Full Paper

Anchoring of Cu(II)–vanillin Schiff base complex on MCM-41: A highly efficient and recyclable catalyst for synthesis of sulfides and 5-substituted 1H–tetrazoles and oxidation of sulfides to sulfoxides

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A copper(II)–vanillin complex was immobilized onto MCM-41 nanostructure and was used as an inexpensive, non-toxic and heterogeneous catalyst in the synthesis of symmetric aryl sulfides by the cross-coupling of aromatic halides with S8 as an effective sulfur source, in the oxidation of sulfides to sulfoxides using 30% H2O2 as a green oxidant and in the synthesis of 5-substituted 1H–tetrazoles from a smooth (3 + 2) cycloaddition of organic nitriles with sodium azide (NaN3). The products were obtained in good to excellent yields. This catalyst could be reused several times without loss of activity. Characterization of the catalyst was performed using Fourier transform infrared, energy-dispersive X-ray and atomic absorption spectroscopies, X-ray diffraction, thermogravimetric analysis, and scanning and transmission electron microscopies.

Keywords
5-substituted 1H–tetrazoles, copper(II), MCM-41 nanostructure, sulfide, sulfoxide

1 | INTRODUCTION

Symmetric and unsymmetric diaryl sulfides are a class of important synthetic reagents and intermediates in organic, bio-organic, heterocyclic and medicinal chemistry. They are found in numerous drugs displaying a broad spectrum of therapeutic activities such as those against diabetes, Alzheimer’s disease, inflammation, cancer, Parkinson’s disease and HIV. Also, sulfides are the starting materials for the preparations of other sulfur compounds, such as sulfonium compounds, sulfones and sulfoxides. The study of oxidation of organic sulfides to sulfoxides is of wide interest because of their antioxidant nature and the important role of sulfur compounds in biological systems and intermediates for pharmaceuticals, polymer materials and ligands in asymmetric catalysis. Tetrazoles are some of the most stable nitrogen-rich heterocyclic compounds that have received considerable attention because tetrazole-containing molecules have several applications in the field of coordination chemistry, organic synthesis, material science and medicinal chemistry including antiprotezoal, antihypertensive and antibiotic effects.

The greatest advantage of heterogeneous catalysis is the facile separation of catalysts from reaction media and products. There are various ways in order to fix catalysts into heterogeneous supports, such as immobilization in zeolites, copolymerization, attachment onto an organic polymer and grafting onto inorganic supports such as silica. The mesoporosity of silica-based materials has come to the forefront as an exciting and novel research field of scientific and technological importance in heterogeneous catalysis. Among the mesoporous silica materials, MCM-41 is of interest due to some of its special properties such as its high thermal stability, high surface area, high pore volume, structural simplicity, narrow pore size distribution and ease of preparation with negligible pore networking and pore blocking. Vanillin has been reported to inhibit mutagenesis induced by chemical and physical mutagens and to suppress the invasion and migration of cancer cells. It also displays antimicrobial and antioxidant properties and is used for medicinal purposes.
Salen Cu(II),\textsuperscript{27} ionic liquids,\textsuperscript{28} CuO,\textsuperscript{29} and CoL\textsubscript{2}, CuL\textsubscript{2}, ZnL\textsubscript{2} and PdL\textsubscript{2} Schiff base complexes.\textsuperscript{30} However, most of them have some drawbacks such as toxicity, instability, expensiveness, require the use of high temperature and long reaction times, and difficulty in synthetic procedure. Hence, in order to overcome some of these drawbacks, in the work reported here a safe and appropriate Schiff base ligand was prepared by immobilization of vanillin onto modified MCM-41 silica support followed by anchoring of Cu\textsuperscript{2+} ions via complex formation into the MCM-41. The aim of the study was to determine a simple and highly efficient protocol for the synthesis of symmetric diaryl sulfides and 5-substituted 1\textsubscript{H}-tetrazoles and for sulfoxidation reactions.

