, separation and recovery of the catalyst is often difficult, costly and time consuming. Therefore, this drawbacks have limited the use of the homogeneous catalysts despite high activity and selectivity.<sup>4</sup> Also, clean technology and green chemistry require the use of heterogeneous and recyclable catalysts.<sup>3–6</sup> While we need to catalytic systems which have high activity and recyclability. This goal is achieved through the use of nanocatalysts which are the bridge between homogeneous and heterogeneous catalysts.<sup>7–8</sup> However, nanoparticles (NPs) are not fully recycled by conventional and inexpensive methods such as centrifugation or filtration due to their very small size. All of these problems can be overcome using magnetic nanocatalysts or stabilizing catalyst species on magnetic substrates.<sup>8–10</sup> In the

absence of an external magnetic field, the magnetic nanoparticles (MNPs) are dispersed in the reaction mixture and make available high surface to the reacting molecules. More important, at the end of the reaction, they are quickly, easily and completely recovered from the reaction mixture using an external magnet.<sup>11–16</sup> But these MNPs are not very stable for long times.<sup>17</sup> Therefore, many organic or inorganic covers have been used to increase the MNPs stability.<sup>18–21</sup> One of the most valuable and cheapest mineral compounds which is rarely used as MNPs cover is boehmite nanoparticles (BNPs) which are synthesized using inexpensive and available materials and very simple method in the aqueous environment.<sup>22</sup> Boehmite is actually one of the polymorphs phases of aluminum oxide which called aluminum oxyhydroxide (AlOOH).<sup>23–27</sup> BNPs with high surface area have high hydroxyl groups on their surface that causes it to be used as a coating.<sup>28,29</sup> Therefore, magnetic boehmite nanoparticles (Fe<sub>3</sub>O<sub>4</sub>@boehmite NPs) have advantages of homogeneous catalyst (such as large surface area and activity), high stability (such as boehmite NPs) and MNPs (such as easily and magnetically separation using an external magnet). For this purpose, in this project, Fe<sub>3</sub>O<sub>4</sub>@boehmite NPs were synthesized and used as a highly efficient, environmentally friendly and magnetically reusable nanocatalyst in the synthesis of 5-substituted 1*H*-tetrazoles. The procedure synthesis of Fe<sub>3</sub>O<sub>4</sub>@boehmite NPs is cheap, simple and environmentally friendly. 5-Substituted tetrazoles were used in drugs and they are used as herbicides, anti-HIV drug

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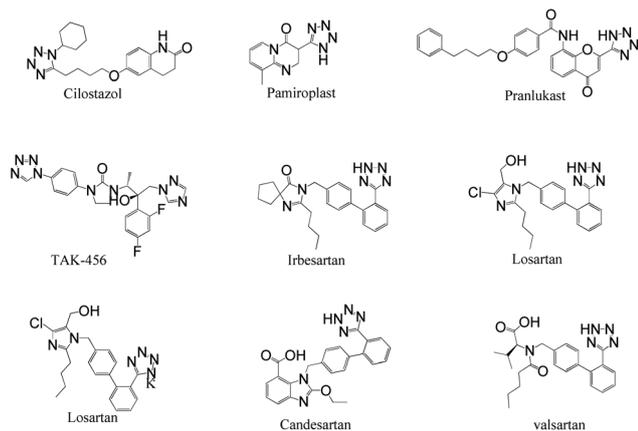


Fig. 1 Several pharmacologically compounds of tetrazoles.

candidates, analgesics, antimicrobial, anti-proliferative, anti-inflammatory, and anticancer agents.<sup>26,30–38</sup> For example, Candesartan, Valsartan, Irbesartan, Losartan, Cilostazol, TAK-456, Pamiroplast and Pranlukast (Fig. 1) are several pharmacologically important of tetrazoles.<sup>39–41</sup>

## 2 Experimental

### 2.1 Preparation of Fe<sub>3</sub>O<sub>4</sub>@boehmite NPs catalyst

The BNPs were synthesized according to previously reported procedure.<sup>44</sup> Then, the obtained BNPs (2 g) dispersed in water at 80 °C, and then FeCl<sub>2</sub>·4H<sub>2</sub>O (7.5 mmol, 1.49 g) and FeCl<sub>3</sub>·6H<sub>2</sub>O (11.5 mmol, 3.1 g) added to the mixture. The reaction mixture stirred under N<sub>2</sub> atmosphere. Under continuous stirring, NaOH (50 mL, 10%) added into the reaction mixture. The obtained mixture stirred for 2 h at 90 °C which black Fe<sub>3</sub>O<sub>4</sub>@boehmite NPs prepared. The obtained Fe<sub>3</sub>O<sub>4</sub>@boehmite NPs washed with distilled water and separated by external magnet each time.

### 2.2 General procedure for synthesis of tetrazoles catalyzed by Fe<sub>3</sub>O<sub>4</sub>@boehmite NPs

A mixture of sodium azide (1.5 mmol) and benzonitrile derivative (1 mmol) stirred in the presence of Fe<sub>3</sub>O<sub>4</sub>@boehmite NPs

catalyst (0.015 g) in PEG at 120 °C. Reaction times controlled by TLC. After completion of the reaction, the Fe<sub>3</sub>O<sub>4</sub>@boehmite NPs catalyst isolated using an external magnet and the tetrazole products extracted by ethyl acetate and aqueous solution of HCl (4 N). The organic solvent dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and evaporated to give the tetrazole products.

### 2.3 Selected spectral data

**2.3.1 2-(1H-Tetrazol-5-yl)benzonitrile.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> = 8.11–8.06 (t, *J* = 8 Hz, 2H), 7.96–7.90 (t, *J* = 12 Hz, 1H), 7.81–7.75 (t, *J* = 20 Hz, 1H) ppm.

**2.3.2 5-(3-Nitrophenyl)-1H-tetrazole.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> = 14.96 (br, 1H), 8.84–8.83 (t, *J* = 4 Hz, 1H), 8.49–8.39 (m, 2H), 7.93–7.88 (t, *J* = 8 Hz, 1H) ppm.

