Iron oxide (Fe₃O₄) magnetic nanoparticles supported on wrinkled fibrous nanosilica (WFNS) functionalized by biimidazole ionic liquid as an effective and reusable heterogeneous magnetic nanocatalyst for the efficient synthesis of N-sulfonylamidines

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Abstract

Wrinkled fibrous nanosilica (WFNS) which functionalized by ionic liquid modified Fe₃O₄ NPs and CuI salts has been synthesized and characterized with FE-SEM, TEM, FT-IR, FAAS, EDX, and, XRD, VSM, and BET-BJH analysis. This new and effective magnetic ceramic nanocatalyst has been applied towards rapid synthesis of N-sulfonylamidines using reaction of phenyl acetylene, substituted sulfonyl azide and various amines under solvent-free conditions in very short reaction time. Higher catalytic activity CuI/Fe₃O₄NPs@IL-DFNS in the reaction is because of special structure of DFNS and existence of ionic liquids on its pores which act as a robust anchors to the loaded various nano-particles. So, this lead to no leaching of them from the pore of the composite. Shorter reaction time, higher yield, recovery of the catalyst using an external magnet and its reusability for 8 series without noteworthy reduction in its activity are the advantages of newly synthetic catalyst toward efficient synthesis of N-sulfonylamidines.

1. Introduction

In recent years, silica materials with porous structure and excellent properties like high thermalization, hydrothermal, and mechanical stability, low density and toxicity, good biocompatibility, cost effectiveness, and simple surface functionalization, have been received a lot of attentions [1, 2, 3, 4, 5, 6]. A new class of silica nanospheres with wrinkled, dendritic and fibrous morphology is DFNS that at the first time introduced by Polshettiwar and co-workers. These materials have exceptional activities in several field of research such as catalysis, synthesis, sensors, energy harvesting, and biomedical applications [7,8].

DFNS is an exceptional nanomaterial with accessibility from all sides in contrast with various silica mesoporous nano-materials like SBA-15 and MCM-41 with tube-shaped or cylindrical pores [9, 10, 11]. In other hand, numerous useful materials like organometallics, some metal nanoparticles, metal oxides, and organic functional groups, can be hosted in the channels of the DFNS without the padlocking of its pores and channels the and above all, availability of freshly produced active positions were improved. Although above mentioned silica mesoporous nanomaterials have higher geometric surface area than DFNS, but the outcomes display that, its honesty is appropriate. Moreover, thin silica walls of DFNS with high mechanical and thermal stability. Also, singular structure and morphology permit the better dispersion and loading of the active sites and functional groups in contrast with MCM-41 and SBA-15.

Recently publications exhibit that functionalization of the various silica nano materials with ionic liquids (ILs) can increase their catalytic activity because of specific futures of ILs such as eco-friendly, good stability, appropriate ionic conductivity, extensive liquid temperature range gap, and high thermal stability [12,13]. Until now, various type of ionic liquids which have been attached to the various supports, they have acted as a catalyst, reaction medium and as a stabilizer of numerous nanomaterials according to their ability in coordination of various metal atoms and ions based on electrostatic interaction [1-4]. Also, the supported ionic liquids can afford a suitable hydrophobic media, and enhance the activity of the catalyst during the reaction procedures. Then, numerous heterocyclic compound synthesis have been generated in the presence of loaded ILs as a nanocatalysts [15].
Scheme 1. Synthesis of N-sulfonylamidines derivatives in the presence of magnetic nanocatalyst CuI/Fe₃O₄ NPs@IL-DFNS.

Scheme 2. Preparation of the CuI/Fe₃O₄ NPs@IL-DFNS nanocatalyst.
One of the significant structural motifs in biologically active compounds and natural products are amidines [16, 17, 18]. They have been broadly used in synthetic, coordination, medicinal, and supramolecular chemistry because of their exceptional chemical properties [19, 20, 21, 22]. N-sulfonylamidines as a new versatile class of compounds are one of the useful synthetic intermediates and efficient ligands with important pharmaceutical and biological activities [16, 17, 18, 21, 22, 23, 24, 25, 26, 27, 28].