2 | EXPERIMENTAL

2.1 | Materials

Tetraethylorthosilicate (TEOS; 98%), cationic surfactant cetyltrimethylammonium bromide (CTAB; 98%), Cu(II) nitrate hexahydrate (Cu(NO\textsubscript{3})\textsubscript{2}⋅6H\textsubscript{2}O), 3-hydroxy-4-methoxybenzaldehyde (vanillin), 30\% H\textsubscript{2}O\textsubscript{2} and other reagents were purchased from Aldrich, Merck or Fluka and used as received.

2.2 | Synthesis of MCM-41 mesoporous material

CTAB (1 g) was added into an aqueous solution containing 3.5 ml of NaOH solution (2 M) and stirred at 80 °C. After the mixture was uniform, 5 ml of TEOS was gradually added and the resulting mixture was refluxed for 2 h at the same temperature. The obtained white solid was washed with deionized water and calcined at 823 K for 5 h at a rate of 2 °C min\textsuperscript{−1} to remove the residual surfactant.

2.3 | Synthesis of aminopropyl-functionalized MCM-41 mesoporous material (nPrNH\textsubscript{2}-MCM-41)

A mixture of pure MCM-41 (4.8 g) suspended in n-hexane (100 ml), and 3-aminoproptriethoxysilane (4.8 g) was refluxed for 24 h. The resulting nPrNH\textsubscript{2}-MCM-41 was filtered, washed with n-hexane and dried under vacuum.

2.4 | Synthesis of Schiff base-functionalized MCM-41 mesoporous material (vanillin-MCM-41)

The prepared nPrNH\textsubscript{2}-MCM-41 (0.5 g) and vanillin (1.2 mmol, 0.182 g) were dissolved in absolute ethanol (25 ml). The reaction mixture was refluxed under nitrogen atmosphere for 3 h. The resultant solid was filtered, washed thoroughly with ethanol and dried for 12 h under vacuum conditions. The synthesized sample was named Vanillin-MCM-41.

2.5 | Synthesis of heterogeneous copper(II) Schiff base catalyst (Cu(II)-vanillin-MCM-41)

For the synthesis of heterogeneous Schiff base catalyst, a mixture of Cu(NO\textsubscript{3})\textsubscript{2}-6H\textsubscript{2}O (0.70 mmol, 0.170 g) and Vanillin-MCM-41 (0.25 g) in ethanol (25 ml) was refluxed for 20 h. The resulting solid was filtered, washed with ethanol and dried at room temperature (Scheme 1).

2.6 | General Procedure for Synthesis of Sulfides

To a solution of aryl halide, KOH and S\textsubscript{8} in dimethylsulfoxide (DMSO), the Cu(II)-Vanillin-MCM-41 catalyst (20 mg) was added and the mixture was stirred magnetically at 110 °C for the required time. The progress of the reaction was monitored by TLC (n-hexane–acetone, 8:2). After completion of the reaction, Cu(II)-Vanillin-MCM-41 was removed from the reaction mixture by filtration. The reaction mixture was decanted using water and dichloromethane and the pure sulfides were obtained by evaporation of dichloromethane.

2.7 | General Procedure for Sulfoxide Oxidation

Typically, a mixture of sulfide (1.0 mmol), H\textsubscript{2}O\textsubscript{2} (0.40 ml) and 5 mg of catalyst was added to a round-bottomed flask (25 ml) equipped with a magnetic stirrer and stirred at room temperature for an appropriate time. After completion of the reaction (the progress of the reaction was monitored by TLC (n-hexane–acetone, 8:2)), the reaction mixture was decanted using water and dichloromethane and the pure sulfides were obtained by evaporation of dichloromethane.
TLC), Cu(II)-Vanillin-MCM-41 was separated from reaction mixture by filtration. Then, the product was extracted from the reaction mixture with dichloromethane. The final product was obtained by evaporating the dichloromethane.

