Surface Modification of Silica-Coated on the Magnetic Nanoparticles with Covalently Immobilized between Imidazolium Cation and Silane Groups for Potential Application as a Green Catalyst

Abstract

The objective of this work is producing a magnetic green Nano catalyst for production of coumarins derivatives by solvent-free protocol. In this research, surface modification silica-coated on the magnetic nanoparticles with covalently immobilized between the imidazolium cation and the 3-chloropropyltrimethoxysilane linker groups. The structure of the catalyst was characterized by XRD, FT-IR, TGA, VSM and SEM. The Fe$_3$O$_4$@SiO$_2$-IM nanoparticle has been used to be an efficient green Nano catalyst for produce of coumarin derivatives by solvent-free protocol. This catalyst is a suitable, owing to its non-toxicity, low-cost and eco-friendly properties. This catalyst can be recovered simply using an external magnetic field. The catalyst was reused several times without losing its catalytic activity.

Keywords: Magnetic nanoparticle; Ionic liquid; Imidazole; Coumarin; Solvent-free

Introduction

In the past decade, ionic liquids (ILs) have attracted increasing attention in organic synthesis and catalysis. The favorable characteristics, such as low vapor pressure, high thermal stability, and peculiar ion environment, make ILs “green” alternatives to replacing traditional organic solvents [1]. Though ionic liquids possessed such promising advantages, their widespread practical application was still hampered by several drawbacks:

i. High viscosity, which resulted in only a minor part of ionic liquids took part in the catalyzed reaction
ii. Homogeneous reaction, which was difficult for product separation and catalyst recovery, and
iii. Consequently high cost for the use of relatively large amounts of ionic liquids [2,3].

Therefore, in order to resolve these issues mentioned earlier, grafting or immobilizing became general concepts applied to heterogenize ILs that is recognized as a green approach in catalytic applications [4,5]. Silica is usually used as an ionic liquid carrier because of its ease of availability, non-toxicity, low cost and high surface area [6-8]. Furthermore, compared with pure ionic liquids, these immobilized ionic liquids show additional advantages, such as significantly decrease of the amounts of ionic liquid, the facilitation of catalyst separation from reaction system and more rapid mass transfer, lower contamination of product, and the ability of using it in gas phase reactions [9-11].

Executing reactions under solvent-free conditions is very important strategy in organic synthesis that appreciably reduces the waste production and precludes post-synthesis steps such as product isolation and solvent recycling. Moreover, in recent years ionic liquids have been successfully employed as solvents with catalytic activity for a variety of reactions but their use as catalyst under solvent free conditions need to be given more attention [12-14].

On the other hand, utilizing magnetic nanoparticles, catalyst separation from reaction system is facilitated [14]. Coumarin derivatives are an important class of natural products with interesting therapeutic and biological properties. These compounds find application in agrochemicals, fragrances, agrochemicals, pharmaceuticals, insecticides and also are extensively used in anticancer for preparation of optical brighteners and laser dyes, anticoagulant, anti-HIV, antibacterial [15-25]. These reactions are usually catalyzed by different Bronsted and Lewis acids in homogeneous and heterogeneous pathway [14,26-33]. This research indicated that Fe$_3$O$_4$@SiO$_2$-IM organic-inorganic hybrid nanostructure can be used as an appropriate heterogeneous acidic catalyst for solvent-free protocol synthesis of coumarin by condensation of phenolic compounds with methyl acetoacetate. Eventually in the context of our work this catalyst is desirable replacement, owing to its low-cost non-toxicity, and eco-friendly properties.
Experimental

Materials and methods

Iron (II) chloride hexahydrate (FeCl$_3$$\cdot$6H$_2$O), iron (II) chloride tetrahydrate (FeCl$_2$$\cdot$4H$_2$O), ammonium hydroxide solution (NH$_4$OH, 25 %), tetraethoxysilicate (TEOS), 3-chloropropyltrimethoxysilane (CPTMS), Imidazole, methyl acetoacetate, phenolic compounds and all chemical solvents were obtained from the Sigma or Merck companies.