Till now diverse copper containing catalysts such as CuI [29, 30, 31, 32, 33], cellulose functionalized with aminomethylpyridine and copper iodide nanoparticles [34], Cu(OTf)2 [35] and, (MOF-Cu2I2(BTTP4) [36] have been widely used for the efficient production of these important active N-sulfonylamidines. Lower yields, longer reaction times and importantly no reusability and recoverability of the used catalyst are disadvantages of the previously reported methods. Hence, developing a green and efficient procedure using the reusable heterogeneous nanocatalysts for the synthesis of these important biological compounds with higher yields is extremely demanded.

Following of previous research work on the application of DFNS as a new heterogeneous nanocatalyst [37, 38, 39, 40], dendritic nanosilica modified with ionic liquid loaded Cu salts and Fe3O4 NPs is the best candidate towards synthesis of N-sulfonylamidines. In this study, DFNS functionalized with biimidazole as a strong anchors to trap Cu salts and Fe3O4 NPs. In the next step, this green and magnetic nanocatalyst has been used in the synthesis of N-sulfonylamidines derivatives. It is noteworthy that, higher catalytic activity of this catalyst is because of its exceptional dendritic and wrinkled structure of DFNS and its alteration by ionic liquids which perform as vigorous anchors to the loaded nano-particles. So, this lead to no leaching of them from the pore of the composite (Scheme 1).

2. Experimental section

2.1. Methods and materials

All of chemicals and materials were purchased from Merck Co.

2.2. Synthesis of N-sulfonylamidines derivatives: a general procedure

A blend of phenyl acetylene (1 mmol), sulfynyl azide (1 mmol), secondary amines (1.2 mmol) and, (CuI/Fe3O4 NPs@IL-DFNS) (1.02 mol %), were involved to the test-tube and stirred for under solvent-free conditions. Surveying of reaction process/completing were performed by TLC (Thin-layer chromatography). Finally, external magnet was used for the separation of nano-catalyst. Also, to increase its purity, obtained material was washed by water/acetone solution several times which the pure products were obtained using preparative layer chromatography in EtOAc/n-Hexan (1:3) as solvent.

2.3. Synthesis of CuI/Fe3O4 NPs@IL-DFNS

After synthesis of dendritic fibrous nanosilica (DFNS) according to our previous report [38]. The obtained precipitate in the previous step was separated using external magnet, washed by deionized water, and dried at 60 °C for 6 h. In the next step, dried precipitate (1 g, Fe3O4 NPs@IL-DFNS) was included to the solution of CuI (0.190 g in 50 ml methanol), and stirred at 30 °C for 24h. Then, the obtained magnetic nanocatalyst was separated by external magnet, washed with ethanol, acetone, and deionized water and dried in air. The schematic of the synthesised nanocatalyst is shown in Scheme 2.
3. Results and discussions

3.1. Characterization of the nanocatalyst

After synthesis and modification of the magnetic nanocatalyst, the morphology and structure of CuI/Fe3O4NPs@IL-DFNS were investigated by FAAS, FT-IR, SEM, TEM, EDX, Mapping, XRD, BET, BJH and VLS analysis.

The amount of copper and iron which loaded on the fibrous dendritic silica was determined by FAAS (flame atomic absorption spectroscopy) which the amount of iron and copper doped in the CuI/Fe3O4NPs@IL-DFNS catalyst were 5.91 and 22.54 wt%, respectively. Hence, according to FAAS the amount of Cu loaded on the catalyst is 0.35 mol.

In the FT-IR spectrum (Figure 1), the peaks appear in 1628 and 1428 cm\(^{-1}\) are related to the stretching vibrations of C=\(\equiv\)N and C=\(\equiv\)C in the imidazolium rings, respectively. The peak at 593 cm\(^{-1}\) is belonging to the

| Material type     | Pore size (nm)
|-------------------|----------------|
| DFNS              | 9.9            |
| CuI/Fe3O4 NPs@IL-DFNS | 13.76         |

| Material type     | Pore volume (cm\(^3\) g\(^{-1}\)) | Surface Area (m\(^2\) g\(^{-1}\)) |
|-------------------|----------------------------------|---------------------------------|
| DFNS              | 1.5                              | 617                             |
| CuI/Fe3O4 NPs@IL-DFNS | 0.77                         | 225                             |

\(^a\) Pore size was calculated by BET method.

\(^b\) Pore volume determined from nitrogen physiosorption isotherm.

Table 1. Porosity evaluation of CuI/Fe3O4 NPs@IL-DFNS and its comparison with DFNS as bare material.