2.8 General Procedure for Synthesis of 5-Substituted 1H-Tetrazoles

Cu(II)-Vanillin-MCM-41 (25 mg), benzonitrile (1 mmol) and sodium azide (0.08 g, 1.2 mmol) were placed in a round-bottom flask and poly(ethylene glycol) (PEG)-400 (3 ml) was added. The mixture was stirred at 120 °C for the appropriate time. After completion of the reaction as indicated by TLC (n-hexane-acetone, 8:2), the catalyst was collected by filtration and treated with ethyl acetate and 0.1 N HCl (2 ml). The resultant organic layer was separated and the aqueous layer was extracted with ethyl acetate (20 ml).

3 RESULTS AND DISCUSSION

3.1 Characterization

The X-ray diffraction (XRD) pattern of MCM-41 presented in Figure 1 shows (100), (110) and (200) reflections of regular hexagonal array of pores at \( \theta = 2.51^\circ, 4.53^\circ \) and \( 5.11^\circ \), respectively. Compared to the parent MCM-41, it can be seen that the intensity of these characteristic peaks in the XRD pattern of the Cu(II)-Vanillin-MCM-41 sample becomes weaker and shift to higher angles when metal is loaded on MCM-41 (Cu(II)-Vanillin-MCM-41). These observations indicate that functionalization occurs mainly inside the MCM-41 channels.[31]

MCM-41 and Cu(II)-Vanillin-MCM-41 were characterized using Fourier transform infrared (FT-IR) spectroscopy. As shown in Figure 2(a), the bands at 1059, 962 and 454 cm\(^{-1}\) can be attributed to asymmetric stretching, symmetric stretching and bending of Si–O–Si, respectively. In addition, the band at 3443 cm\(^{-1}\) is assigned to the vibration of the hydrogen-bonding silanol groups. After the functionalization of MCM-41 with 3-aminopropyltriethoxysilane, a band at around 2928 cm\(^{-1}\) is observed that is associated with the CH\(_2\) vibrations corresponding to C–H stretching (Figure 2b). In Figure 2(c), the bands at about 1519 cm\(^{-1}\) (C=C) and

![FIGURE 2 FT-IR spectra of (a) MCM-41, (b) nPrNH\(_2\)-MCM-41, (c) Vanillin-MCM-41 and (d) Cu(II)-Vanillin-MCM-41](image)

![FIGURE 3 SEM micrographs of (a) MCM-41 and (b) Cu(II)-Vanillin-MCM-41](image)
1649 cm\(^{-1}\) (C=N) are characteristic bands of vanillin. It is clearly observed that the band at 1649 cm\(^{-1}\), assigned to azomethine nitrogen present in the Schiff base ligand, is shifted near 1626 cm\(^{-1}\) in the FT-IR spectrum of Cu(II)-Vanillin-MCM-41 after immobilization of copper on the surface of Vanillin-MCM-41 (Figure 2d).

Scanning electron microscopy (SEM) images of MCM-41 and Cu(II)-Vanillin-MCM-41 are shown in Figure 3. The SEM images confirm that MCM-41 and Cu(II)-Vanillin-MCM-41 have regular and spherical morphology. The average nanoparticle diameter of Cu(II)-Vanillin-MCM-41 is around 51–262 nm. As shown in Figure 4, the energy-dispersive X-ray spectrum (EDS) of the catalyst reveals the presence of Si (42.02%), O (37.30%), C (10.77%), N (6.75%) and Cu (3.16%) species in the catalyst.

The amount of Cu(II) of the catalyst immobilized onto MCM-41 nanoparticles is found to be 0.45 mmol g\(^{-1}\) based on atomic absorption spectroscopy (AAS).

The weight changes of catalyst and support were measured using thermogravimetric analysis (TGA; Figure 6). The TGA curve for MCM-41 sample shows a one-step weight loss of approximately 4% below 100 °C, which is due to desorption of physically adsorbed water. It is possible to observe a three-step weight loss for the Cu(II)-Vanillin-MCM-41 sample. The initial weight loss below 200 °C is due to removal of the physically adsorbed water and other solvents attached to the particle surfaces. In addition, on increasing the temperature from 200 to 800 °C, the TGA curve seems to show two weight loss stages which are related to the decomposition of organic moieties (200–400 °C) and silanol groups (500 to ca 800 °C), respectively. These three steps involve a total weight loss of about 25%.