**2.3.3 5-(4-Bromophenyl)-1H-tetrazole.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> = 7.98–7.96 (d, *J* = 8 Hz, 2H), 7.84–7.82 (d, *J* = 8 Hz, 2H) ppm.

**2.3.4 5-(4-Nitrophenyl)-1H-tetrazole.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> = 14.76 (br, 1H), 8.45–8.41 (d, *J* = 12 Hz, 2H), 8.30–8.27 (d, *J* = 12 Hz, 2H) ppm.

## 3 Results and discussion

In this project, to combine the advantages of both MNPs and boehmite nanoparticles, magnetic boehmite nanoparticles (Fe<sub>3</sub>O<sub>4</sub>@boehmite NPs) synthesized using Fe<sub>3</sub>O<sub>4</sub> nanoparticles and available materials through environmentally friendly and very simple procedure in aqueous media. In the next step, Fe<sub>3</sub>O<sub>4</sub>@boehmite NPs characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), wavelength dispersive X-ray spectroscopy (WDX), energy-dispersive X-ray spectroscopy (EDS), Inductively coupled plasma (ICP), Fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy, X-ray diffraction (XRD) and vibrating-sample magnetometer (VSM) techniques. The scanning electron microscope was used to obtain high-resolution SEM images of Fe<sub>3</sub>O<sub>4</sub>@boehmite NPs. The SEM images were used to studying the morphology and diameter size of Fe<sub>3</sub>O<sub>4</sub>@boehmite NPs. SEM images of Fe<sub>3</sub>O<sub>4</sub>@boehmite NPs are shown in Fig. 2 which

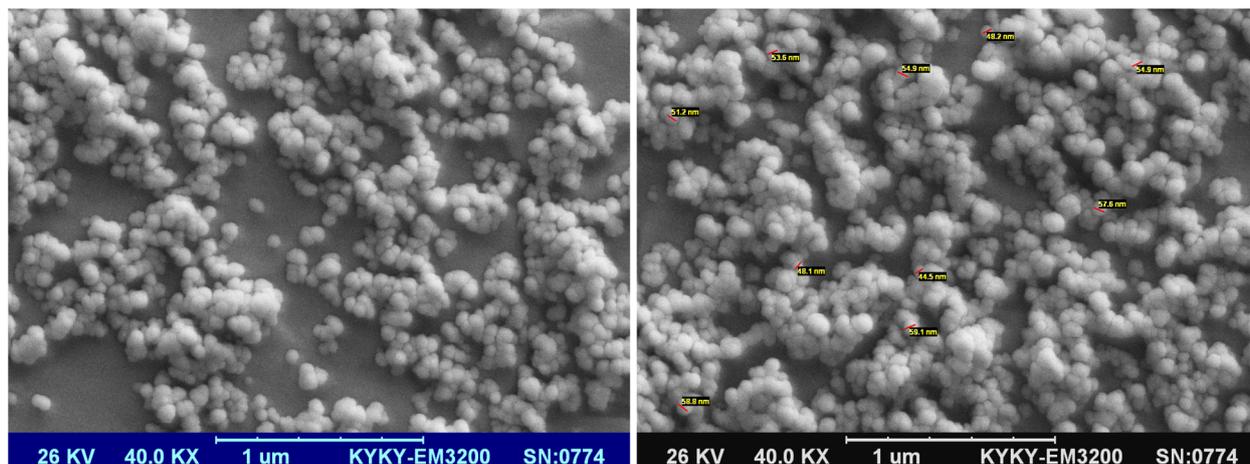


Fig. 2 SEM images of Fe<sub>3</sub>O<sub>4</sub>@boehmite NPs.



indicate particles size of  $\text{Fe}_3\text{O}_4$ @boehmite NPs are less than 60 nm.

Also, the TEM images were used to studying the morphology and size of  $\text{Fe}_3\text{O}_4$ @boehmite NPs. As shown in TEM images (Fig. 3),  $\text{Fe}_3\text{O}_4$ @boehmite NPs were formed in uniform shapes with quite homogeneous diameter.

The elements content of  $\text{Fe}_3\text{O}_4$ @boehmite NPs was studied by EDS analysis. The EDS analysis of  $\text{Fe}_3\text{O}_4$ @boehmite NPs is shown in Fig. 4 which indicate the presence of oxygen, iron and aluminum species. Also, the elements distribution of

$\text{Fe}_3\text{O}_4$ @boehmite NPs was studied by WDX analysis. The WDX analysis of  $\text{Fe}_3\text{O}_4$ @boehmite NPs is shown in Fig. 5 which indicate the uniform distribution of the elements in  $\text{Fe}_3\text{O}_4$ @boehmite NPs. As shown in the EDS diagram, no elements except oxygen, iron and aluminum elements were seen.

The exact amount of iron and aluminum elements in  $\text{Fe}_3\text{O}_4$ @boehmite NPs was obtained by ICP analysis, which found to be  $5.7 \times 10^{-3} \text{ mol g}^{-1}$  and  $3.5 \times 10^{-3} \text{ mol g}^{-1}$  respectively.

The normal XRD pattern of  $\text{Fe}_3\text{O}_4$ @boehmite NPs is shown in Fig. 6. The XRD pattern of  $\text{Fe}_3\text{O}_4$ @boehmite NPs shows the