Table 2. Optimization of the type of solvent and time of reaction for the synthesis of N-sulfonylamidines.

| Entry | Catalyst (mol %) | Solvent     | Time (min) | Yield (%) |
|-------|------------------|-------------|------------|-----------|
| 1     | CuI/Fe3O4 NPs@IL-DFNS (1.73, 3.46, 5.2) | DMF         | 100        | 80, 86, 95 |
| 2     | CuI/Fe3O4 NPs@IL-DFNS (5.2) | THF         | 100        | 87        |
| 3     | CuI/Fe3O4 NPs@IL-DFNS (5.2) | CH\(_2\)CN   | 100        | 84        |
| 4     | CuI/Fe3O4 NPs@IL-DFNS (5.2) | CH\(_2\)Cl   | 100        | 83        |
| 5     | CuI/Fe3O4 NPs@IL-DFNS (5.2) | CHCl\(_3\)   | 100        | 83        |
| 6     | CuI/Fe3O4 NPs@IL-DFNS (5.2) | Solvent-free | 5          | 96        |
| 7     | CuI/Fe3O4 NPs@IL-DFNS (6.93) | Solvent-free | 5          | 96        |
| 8     | Cu (10% mol)     |             | 40         | 81        |
| 9     | CuBr (10% mol)   |             | 60         | 78        |
| 10    | CuCl (10% mol)   |             | 60         | 73        |
| 11    | Fe3O4 NPs (40 mg) |             | 500        |           |
| 12    | Fe3O4 NPs@IL-DFNS |             | 500        |           |

Scheme 3. A model reaction for the catalytically synthesis of N-sulfonylamidines derivatives in the presence CuI/Fe3O4 NPs@IL-DFNS.
vibration of Fe–O in Fe₃O₄. Also, the weak peak at 670 cm⁻¹ can be attributed to copper iodide bond and the sharp peak at 3426 cm⁻¹ is assigned to O–H bonds of nanocatalyst [45].

In order to study the structure and morphology of the nanocatalyst, TEM and FE-SEM analyses were used. Uniform spheres with dendritic and fibrous structure of DFNS were confirmed by FE-SEM and TEM images (Figure 2). Also, based on TEM images, the average size of particle was obtained as 30 nm and existence of MNPs on the structure was approved.

To determine the successful coating of Fe₃O₄ and CuI on the surface of CuI/Fe₃O₄ NPs@IL-DFNS, EDX was employed (Fig. S1A). The EDX analysis paved the presence of Cu, N, C, Si, and O characteristic peaks. Also, Map analysis was applied to confirm the all mentioned results (Fig. S1B).

In the following stage, to assess the crystal structure of the CuI/Fe₃O₄ NPs@IL-DFNS nanocatalyst, X-ray diffraction (XRD) analysis was applied (Figure 3). Results shown that, the peaks at 2θ = 63.08°, 58.09°, 54.14°, 43.53°, 35.24° and 30.39° are associated for cubic CuI and the peaks at 89.21°, 79.30°, 77.49°, 69.30°, 67.24°, 61.76°, 52.60°, 49.85°, 42.01°, 29.33°, 25.20°, and 12.46° are related to cubic Fe₃O₄. Moreover, a wide peak in the range of 2θ = 19–30° is belong to amorphous silica.

The porous nature of CuI/Fe₃O₄ NPs@IL-DFNS and bare DFNS was investigated using BJH-BET analysis (Fig. S2). Using these methods, surface area and porosity of the nanocatalyst were measured. In addition, the pore volume of the CuI/Fe₃O₄ NPs@IL-DFNS and DFNS were calculated by using BJH analysis and compared in Table 1. According to these data, the pore volumes changed from 1.52 to 0.77 cm³/g for DFNS (bare material) and CuI/Fe₃O₄ NPs@IL-DFNS, respectively. Also, surface area was obtained as 225 m²/g, 617 m²/g for CuI/Fe₃O₄ NPs@IL-DFNS and bare materials (DFNS), respectively. In addition, the mean pore diameter of CuI/Fe₃O₄ NPs@IL-DFNS and DFNS was obtained as 13.76 and 9.9 nm, respectively.

The VSM magnetization curve of prepared nanaocatalyst is shown in Fig. S3. The saturation magnetization of the prepared catalyst is obtained as 22.47 emu g⁻¹. All of these results was confirmed by FESEM (Fig. S3) and TEM (Fig. S4) images of nanocatalyst.