### 3.2 Application of Cu(II)-Vanillin-MCM-41 Heterogeneous Catalyst

In continuation of our previous study of organic functional group transformations,[32–36] we were interested in finding a simple and efficient method for the synthesis of symmetric diaryl sulfide derivatives.

The weight changes of catalyst and support were measured using thermogravimetric analysis (TGA; Figure 6). The TGA curve for MCM-41 sample shows a one-step weight loss of approximately 4% below 100 °C, which is due to desorption of physically adsorbed water. It is possible to observe a three-step weight loss for the Cu(II)-Vanillin-MCM-41 sample. The initial weight loss below 200 °C is due to removal of the physically adsorbed water and other solvents attached to the particle surfaces. In addition, on increasing the temperature from 200 to 800 °C, the TGA curve seems to show two weight loss stages which are related to the decomposition of organic moieties (200–400 °C) and silanol groups (500 to ca 800 °C), respectively. These three steps involve a total weight loss of about 25%.

### Heterogeneous Catalyst

In continuation of our previous study of organic functional group transformations,[32–36] we were interested in finding a simple and efficient method for the synthesis of symmetric diaryl sulfide derivatives.

### Table 1 Optimization of reaction conditions using phenyl iodide (1 mmol), S\(_8\) (1 mmol) and KOH

<table>
<thead>
<tr>
<th>Entry</th>
<th>Amount of catalyst (mg)</th>
<th>Amount of base (g)</th>
<th>Temperature (°C)</th>
<th>Solvent</th>
<th>Time (min)</th>
<th>Yield (%)(^{a})</th>
</tr>
</thead>
<tbody>
<tr>
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<td>None</td>
<td>1</td>
<td>120</td>
<td>DMSO</td>
<td>600</td>
<td>Trace</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>1</td>
<td>120</td>
<td>DMSO</td>
<td>45</td>
<td>25</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>1</td>
<td>120</td>
<td>DMSO</td>
<td>45</td>
<td>67</td>
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<tr>
<td>4</td>
<td>15</td>
<td>1</td>
<td>120</td>
<td>DMSO</td>
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<td>83</td>
</tr>
<tr>
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<td>1</td>
<td>120</td>
<td>DMSO</td>
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<tr>
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<td>0.5</td>
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<td>DMSO</td>
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<td>65</td>
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<td>13</td>
<td>20</td>
<td>1</td>
<td>100</td>
<td>DMSO</td>
<td>45</td>
<td>84</td>
</tr>
</tbody>
</table>

\(^{a}\)Isolated yield.

\(^{b}\)No reaction.
diaryl sulphides and tetrazoles and also for the oxidation of sulfides using Cu(II)-Vanillin-MCM-41 as a reusable and non-toxic heterogeneous catalyst.

### 3.2.1 Synthesis of symmetric diaryl sulfide derivatives

The reaction parameters of catalyst amount, nature of solvent and temperature were optimized in the synthesis of sulfides. For this propose phenyl iodide (1 mmol), S₈ (1 mmol) as a