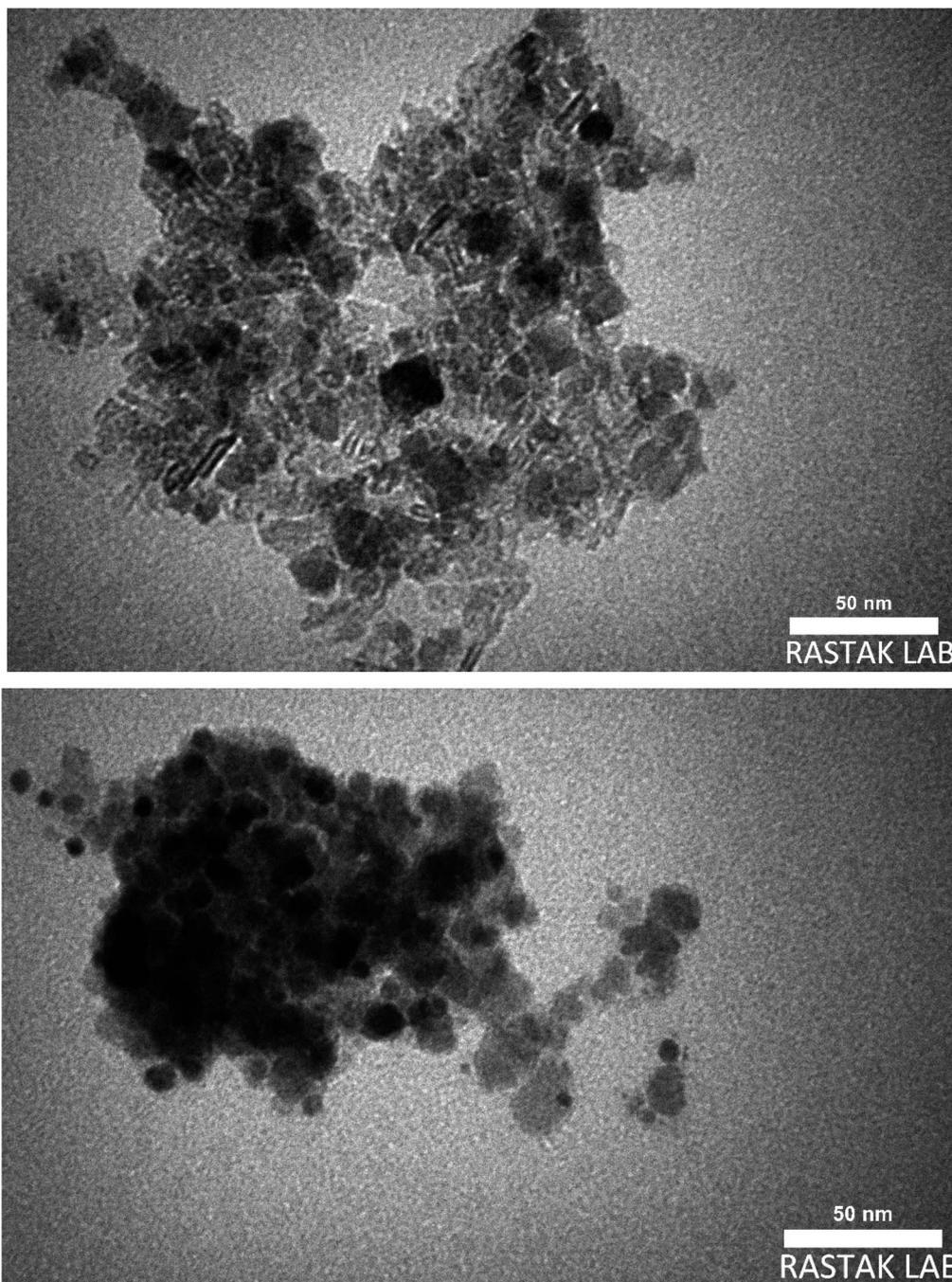


Fig. 3 TEM images of  $\text{Fe}_3\text{O}_4$ @boehmite NPs.



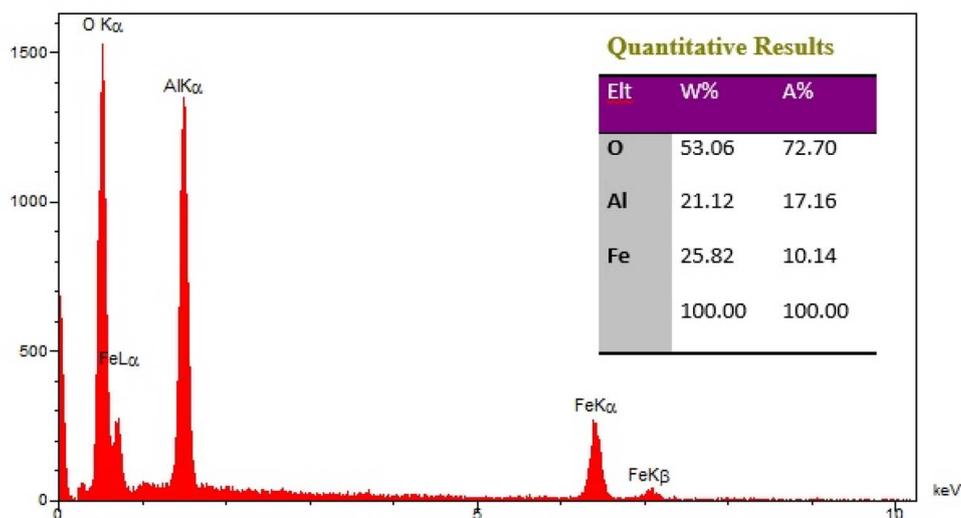


Fig. 4 EDX spectrum of  $\text{Fe}_3\text{O}_4$ @boehmite NPs.

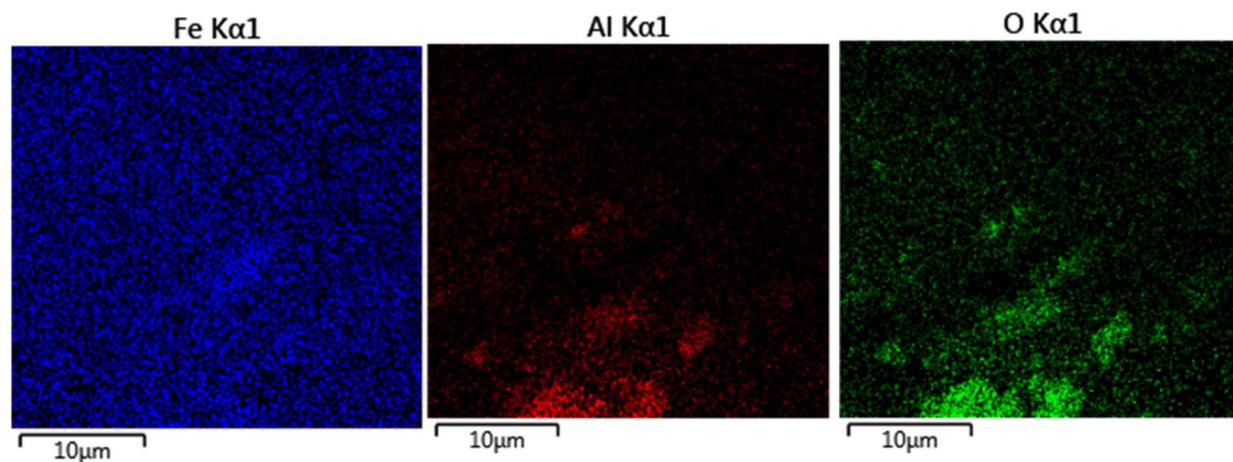


Fig. 5 Elemental mapping of iron, aluminum and oxygen for  $\text{Fe}_3\text{O}_4$ @boehmite NPs.