Synthesis of magnetite nanoparticles

Magnetic nanoparticles were synthesized by chemical co-precipitation method under alkaline condition [34]. 3.18 gr of FeCl$_3$$\cdot$6H$_2$O and 1.85 gr of FeCl$_2$$\cdot$4H$_2$O were dissolved in 50 ml of water in a round bottom flask and under N$_2$ atmosphere with vigorous stirring. The mixed solution was stirred under N$_2$ at 80°C for 2 h. 10 ml of NH$_4$OH was added into the reaction mixture drop wise, stirred under N$_2$ for another 2h and then cooled to room temperature. The precipitated black powders were collected and washed for several times with deionized water and EtOH. Lastly, magnetite nanoparticles were dried under vacuum at 8°C (Figure 1).

Synthesis of citrate-coated magnetite nanoparticles

To obtain the well-dispersed magnetite nanoparticles, the prepared magnetic nanoparticles were added to 30 ml of 0.1 M citric acid with ultrasonic treatment for 30 min and the reaction was maintained for 12 h at room temperature, and the final product was washed several times with water. The obtained citrate-coated magnetite nanoparticles were separated with external magnetic field [35] (Figure 2).

Modification of nanoparticles surface

The obtained synthesized nanoparticles were dispersed in 100 ml of EtOH and then 2 ml of toluene was added to the solution and the resulting solution was sonicated for 30 min, then 2 ml of CPTMS was added drop wise to the solution. The mixture was stirred for 2 days under nitrogen atmosphere. The modified nanoparticles were again isolated with a magnet and at that time the precipitated particles were washed with MeOH for several times (Figure 4).

Synthesis of Fe$_3$O$_4$@SiO$_2$-IM

1.2 gr of Imidazole was added to 10 ml of CHCl$_3$ and then the modified nanoparticles were added to the resulting solution. The suspension was vigorous stirred and refluxed for two days and then the brown solid washed by CHCl$_3$ and was dried (Figure 5).

Catalyst characterization

SEM images were obtained using a KYKY EM-3200 instrument. FT-IR spectra of the materials were recorded over the range of 400-4000 cm$^{-1}$ region by using a Bruker Tensor 27 series FT-IR spectrometer. TGA was recorded in the range of 25-800 centigrade and XRD on a Siemens D=5000 X-ray Diffractometer, using CuKα radiation (λ=1.5418 Å) at 30 kV and 30 mA.

Typical procedure for the synthesis of coumarin derivatives

The phenolic compound (1mmol), methyl acetoacetate (1mmol) and synthesized nanocatalyst (Fe$_3$O$_4$@SiO$_2$-IM) (0.15 gr) were placed in a glass flask equipped with a magnetic stirrer
at 80°C for suitable times. The reaction was monitored by TLC, and after completion of reaction, the reaction mixture was diluted with cold water and stirred for 15 min. EtOH was added to the reaction mixture and sample were separated by external magnet then the product was purified by recrystallization from EtOH (Figure 6).

**Figure 6:** Typical procedure for the synthesis of coumarin derivatives.

**Results and Discussion**

**Preparation and characterization of the catalyst**

The magnetite nanoparticles were simply synthesized via the co-precipitation method. Citric acid was used as a coating agent and completed stable colloidal dispersion [35]. The choice of citric acid over other frequently offered coating agents is to control the prevent aggregation of magnetite nanoparticles, coating the magnetite nanoparticles with the silica would be a good solution. Likewise, the silica hydroxyl groups were modified by silane groups with covalently bond. In conclusion, imidazole was immobilized on the core-shell nanostructure with covalently bond between Silane groups and imidazole under the S_N2 reaction.

Figure 7 shows the XRD powder diffraction pattern of Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}-IM. All of the observed diffraction peaks are indexed by the cubic structure of Fe\textsubscript{3}O\textsubscript{4} (PDF: 00-011-0614). As can be seen, the XRD pattern of Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}-IM was in agreement with that of the standard magnetite structure indicated that these particles have phase stability and the structural integrity was preserved. A broad diffraction peak near 2θ = 10-30° is observed in the Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}-IM powder. This may be attributed to the amorphous silica.