**TABLE 2** Synthesis of symmetric sulfides from reaction of aryl halides (1 mmol) with S₈ (1 mmol), KOH (1 g) in DMSO at 110 °C in the presence of Cu(II)-Vanillin-MCM-41 (20 mg)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product</th>
<th>Time (min)</th>
<th>Yield (%)a</th>
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<tbody>
<tr>
<td>1</td>
<td>I</td>
<td>S_2</td>
<td>45</td>
<td>90</td>
</tr>
<tr>
<td>2</td>
<td>Br</td>
<td>S_2</td>
<td>70</td>
<td>83</td>
</tr>
<tr>
<td>3</td>
<td>OCH₃</td>
<td>OCH₃ OCH₃</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>4</td>
<td>Br</td>
<td>S_2</td>
<td>80</td>
<td>87</td>
</tr>
<tr>
<td>5</td>
<td>N₃</td>
<td>S_2</td>
<td>75</td>
<td>85</td>
</tr>
<tr>
<td>6</td>
<td>HO</td>
<td>S_2</td>
<td>70</td>
<td>83</td>
</tr>
<tr>
<td>7</td>
<td>O₂N</td>
<td>S_2</td>
<td>65</td>
<td>80</td>
</tr>
<tr>
<td>8</td>
<td>Br</td>
<td>S_2</td>
<td>120</td>
<td>82</td>
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<td>9</td>
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<tr>
<td>10</td>
<td>Cl</td>
<td>S_2</td>
<td>150</td>
<td>80</td>
</tr>
<tr>
<td>11</td>
<td>Br</td>
<td>S_2</td>
<td>1020</td>
<td>87</td>
</tr>
<tr>
<td>12</td>
<td>Br</td>
<td>S_2</td>
<td>2280</td>
<td>84</td>
</tr>
</tbody>
</table>

*Isolated yield.

### SCHEME 3 Oxidation of sulfides to sulfoxides

**TABLE 3** Oxidation of various sulfides (1 mmol) with 30% H₂O₂ (0.4 ml) catalysed by Cu(II)-Vanillin-MCM-41 (5 mg) under solvent-free conditions at room temperature

<table>
<thead>
<tr>
<th>Entry</th>
<th>Amount of catalyst (mg)</th>
<th>Solvent</th>
<th>Time (min)</th>
<th>Yield (%)a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>Solvent free</td>
<td>300</td>
<td>Trace</td>
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<tr>
<td>2</td>
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<td>Dichloromethane</td>
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<td>85</td>
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<td>7</td>
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<td>Ethyl acetate</td>
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<td>8</td>
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<td>Acetonitrile</td>
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<td>90</td>
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<tr>
<td>9</td>
<td>5</td>
<td>Ethanol</td>
<td>80</td>
<td>80</td>
</tr>
</tbody>
</table>

*aIsolated yield.

*Reaction conditions: 1 mmol of methylphenyl sulfide, 4 ml of 30% H₂O₂ at room temperature.

### TABLE 4 Effect of catalyst load and various solvents on oxidation reaction

<table>
<thead>
<tr>
<th>Entry</th>
<th>Amount of catalyst (mg)</th>
<th>Solvent</th>
<th>Time (min)</th>
<th>Yield (%)b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>Solvent free</td>
<td>80</td>
<td>96</td>
</tr>
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<tr>
<td>6</td>
<td>5</td>
<td>Dichloromethane</td>
<td>80</td>
<td>85</td>
</tr>
<tr>
<td>7</td>
<td>5</td>
<td>Ethyl acetate</td>
<td>80</td>
<td>85</td>
</tr>
<tr>
<td>8</td>
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<td>Acetonitrile</td>
<td>80</td>
<td>90</td>
</tr>
<tr>
<td>9</td>
<td>5</td>
<td>Ethanol</td>
<td>80</td>
<td>80</td>
</tr>
</tbody>
</table>

*aIsolated yield.

*bReaction conditions: 1 mmol of methylphenyl sulfide, 4 ml of 30% H₂O₂ at room temperature.
sulfur source and KOH were chosen for a model reaction (Scheme 2).

When we carried out the model reaction in the absence of catalyst, the reaction does not go well even after prolonged heating (120 °C, 10 h) (Table 1, entry 1) and in the presence of 5 mg of catalyst, the sulfide product is formed in low yield (Table 1, entry 2). On increasing the amount of catalyst up to 20 mg, high isolated yield (90%) is achieved after 45 min (Table 1, entry 5). Among various solvents screened (Table 1, entries 7–9), it is found that the desired product is not obtained in solvents such as water and PEG-400. However, when we carried out the reaction in polar aprotic solvents such as DMSO and dimethylformamide (DMF), the reaction is highly effective (Table 1, entries 5 and 7). The important role of the amount of KOH in the synthesis of sulfides is often overlooked (Table 1, entries 5, 10 and 11). With 1 g of KOH the best result is obtained. In addition, the effect of temperature was evaluated and the desired product is obtained at 110 and 120 °C (Table 1, entries 5, 12 and 13). Therefore, 110 °C was selected for this reaction.