several peaks of  $2\theta$  values at  $30.5^\circ$  (220),  $35.7^\circ$  (311),  $43.3^\circ$  (400),  $53.6^\circ$  (422),  $57.8^\circ$  (511), and  $62.9^\circ$  (440), which are related to the crystal phase of  $\text{Fe}_3\text{O}_4$  nanoparticles.<sup>11</sup> These results confirmed that  $\text{Fe}_3\text{O}_4$  MNPs were successfully synthesized and did not any changes during synthesis of  $\text{Fe}_3\text{O}_4$ @boehmite NPs. These results are in agreement with the standard XRD pattern of  $\text{Fe}_3\text{O}_4$  MNPs. Also, the boehmite phase in  $\text{Fe}_3\text{O}_4$ @boehmite NPs was characterized by the peak positions at 14.9 (020), 28.5 (120), 38.7 (031), 45.7 (131), 49.4 (051), 51.9 (200), 55.8 (151), 60.1 (080), 65.2 (231), 66.6 (002), 68.6 (171), and 72.1 (251) in the XRD pattern.<sup>27</sup> These results confirmed that BNPS did not any changes after modification of  $\text{Fe}_3\text{O}_4$  MNPs.

The FT-IR spectrum of  $\text{Fe}_3\text{O}_4$  NPs, boehmite NPs and  $\text{Fe}_3\text{O}_4$ @boehmite NPs are shown in Fig. 7. Two bands at region 443 and  $587\text{ cm}^{-1}$  in the FT-IR spectrum of the  $\text{Fe}_3\text{O}_4$  NPs (Fig. 7(a)) are correspond to the vibrations of the Fe-O bonds,<sup>18,42</sup> which these bands are present in the FT-IR spectrum of  $\text{Fe}_3\text{O}_4$ @boehmite NPs (Fig. 7(c)). The peaks at (490, 621 and  $744\text{ cm}^{-1}$ ) in the FT-IR spectrum of the boehmite NPs (Fig. 7(b)) related to

the Al-O bonds vibrations,<sup>27,44</sup> which these bands are also present in the FT-IR spectrum of  $\text{Fe}_3\text{O}_4$ @boehmite NPs (Fig. 7(c)). Hydrogen bands of OH $\cdots$ OH and nitrate impurity vibration were indicated by the several bands at ( $1158$  and  $1077\text{ cm}^{-1}$ ) and ( $1637\text{ cm}^{-1}$ ) respectively in FT-IR spectrum of the boehmite NPs (Fig. 7(b)).<sup>42,43,45</sup>

The surface of  $\text{Fe}_3\text{O}_4$ @boehmite NPs has a large number of hydroxyl groups which the stretching vibration of them appeared above  $3000\text{ cm}^{-1}$  in the FT-IR spectrum.<sup>17</sup> Also, the vibrations of their hydrogen bands of OH $\cdots$ OH are presented at  $1159$  and  $1075\text{ cm}^{-1}$ .<sup>44,45</sup> The several bands at 492, 627 and  $743\text{ cm}^{-1}$  are corresponds to the vibration of the Al-O bonds.<sup>27,46</sup> The characteristic the nitrate impurity were emerged at  $1628\text{ cm}^{-1}$ .<sup>44,47</sup> The peaks which shown in region 452 and  $568\text{ cm}^{-1}$  are related to the vibrations of the Fe-O bond of  $\text{Fe}_3\text{O}_4$  NPs<sup>18</sup> that overlap with the vibrations of the Al-O bonds.

The Raman spectrum of  $\text{Fe}_3\text{O}_4$ @boehmite NPs is shown in Fig. 8. The several bands at 312, 348, 513, 545, 663, 798, 1027, 1297, 1362, 1478, 1520, 1578, 1624, 1762, 2820, 2942 and