The Fourier transform infrared (FT-IR) spectra of (a) Fe\textsubscript{3}O\textsubscript{4} and (b) Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}-IM are shown in Figure 8a. The FT-IR spectrum of Fe\textsubscript{3}O\textsubscript{4} nanoparticles (Figure 2a) the absorption bands around 3425 cm\textsuperscript{-1} is attributed to the stretching vibrations of -OH and the peak at 1629 cm\textsuperscript{-1} is assigned to the bending vibrations of Si-OH [36]. There are two characteristic bonds include C-H stretching 3128 and 2948 cm\textsuperscript{-1} and bending bonds at, 1531 and 1398 cm\textsuperscript{-1} of the C=N and C=C in IM rings. The IR spectrum represented in the Figure 8b. Reveals the characteristic bonds of ILs modified on the silica-coated nanoparticles. The broad high-intensity bands at 1084 and 748 cm\textsuperscript{-1} are assigned to the Si-O-Si asymmetric and symmetric vibration, owing to the asymmetric stretching bonds of Si-O-Si in silica shell. The band at 1629 cm\textsuperscript{-1} corresponds to the bending vibrations of Si-OH [36].

**Thermo gravimetric analysis of Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}-IM nanoparticles**

Test thermal stability of Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}-IM nanoparticles, Thermo gravimetric analysis (TGA) between 25 and 800 centigrade in a nitrogen atmosphere were static. Analysis TGA, the Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}-IM nanoparticles have phase stability and the structural integrity was preserved. A broad diffraction peak near 2θ = 10-30° is observed in the Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}-IM powder. This may be attributed to the amorphous silica.
IM nanoparticles is a weight loss owing to water absorption below 160 centigrade. The other weight loss due to loss of organic groups was indicated between 185 and 384 (Figure 10).

Vibrating sample magnetometer of Fe$_3$O$_4$@SiO$_2$-IM nanoparticles

In the analysis of VSM, the magnetic properties of synthesized nanocatalysts 42 emu/g, respectively (Figure 11).

Catalytic activity of Fe$_3$O$_4$@SiO$_2$-IM nanoparticles for synthesis of coumarin derivatives

The catalytic application of Fe$_3$O$_4$@SiO$_2$-IM nanoparticle was used as a suitable heterogeneous catalyst for solvent-free protocol synthesis of coumarin by condensation of phenolic compounds with methyl acetoacetate. To optimize the reaction conditions, phenol and methyl acetoacetate were selected as the model substrates to examine the effects of different solvents and molar ratios of the catalyst at different temperatures. The effect of different solvents on the course of reaction was studied (Table 1). From the results given in Table 1, it was found that among various solvents tried, solvent-free was found to give optimum results in term of reaction time and yield. Consequently, the optimum conditions for the reaction are: 0.15 g of Fe$_3$O$_4$@SiO$_2$-IM nanoparticle, 80°C was found to be the optimum reaction temperature and solvent-free protocol.

Table 1: Optimization condition for synthesis of coumarin derivatives by Fe$_3$O$_4$@SiO$_2$-IM.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Temperature</th>
<th>Time</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Dichloromethane</td>
<td>rt.</td>
<td>4 h</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>Toluene</td>
<td>rt.</td>
<td>4 h</td>
<td>15</td>
</tr>
<tr>
<td>3</td>
<td>Toluene</td>
<td>Reflux</td>
<td>4 h</td>
<td>40</td>
</tr>
<tr>
<td>4</td>
<td>Acetonitrile</td>
<td>rt.</td>
<td>4 h</td>
<td>50</td>
</tr>
<tr>
<td>5</td>
<td>Acetonitrile</td>
<td>Reflux</td>
<td>4 h</td>
<td>30</td>
</tr>
<tr>
<td>6</td>
<td>Water</td>
<td>rt.</td>
<td>4 h</td>
<td>50</td>
</tr>
<tr>
<td>7</td>
<td>Ethanol</td>
<td>rt.</td>
<td>4 h</td>
<td>70</td>
</tr>
<tr>
<td>8</td>
<td>Solvent-free</td>
<td>80°C</td>
<td>15 min</td>
<td>97</td>
</tr>
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</table>

In order to generalize the scope of reaction, a variety of phenols was subjected for reaction with methyl acetoacetate under the solvent-free optimized reaction conditions, and the results are presented in Table 2. The spectral data and melting points are in good agreement with those reported in literature. The reactions went on well to afford products in good to high yields and short times [37]. It was obvious, which the recycle of a heterogeneous system and the lifetime of the catalyst are highly better in terms of green chemistry. This research used the reused catalytic five times without any reduction in the chemical reaction. The competence of the catalytic activity after five times recycling illustrated in Figure 12.