3.2. Catalytically synthesis of N-sulfonylamidines derivatives in the presence CuI/Fe₃O₄ NPs@IL-DFNS

To the obtain of optimum reaction conditions towards synthesis of N-sulfonylamidines derivatives, a mixture of phenyl acetylene (1 mmol), 4-toluenesulfonyl azide (1 mmol), morpholine (1.2 mmol) were designated as a model reaction and the effect of the various solvents, different catalysts and also amount of the catalysts has been investigated (Scheme 3).

Various amount of magnetic nanocatalyst (CuI/Fe₃O₄ NPs@IL-DFNS) was used for the optimization of synthesis of N-sulfonylamidines derivatives in the presence of DMF at room temperature. Based on obtained results, yield of the reaction has association with the amount of applied nanocatalyst which increasing of this nanocomposite from 1.73 to 6.93 mol% lead to increasing of reaction yield. However, after increment the amount of CuI/Fe₃O₄ NPs@IL-DFNS to 5.2 mol% has not effect on the yield of the reaction (synthesis of N-sulfonylamidines derivatives). So, 5.2 mol% of the synthesized magnetic nano-catalyst was selected as an optimized amount for the reaction (synthesis of N-sulfonylamidines derivatives) under solvent-free condition and rt (Table 1, entry 1).

In continue, different solvents such as DMF, THF, CH₃CN, CH₂Cl₂, and CH₃Cl in the presence of CuI/Fe₃O₄ NPs@IL-DFNS (5.2 mol%) were investigated as a solvent for the model reaction (Table 1, entries 1–5). In these solvents, the yields of the reaction were obtained as 95%, 87%, 84%, 83% and 83%, respectively at 100 min. Surprisingly, when the model reaction was done in the solvent-free conditions, the yield of the reaction was increased. Therefore, the reaction time was significantly reduced. Also, solvent-free condition was preferred towards synthesis of N-sulfonylamidines in the presence of candidate magnetic nanocatalyst (5.2 mol%) as an efficient magnetic nanocatalyst and all of the reactions were performed in this condition (Table 1, entry 6).
| Entry | Product | Time (Min) | Yield* (%) |
|-------|---------|------------|------------|
| 4a    | ![Chemical Structure](image) | 4          | 96         |
| 4b    | ![Chemical Structure](image) | 4          | 96         |
| 4c    | ![Chemical Structure](image) | 10         | 84         |
| 4d    | ![Chemical Structure](image) | 5          | 90         |
| 4e    | ![Chemical Structure](image) | 4          | 91         |
| 4f    | ![Chemical Structure](image) | 4          | 91         |
| 4g    | ![Chemical Structure](image) | 4          | 95         |
| 4h    | ![Chemical Structure](image) | 4          | 92         |

(continued on next page)
In addition, various Cu sources like CuI, CuBr, CuCl (10% mol) were tested for the model reaction under solvent-free conditions (Table 1, entries 8–10). The results show that among the copper halides, CuI is an effective catalyst for this reaction, but it is not a recoverable and reusable catalyst in various coupling reactions. Hence, by supporting of this useful catalyst by appropriate substrate such as dendritic fibrous nanosilica, its catalytic efficiency can be improved significantly. It is found that, in the presence of Fe3O4 NPs and Fe3O4 NPs@IL-DFNS as a nanocatalyst, no product was formed (Table 1, entries 11–12). But, by the incorporation of copper iodide on the surface and pores of the fibrous nanosilica the favorite products achieved with short reaction times in high yield. Hence, CuI/Fe3O4 NPs@IL-DFNS was preferred as an effective and reusable nanocatalyst towards synthesis of N-sulfonylamidines in solvent-free conditions. The effectiveness of the catalyst is because of the uniform distribution of copper iodide on the substrate and simple diffusion of the reactants on the channels and so on their interactions with the active sites of the magnetic candidate nanocatalyst.

Based on Table 1, CuI/Fe3O4 NPs@IL-DFNS (with the amount of 5.2 mol%) is an active nanocatalyst for the reaction of the phenylacetylene (1 mmol), sulfonyl azide (1 mmol), and secondary amines (1.1 mmol), under solvent-free conditions to generate N-sulfonylamidines derivatives in high yields.