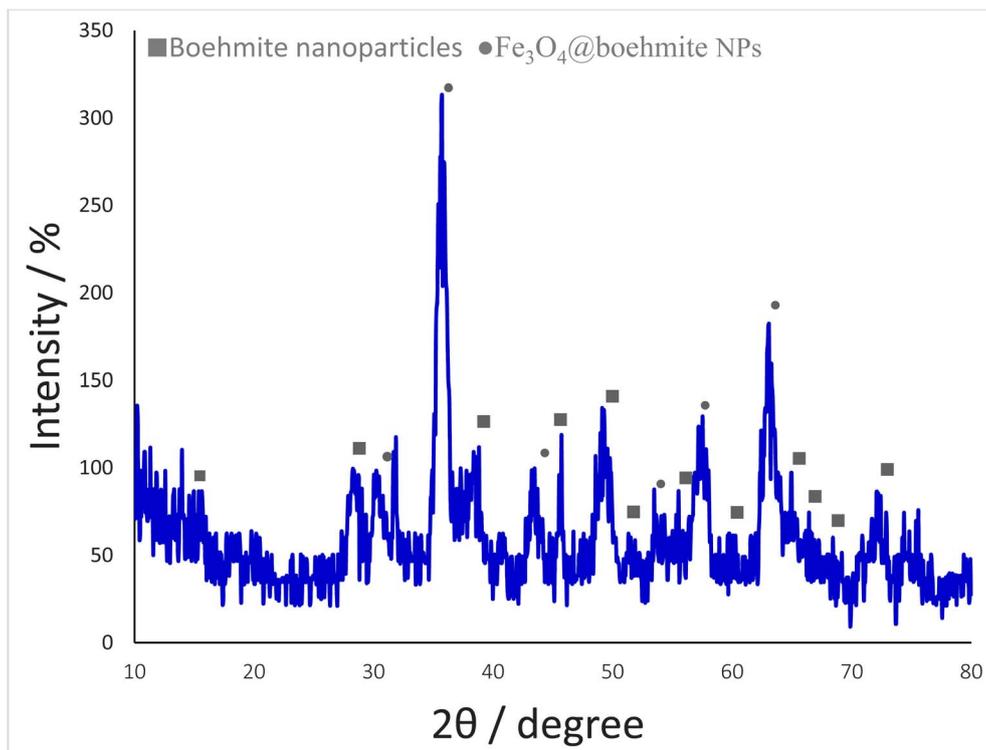


Fig. 6 Normal XRD pattern of  $\text{Fe}_3\text{O}_4$ @boehmite NPs.

$3150\text{ cm}^{-1}$  were observed in the Raman spectrum of  $\text{Fe}_3\text{O}_4$ @boehmite NPs. According to authentic literature,  $\text{Fe}_3\text{O}_4$  NPs characterized by several peaks on  $311$ ,  $540$  and  $665\text{ cm}^{-1}$  in Raman spectroscopy.<sup>48</sup> Therefore, the Raman spectrum shows that  $\text{Fe}_3\text{O}_4$ @boehmite NPs contains  $\text{Fe}_3\text{O}_4$  NPs, not  $\text{Fe}_2\text{O}_3$  NPs.

Also, based on another previous literature,<sup>49,50</sup>  $\text{Fe}_3\text{O}_4$  nanoparticles characterized by several peaks on  $305$ ,  $513$ ,  $534$  and  $660\text{ cm}^{-1}$  in Raman spectroscopy. These peaks are observed in Raman spectrum of  $\text{Fe}_3\text{O}_4$ @boehmite NPs which are indexed to  $\text{Fe}_3\text{O}_4$  NPs in  $\text{Fe}_3\text{O}_4$ @boehmite NPs. Meanwhile, based on same literature,<sup>49,50</sup>  $\gamma\text{-Fe}_2\text{O}_3$  nanoparticles characterized by several peaks on  $350$ ,  $500$  and  $700\text{ cm}^{-1}$  in Raman spectroscopy and  $\alpha\text{-Fe}_2\text{O}_3$  nanoparticles characterized by several peaks on  $221$ ,  $244$ ,  $292$ ,  $406$ ,  $497$  and  $611\text{ cm}^{-1}$  in Raman spectroscopy. These peaks were not observed in the Raman spectrum of  $\text{Fe}_3\text{O}_4$ @boehmite NPs. Therefore,  $\text{Fe}_3\text{O}_4$ @boehmite NPs only includes  $\text{Fe}_3\text{O}_4$  NPs.

The magnetic property of  $\text{Fe}_3\text{O}_4$ @boehmite NPs was studied by VSM technique using LBKFB device from “Magnetic Kavir

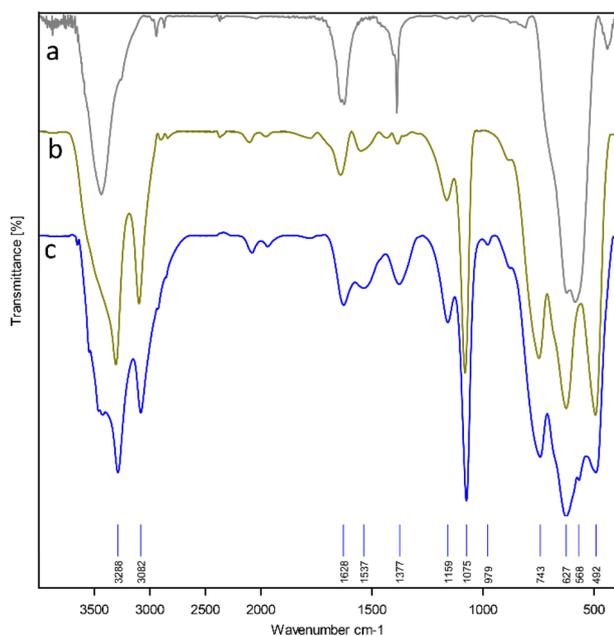


Fig. 7 FT-IR spectra of  $\text{Fe}_3\text{O}_4$  NPs (a), boehmite NPs (b) and  $\text{Fe}_3\text{O}_4$ @boehmite NPs (c).

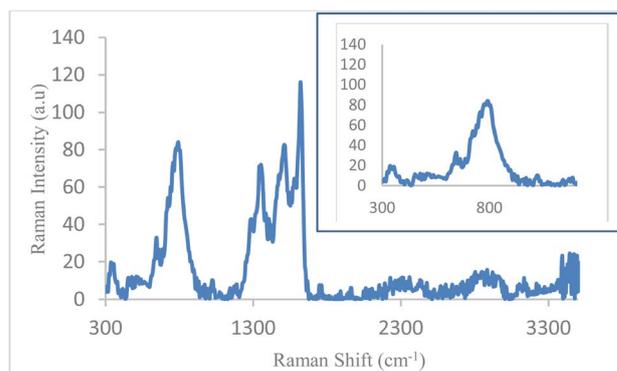


Fig. 8 Raman spectrum  $\text{Fe}_3\text{O}_4$ @boehmite NPs.



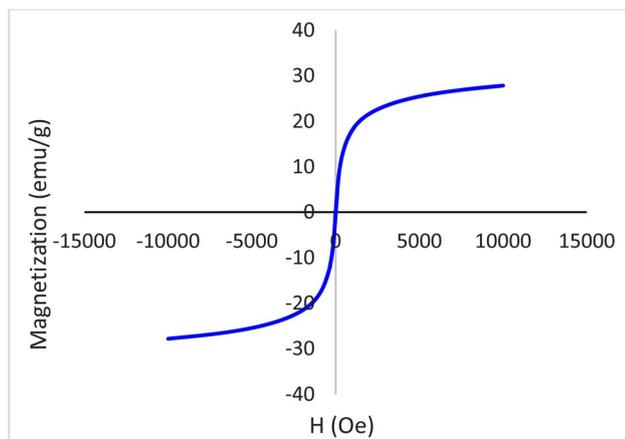
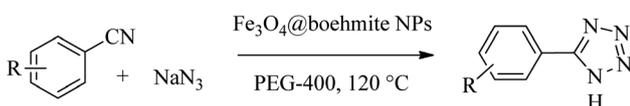


Fig. 9 Magnetization curves for  $\text{Fe}_3\text{O}_4$ @boehmite NPs.