Selected spectral data of the products

2a: 4-Methyl-2H-chromen-2-one: Mp.: 78-80 °C; IR (KBr): 1702, 1638, 1543, 1450, 1385, 1085, 928, 852, 755 cm$^{-1}$; ¹H-NMR (400 MHz, DMSO-d$_6$) δ (ppm) 7.8-6.63 (m, 4H), 6.12 (s, 1H), 2.32 (s, 3H).

2b: 7-Hydroxy-4-methyl-2H-chromen-2-one: Mp.: 184-187°C;
IR (KBr): 3163, 1690, 1590, 1382, 1275, 1233, 1059, 850, 803, 750 cm⁻¹; ¹H-NMR (400 MHz, DMSO-d₆) δ (ppm) 10.53 (br, 1H), 7.61-7.53 (br, 1H), 6.81-6.66 (m, 2H), 6.14 (br, 3H), 2.36-2.31 (br, 3H).

2c: 6-Hydroxy-4-methyl-2H-chromen-2-one: Mp.: 241-244 °C; ¹H-NMR (400 MHz, DMSO-d₆) δ (ppm) 9.67 (s, 1H), 7.27-7.20 (br, 1H), 6.78-6.67 (br, 2H), 6.09 (s, 1H), 2.32 (s, 3H).

2g: 4,7-Dimethyl-2H-chromen-2-one: Mp.: 125-129°C; IR (KBr): 3015, 2920, 1704, 1620, 1590, 1384, 1321, 1248, 1263, 1144, 1070, 954, 879, 710, 580 cm⁻¹; ¹H-NMR (400 MHz, DMSO-d₆) δ (ppm) 10.51 (s, 1H), 10.29 (s, 1H), 6.23 (br, 1H), 6.14 (br, 1H), 5.82 (s, 1H), 2.46 (s, 3H).

Table 2: Synthesis of coumarin derivatives catalyzed by Fe₃O₄@SiO₂-IM.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Phenol</th>
<th>Time (min)</th>
<th>Product</th>
<th>Melting Point</th>
<th>Yield (%)</th>
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<tbody>
<tr>
<td>1</td>
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<td>15</td>
<td>2a</td>
<td>77-81</td>
<td>97</td>
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<tr>
<td>2</td>
<td><img src="" alt="OH" /></td>
<td>20</td>
<td>2b</td>
<td>182-185</td>
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<tr>
<td>3</td>
<td><img src="" alt="OH" /></td>
<td>25</td>
<td>2c</td>
<td>241-243</td>
<td>92</td>
</tr>
<tr>
<td>4</td>
<td><img src="" alt="OH" /></td>
<td>15</td>
<td>2d</td>
<td>162-165</td>
<td>92</td>
</tr>
<tr>
<td>5</td>
<td><img src="" alt="OH" /></td>
<td>20</td>
<td>2e</td>
<td>247-249</td>
<td>95</td>
</tr>
<tr>
<td>6</td>
<td><img src="" alt="OH" /></td>
<td>25</td>
<td>2f</td>
<td>132-134</td>
<td>90</td>
</tr>
<tr>
<td>7</td>
<td><img src="" alt="OH" /></td>
<td>20</td>
<td>2g</td>
<td>126-128</td>
<td>92</td>
</tr>
<tr>
<td>8</td>
<td><img src="" alt="OH" /></td>
<td>15</td>
<td>2h</td>
<td>151-155</td>
<td>91</td>
</tr>
<tr>
<td>9</td>
<td><img src="" alt="OH" /></td>
<td>20</td>
<td>2i</td>
<td>88-89</td>
<td>92</td>
</tr>
<tr>
<td>10</td>
<td><img src="" alt="OH" /></td>
<td>25</td>
<td>2j</td>
<td>154-156</td>
<td>88</td>
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