In subsequent experiments, C—S cross-coupling reactions of S8 and aryl halides catalysed by the copper(II) complex were investigated under the optimized reaction conditions (Table 2). The C—S coupled products are isolated in good to excellent yields for all derivatives.

### 3.2.2 Oxidation of sulfides to sulfoxides

To optimize the reaction conditions for the oxidation of sulfides to sulfoxides, we chose the reaction of methylphenyl sulfide (1 mmol) and 30% H2O2 (0.4 ml) as a model reaction under solvent-free conditions at room temperature (Scheme 3).

**SCHEME 3** Synthesis of 5-substituted 1H-tetrazoles

![Chemical Structure](image)

The amount of catalyst has a considerable effect on the yield of the reaction of methylphenyl sulfide to the corresponding sulfoxide. Therefore, various amounts of catalyst were used for this oxidation reaction. In the absence of catalyst, no product is detectable after 5 h (Table 3, entry 1). Among various amounts of catalyst screened (Table 3, entries 2–5), the maximum yield is observed with 5 mg of catalyst, but there is no considerable difference in the yield when 8 and 10 mg of catalyst are employed. Therefore, 5 mg of catalyst was chosen as the optimum amount. We also studied the influence of various solvents on the product yield, namely dichloromethane, ethanol, acetonitrile and ethyl acetate (Table 3, entries 6–9). It is found that the best result is obtained in the oxidation reactions of sulfide to sulfoxide under solvent-free conditions.

With the optimal reaction conditions in hand, we extended the scope of the method with various sulfides. The results of the chemoselective oxidation of sulfides to sulfoxides with 30% H2O2 under solvent-free conditions in the presence of 5 mg of Cu(II)-Vanillin-MCM-41 at room temperature are summarized in Table 4.

### 3.2.3 Synthesis of 5-substituted 1H-tetrazole derivatives

The first step of the synthetic approach for 5-substituted 1H-tetrazoles involved optimization of reaction conditions and exploring the catalytic activity of Cu(II)-Vanillin-MCM-41 as catalyst. Initially, we investigated the reaction of benzonitrile (1 mmol) with sodium azide (1.2 mmol) as a model reaction to synthesize the corresponding tetrazoles (Scheme 4).

**SCHEME 4** Synthesis of 5-substituted 1H-tetrazoles

![Chemical Structure](image)

**TABLE 5** Catalytic results for the synthesis of 5-substituted 1H-tetrazoles

<table>
<thead>
<tr>
<th>Entry</th>
<th>Temperature (°C)</th>
<th>Solvent</th>
<th>Catalyst (mg)</th>
<th>Time (h)</th>
<th>Yield (%)b</th>
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<tbody>
<tr>
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<td>PEG-400</td>
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<td>3.5</td>
<td>Trace</td>
</tr>
<tr>
<td>2</td>
<td>120</td>
<td>PEG-400</td>
<td>5</td>
<td>3.5</td>
<td>25</td>
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<td>3</td>
<td>120</td>
<td>PEG-400</td>
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<td>3.5</td>
<td>45</td>
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<td>4</td>
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<td>3.5</td>
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<tr>
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<td>Water</td>
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<td>3.5</td>
<td>25</td>
</tr>
<tr>
<td>13</td>
<td>120</td>
<td>EtOH</td>
<td>25</td>
<td>3.5</td>
<td>—c</td>
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</tbody>
</table>

*aReaction mixture consisted of benzonitrile (1.0 mmol), sodium azide (1.2 mmol), catalyst and 2 ml of solvent. Reaction time was 3.5 h.

bIsolated yield.

cNo reaction.
A greater amount of catalyst (25 mg) improves the yield of product (Table 5, entries 2–6).