Scheme 1 Synthesis of 5-substituted 1H-tetrazoles in the presence of  $\text{Fe}_3\text{O}_4$ @boehmite NPs.

Kashan". The VSM curve of  $\text{Fe}_3\text{O}_4$ @boehmite NPs is shown in Fig. 9. Magnetic properties of  $\text{Fe}_3\text{O}_4$ @boehmite NPs was found to be  $27.5 \text{ emu g}^{-1}$ . As expected,  $\text{Fe}_3\text{O}_4$ @boehmite NPs showed the lower magnetic value in comparison to  $\text{Fe}_3\text{O}_4$  NPs (which is about  $74.09 \text{ emu g}^{-1}$ )<sup>12</sup> due to the coating of  $\text{Fe}_3\text{O}_4$  nanoparticles by boehmite layers.

After characterization of  $\text{Fe}_3\text{O}_4$ @boehmite NPs, its catalytic application was studied in the synthesis of 5-substituted 1H-tetrazole derivatives (Scheme 1).

Firstly, the [3+2] cycloaddition of  $\text{NaN}_3$  with benzonitrile in the presence of  $\text{Fe}_3\text{O}_4$ @boehmite NPs was selected for optimizing reaction conditions (Table 1). The effect of solvent, amount of  $\text{NaN}_3$  and temperature was studied in the presence of various catalytic amount of  $\text{Fe}_3\text{O}_4$ @boehmite NPs. As shown, the [3+2] cycloaddition of  $\text{NaN}_3$  with benzonitrile was tested in the presence of (30, 20, 15 and 10) mg of  $\text{Fe}_3\text{O}_4$ @boehmite NPs

catalyst (Table 1, entries 2–5), which 15 mg of  $\text{Fe}_3\text{O}_4$ @boehmite NPs is optimal amount of this catalyst for completing of the reaction in acceptable time (Table 1, entry 4). Reducing the amount of catalyst from 15 mg to 10 mg significantly increases in the reaction time and reduces in the product yield (Table 1, entry 5). While increasing the amount of catalyst has insignificant effect on reaction time or yield (Table 1, entry 3). Then, the optimization conditions were continued in various solvents (Table 1, entries 6–9) in the presence of 15 mg (optimal amount) of  $\text{Fe}_3\text{O}_4$ @boehmite NPs catalyst. Among various solvents, the best results were obtained when PEG was used as solvent (Table 1, entry 4). Also in continuation of our studying the effect of temperature and sodium azide content was examined, which the best result was observed at  $120 \text{ }^\circ\text{C}$  using 1.5 mmol sodium azide (Table 1, entry 4).

After optimization of reaction conditions, the catalytic application of  $\text{Fe}_3\text{O}_4$ @boehmite NPs was extended to aromatic (Table 2, entries 1–12) and aliphatic (Table 2, entries 13–15) nitrile derivatives. In this regard, aromatic nitriles; including, an electron-donating or electron-withdrawing groups on aromatic ring were investigated for the synthesis of corresponding tetrazole derivatives. As shown in Table 2, all products were obtained in acceptable times and excellent yields which indicated the excellent efficiency of  $\text{Fe}_3\text{O}_4$ @boehmite NPs. Also, *ortho*-, *meta*- and *para*-substituted benzonitriles were successfully investigated. More additions, aliphatic nitriles were investigated and corresponding tetrazoles were obtained in excellent yields.

Homoselectivity is an interesting property which indicate in the quite the same functional groups that only one of them take part in the reaction.<sup>51,52</sup> For example, malononitrile which has two identical cyano groups, was investigated for the synthesis of corresponding tetrazoles in the presence of  $\text{Fe}_3\text{O}_4$ @boehmite NPs catalyst (Table 2, entry 15). Interestingly, this catalyst shown a good selectivity in the synthesis of tetrazoles and only one of identical cyano groups in malononitrile was reacted with sodium azide and another cyano groups was remained without any change (Scheme 2).

Also, benzylidenemalononitrile derivatives bearing electron-withdrawing (Table 2, entry 16) and electron-donor (Table 2, entry 17) functional groups were investigated for the synthesis

Table 1 Optimization reaction conditions for [3+2] cycloaddition of  $\text{NaN}_3$  with benzonitrile in the presence of  $\text{Fe}_3\text{O}_4$ @boehmite NPs catalyst

| Entry | Catalyst (mg) | Solvent              | $\text{NaN}_3$ (mmol) | Temperature ( $^\circ\text{C}$ ) | Time (min) | Yield (%) <sup>a</sup> |
|-------|---------------|----------------------|-----------------------|----------------------------------|------------|------------------------|
| 1     | —             | PEG                  | 1.5                   | 120                              | 600        | —                      |
| 2     | 30            | PEG                  | 1.5                   | 120                              | 210        | 95                     |
| 3     | 20            | PEG                  | 1.5                   | 120                              | 220        | 93                     |
| 4     | 15            | PEG                  | 1.5                   | 120                              | 240        | 97                     |
| 5     | 10            | PEG                  | 1.5                   | 120                              | 600        | 88                     |
| 6     | 15            | PEG                  | 1.7                   | 120                              | 230        | 90                     |
| 7     | 15            | $\text{H}_2\text{O}$ | 1.5                   | 120                              | 240        | 25                     |
| 8     | 15            | DMSO                 | 1.5                   | 120                              | 240        | 68                     |
| 9     | 15            | DMF                  | 1.5                   | 120                              | 240        | 73                     |
| 10    | 15            | PEG                  | 1.5                   | 100                              | 240        | 60                     |

<sup>a</sup> Isolated yield.