In order to show the efficiency of CuI/Fe3O4 NPs@IL-DFNS as innovative nanocatalyst, several types of secondary amines were applied to react with phenylacetylene and sulfonyl azide at r.t., and solvent-free conditions (See Table 2).

Suggested mechanism for the synthesis procedure of N-sulfonylamidines in the existence of candidate magnetic nano-catalyst (CuI@Fe3O4 NPs@IL-DFNS) is illustrated in Scheme 4. As seen, in the presence of nanocatalyst functionalized with ionic liquid and trapped Fe3O4 NPs and Cu salts, the triazole was formed by the cycloaddition reaction between phenylacetylene and sulfonyl azide. In the next step, after the elimination of the nitrogen, the ketenimine intermediate is created with nucleophilic addition of morphine gives the major product with high yields.

Table 3 (continued)

| Entry | Product | Time (Min) | Yield (%) |
|-------|---------|------------|-----------|
| 4i    | ![Product Image] | 5          | 94        |
| 4j    | ![Product Image] | 7          | 91        |

* Isolated yields.

Table 4. Comparison of prepared nanocatalyst with other reported catalysts in N-sulfonylamidine synthesis.

| Entry | Catalyst | Conditions | Time (min) | Yield (%) | Ref. |
|-------|----------|------------|------------|-----------|------|
| 1     | CuI      | r.t., THF  | 120        | 89        | [41] |
| 2     | CuI@C    | r.t., CH3CN| 180        | 92        | [42] |
| 3     | MOF-CuO2 (BTPA) | r.t., CH3CN | 120        | 88        | [36] |
| 4     | CuI/Fe3O4 NPs@AMPCs | r.t., solvent-free | 5          | 94        | [34] |
| 5     | CuI@scolecite | r.t., THF   | 80         | 90        | [43] |
| 6     | CuI@Fe3O4 NPs-g-CS | r.t., solvent-free | 10        | 92        | [44] |
| 7     | CuI@Fe3O4 NPs-IL-DFNS | r.t., solvent-free | 5         | 97        | This work |

Figure 4. A) Effective separation of nanocatalyst (CuI/Fe3O4 NPs@IL-DFNS) from the reaction mixture by means of external magnet. B) Histogram of catalyst reusability (Yield %) versus number of use.
Table 3, compare catalytically activity of Cu@Fe3O4 NPs-IL-DNFNS on the synthesis of N-sulfonylamidines derivatives with previous reports. According to the obtained results, engineered magnetic nanocatalyst is an appropriated candidate nanocomposite/nanocatalyst towards synthesis of N-sulfonylamidines because of its eco-friendliness, simple recovery and reusability. Also, higher yields, shorter reaction times and solvent free conditions are another advantages of using of this catalyst (see Table 4).

3.3. Re-usability of the candidate magnetic catalyst

In industrial applications the simple recovery and reusability of nanocatalysts is too important. In the present work, reusability of the proposed magnetic nanocatalyst was investigated by running in various number. For this purpose, after the completion of the reaction, an external magnet was used for the easily separation of the Cu@Fe3O4 NPs-IL-DNFNS from the reaction mixture. Then the separated catalyst was washed with acetone and water and as can be seen in Figure 1, proposed magnetic nano-catalyst (Cu@Fe3O4 NPs-IL-DNFNS) is recyclable eight times with slightly decrease in its catalytic intrinsic (Figure 4).

4. Conclusion

In conclusion, Cu@Fe3O4 NPs-IL-DNFNS was used as a green magnetic nanocatalyst towards efficient catalytically synthesis of N-sulfonylamidines by one-pot reaction of sulfonyl azides, phenyl acetylene, and secondary amines. Higher surface area and porous structure of the nanocatalyst with its exceptional catalytic activity, magnetically recoverable of the catalyst, shorter reaction times, and excellent yields in comparison with previous reported methods, and no using of toxic solvents are the benefits of this work.

Declarations

Author contribution statement

Sajjad Azizi: Performed the experiments; Wrote the paper. Nazrin Shadjou: Conceived and designed the experiments; Analyzed the data; Wrote the paper.

Funding statement

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Data availability statement

Data included in article supplementary material/referenced in article.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

Supplementary content related to this article has been published online at https://doi.org/10.1016/j.heliyon.2021.e05915.

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