Indeed, the highest yield is attained at 120 °C, while lower temperature has a negative effect on the reaction (Table 5, entries 5 and 7–9). In a further attempt to improve the conversion, we also examined the reaction in several solvents (Table 5, entries 10–13). PEG-400, DMF and DMSO are the most appropriate solvents for this reaction (Table 5, entries 6, 10 and 11). But from an environmental viewpoint, PEG-400 is the more desirable solvent. Therefore, PEG-400 was chosen for this reaction (Table 5, entry 5). Results are summarized in Table 5.

Finally, the catalyst efficiency was investigated in the synthesis of 5-substituted 1H-tetrazoles under the optimized reaction conditions. This investigation shows that the presence of electron-donating or electron-withdrawing group has no significant role in this reaction and the reactions successfully proceed in good to excellent yields (Table 6).

**TABLE 6** Synthesis of 5-substituted 1H-tetrazoles with sodium azide in the presence of Cu(II)-Vanillin-MCM-41 catalyst (25 mg) in PEG-400 at 120 °C

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product</th>
<th>Time (h)</th>
<th>Yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Melting point (°C)</th>
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<tr>
<td>1</td>
<td></td>
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<td>3.5</td>
<td>92</td>
<td>211–214&lt;sup&gt;137&lt;/sup&gt;</td>
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<td></td>
<td></td>
<td>2</td>
<td>91</td>
<td>219–221&lt;sup&gt;137&lt;/sup&gt;</td>
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<td></td>
<td>3</td>
<td>92</td>
<td>254–256&lt;sup&gt;137&lt;/sup&gt;</td>
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<td>207–209&lt;sup&gt;137&lt;/sup&gt;</td>
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<td>164–167&lt;sup&gt;400&lt;/sup&gt;</td>
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<td></td>
<td>12</td>
<td>75</td>
<td>242–245&lt;sup&gt;400&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup>Isolated yield.
3.3 | Catalyst Integrity and Leaching

To determine whether the catalyst is actually functioning in a heterogeneous manner, we performed a hot filtration test for the reaction using a mixture of benzonitrile (1 mmol) with sodium azide (1.2 mmol) and 25 mg of Cu(II)-Vanillin-MCM-41 in 3 ml of PEG-400 as a model reaction that was stirred at 120 °C. When 50% of the reaction was completed (monitored by TLC) the reaction mixture was filtered at the reaction temperature and the reaction of the filtrate was continued under the same reaction conditions. After 2 h at 120 °C under the optimized conditions, we found that the filtrate mixture did not indicate any catalytic activity towards the synthesis of 5-substituted 1H-tetrazoles. Also, to determine if Cu(II) is leached out from the catalyst during reaction, we performed AAS analysis of the liquid phase of the reaction mixture that was collected by filtration after completion of the reaction at 120 °C. We found that copper was not present in the filtrate.

3.4 | Catalyst Reusability

Catalyst recycling was performed for the oxidation of methylphenyl sulfide under the optimized reaction conditions (methylphenyl sulfide (1 mmol), with 30% H$_2$O$_2$ (0.4 ml) at room temperature). At the end of each reaction, the catalyst was separated by simple filtration, washed with ethanol, dried at 80 °C and reused for the next run under the same reaction conditions as for the first run. After five cycles the immobilized catalyst retains its catalytic efficiency and selectivity (Figure 7). This is evidence of the potential of the immobilized catalyst in large-scale processes.

4 | CONCLUSIONS

In summary, we have developed a recyclable Cu(II) complex immobilized on MCM-41 nanoparticles to catalyse the synthesis of symmetric diaryl sulfides and 5-substituted 1H-tetrazoles and selective H$_2$O$_2$ (30%) oxidation of organic sulfides to sulfoxides under mild reaction condition. The use of 30% H$_2$O$_2$ as a green oxidant and with no solvent and green solvents in these reactions and also the use of vanillin in the synthesis of the catalyst make these reactions interesting from environmental and economic points of view. More importantly, this catalyst can be reused several times without loss of its catalytic activity.

REFERENCES


**SUPPORTING INFORMATION**

Additional Supporting Information may be found online in the supporting information tab for this article.

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