Table 2 Synthesis of tetrazoles in the presence of Fe<sub>3</sub>O<sub>4</sub>@boehmite NPs

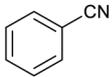
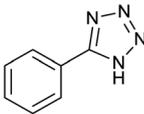
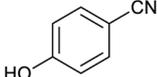
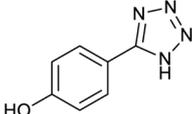
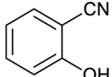
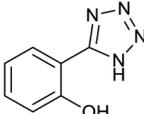
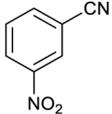
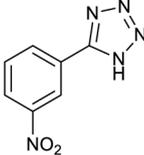
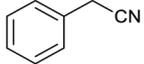
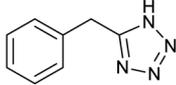
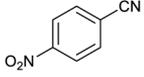
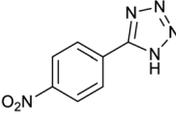
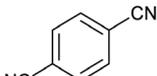
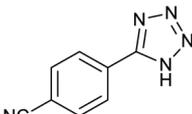
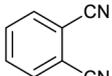
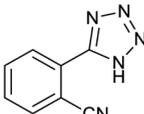
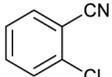
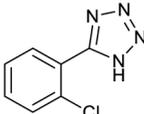
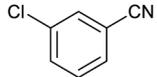
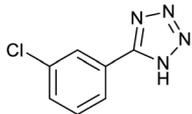
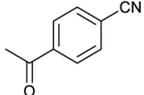
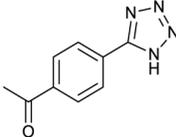
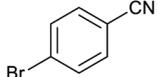
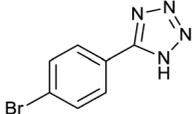
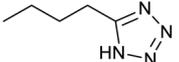
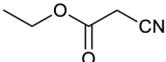
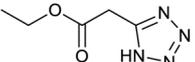
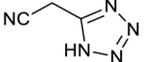
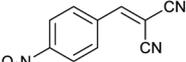
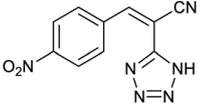
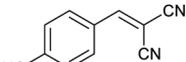
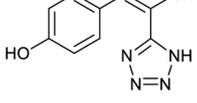
| Entry | Nitrile                                                                             | Product                                                                             | Time (min) | Yield <sup>a</sup> (%) |
|-------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|------------|------------------------|
| 1     |    |    | 240        | 97                     |
| 2     |    |    | 335        | 95                     |
| 3     |    |    | 300        | 96                     |
| 4     |    |    | 360        | 93                     |
| 5     |    |    | 260        | 91                     |
| 6     |    |   | 28 h       | 90                     |
| 7     |  |  | 24 h       | 92                     |
| 8     |  |  | 375        | 94                     |
| 9     |  |  | 610        | 92                     |
| 10    |  |  | 12.5 h     | 90                     |
| 11    |  |  | 37 h       | 85                     |
| 12    |  |  | 25         | 95                     |



Table 2 (Contd.)

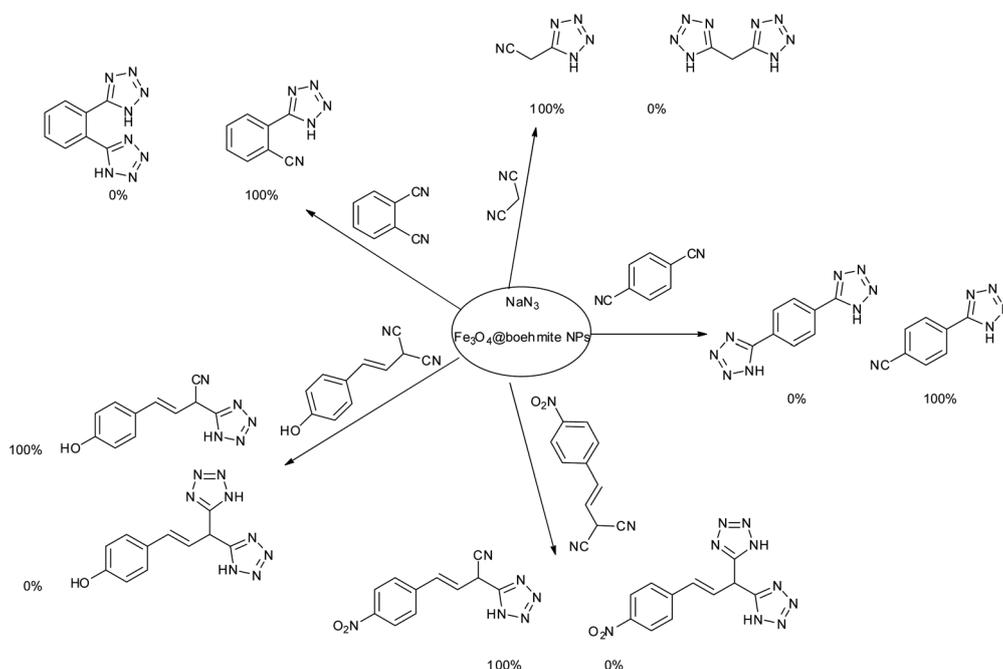
| Entry | Nitrile                                                                           | Product                                                                           | Time (min) | Yield <sup>a</sup> (%) |
|-------|-----------------------------------------------------------------------------------|-----------------------------------------------------------------------------------|------------|------------------------|
| 13    |  |  | 12 h       | 87                     |
| 14    |  |  | 105        | 93                     |
| 15    |  |  | 65         | 85                     |
| 16    |  |  | 135        | 95                     |
| 17    |  |  | 200        | 93                     |

<sup>a</sup> Isolated yield.

of tetrazoles in the presence of  $\text{Fe}_3\text{O}_4$ @boehmite NPs catalyst. These substrate have two cyano-functional groups with same position in their structure which afforded the mono [3+2] cycloaddition with sodium azide in the presence of  $\text{Fe}_3\text{O}_4$ @boehmite NPs catalyst. Phthalonitrile and terphthalonitrile (Table 2, entries 7 and 8) were also investigated and the products were obtained in high yield and excellent homoselectivity (Scheme 2). Therefore, these results were indicated the high

efficiency of  $\text{Fe}_3\text{O}_4$ @boehmite NPs catalyst in the synthesis of the wide range of tetrazoles.

Reusability of catalysts is one of the principles of green chemistry in the design of chemical processes, which is the most important advantage of heterogeneous catalysts over homogeneous catalysts. Therefore, the reusability of  $\text{Fe}_3\text{O}_4$ @boehmite NPs catalyst was studied in the [3+2] cycloaddition of  $\text{NaN}_3$  with benzonitrile (Fig. 10). In this studying, in the end of

Scheme 2 Homoselectivity of  $\text{Fe}_3\text{O}_4$ @boehmite NPs catalyst in the [3+2] cycloaddition of  $\text{NaN}_3$  with dicyano substituted derivatives.

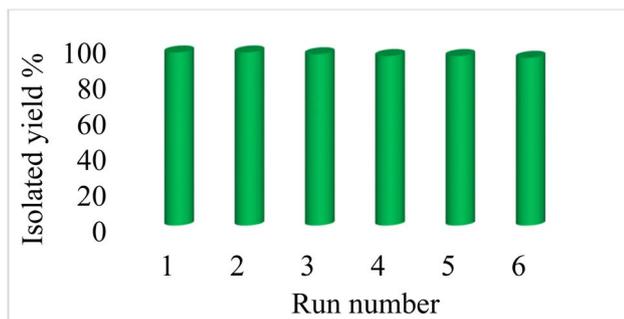


Fig. 10 Recyclability of Fe<sub>3</sub>O<sub>4</sub>@boehmite NPs catalyst in the [3+2] cycloaddition of NaN<sub>3</sub> with benzonitrile.

each reaction, Fe<sub>3</sub>O<sub>4</sub>@boehmite NPs catalyst was recovered using an external magnet and washed with water and ethyl acetate. Subsequently the recovered catalyst was charged by same reactants for next run. As shown in Fig. 10, Fe<sub>3</sub>O<sub>4</sub>@boehmite NPs catalyst reused up to 6 times.

In order to studying the iron leaching from Fe<sub>3</sub>O<sub>4</sub>@boehmite NPs catalyst in the reaction mixture, the [3+2] cycloaddition of NaN<sub>3</sub> with benzonitrile was repeated under optimized conditions. In the end of the reaction, the catalyst was isolated by external magnet and the amount of probably leached iron in the reaction solution was calculated by AAS analysis, which a significant amount of iron was not detected in the reaction solution. Therefore, Fe<sub>3</sub>O<sub>4</sub>@boehmite NPs are formed by strong bonds between boehmite and Fe<sub>3</sub>O<sub>4</sub> NPs.

The efficiency and practically of Fe<sub>3</sub>O<sub>4</sub>@boehmite NPs catalyst was compared to previously catalysts in the synthesis of 5-phenyl-1H-tetrazole from the [3+2] cycloaddition of NaN<sub>3</sub> with benzonitrile (Table 3). As shown the higher yield of the product was obtained in the presence of Fe<sub>3</sub>O<sub>4</sub>@boehmite NPs catalyst than other catalysts. Also, the reaction time in the presence of Fe<sub>3</sub>O<sub>4</sub>@boehmite NPs catalyst is shorter than other catalysts. Fe<sub>3</sub>O<sub>4</sub>@boehmite NPs catalyst has the advantages of both MNPs and BNPs and it can be reused for several times. While purification of the products and reusing of the homogeneous

catalysts are often difficult, costly and time consuming. The synthesis of tetrazole derivatives were out come in PEG as green solvents in the presence of Fe<sub>3</sub>O<sub>4</sub>@boehmite NPs catalyst, while some previously procedures used organic solvents.

## 4 Conclusions

In conclusion, magnetic boehmite nanoparticles was synthesized as an efficient and reusable heterogeneous catalyst for the homoselective synthesis of 5-substituted 1H-tetrazoles. This catalyst is composed of boehmite nanoparticles and Fe<sub>3</sub>O<sub>4</sub> nanoparticles, therefore it has advantages of both boehmite nanoparticles (such as high surface area and stability) and Fe<sub>3</sub>O<sub>4</sub> (such as easy separation by an external magnet) systems. Magnetic boehmite nanoparticles can be recovered and reused up to 6 times without any significant loss of its activity. Magnetic boehmite nanoparticles was characterized by TEM, SEM, EDS, WDX, ICP, FT-IR, Raman, XRD and VSM techniques.

## Conflicts of interest

There are no conflicts to declare.

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Table 3 Comparison of Fe<sub>3</sub>O<sub>4</sub>@boehmite NPs catalyst in the [3+2] cycloaddition of NaN<sub>3</sub> with benzonitrile

| Entry | Catalyst                                                       | Time (h) | Yield (%) | Ref.      |
|-------|----------------------------------------------------------------|----------|-----------|-----------|
| 1     | Cu-TBA@biochar                                                 | 7        | 98        | 26        |
| 2     | CoY zeolite                                                    | 14       | 90        | 53        |
| 3     | Cu-Zn alloy nanopowder                                         | 10       | 95        | 54        |
| 4     | B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>                 | 8        | 94        | 55        |
| 5     | Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> /Salen Cu(II) | 7        | 90        | 56        |
| 6     | Fe <sub>3</sub> O <sub>4</sub> /ZnS HNSs                       | 24       | 81.1      | 57        |
| 7     | Mesoporous ZnS                                                 | 36       | 86        | 58        |
| 8     | Cu(OAc) <sub>2</sub>                                           | 12       | 98        | 59        |
| 9     | CuFe <sub>2</sub> O <sub>4</sub>                               | 12       | 82        | 60        |
| 10    | Nano ZnO/Co <sub>3</sub> O <sub>4</sub>                        | 12       | 90        | 61        |
| 11    | Cu(II)-adenine-MCM-41                                          | 5        | 92        | 62        |
| 12    | Pd-isatin-boehmite                                             | 8        | 94        | 63        |
| 13    | Fe <sub>3</sub> O <sub>4</sub> @boehmite NPs                   | 4        | 97        | This work |



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