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Magnetic nanocrystallites strontium hexaferrite as an efficient catalyst in the green Betti reaction

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Abstract

The sol–gel auto-combustion method was applied for preparation of SrFe\textsubscript{12}O\textsubscript{19} magnetic nanoparticles (MNPs). Then, the prepared SrFe\textsubscript{12}O\textsubscript{19} was analyzed by VSM, FT-IR, SEM, N\textsubscript{2} adsorption-desorption and XRD pattern. According to the hysteresis loops of SrFe\textsubscript{12}O\textsubscript{19} MNPs, its magnetic saturation was about 79 emu/g and also it is a typical feature of ferromagnetic compound. SEM image showed semi-spherical particles with average size of 70 nm. The BET surface area of SrFe\textsubscript{12}O\textsubscript{19} MNPs was 10.4 m\textsuperscript{2}/g. Moreover, the catalytic activity of SrFe\textsubscript{12}O\textsubscript{19} MNPs was tested for the first time toward the Betti reaction. The results showed that it is an efficient catalyst which can be easily separated from the reaction mixture using an external magnet and gives the pure products in high yields within short reaction time.

Introduction

A ferrite, as a kind of ceramic compounds, is a composition of iron oxide (Fe\textsubscript{2}O\textsubscript{3}) which can combined chemically with different metallic elements.\textsuperscript{[1]} Up to now, diverse types of ferrite compounds have been synthesized and applied in many research areas especially as catalysis.\textsuperscript{[2–6]} Hexagonal strontium ferrites (SrFe\textsubscript{12}O\textsubscript{19}) with a magnetoplumbite structure have been intensively considered during the last few decades due to their excellent properties such as relatively large magnetization, superior chemical stability, superior coercivity, and excellent resistivity.\textsuperscript{[7]} So far, various preparation approaches have been developed for the synthesis of strontium ferrite nanoparticles which are sol–gel,\textsuperscript{[8]} hydrothermal,\textsuperscript{[9]} chemical co-precipitation,\textsuperscript{[10]} salt melt methods,\textsuperscript{[11]} and ball milling.\textsuperscript{[12]} The best method among the mentioned approaches is the sol–gel auto-combustion technique because of many advantages such as relatively low procedure temperatures, short reaction time and simple synthesis. This approach involves gelling a solution of metal salts and organic complexant following by a combustion process to produce a fluffy product with high specific surface area.

Multicomponent reaction of an aldehyde, an amine and phenols was firstly developed by Mario Betti in the 20th century.\textsuperscript{[13]} Betti reaction produces \textit{a}-aminobenzylphenols that is a special form of the Mannich reaction. In continuation of our previous works,\textsuperscript{[14–19]} herein, SrFe\textsubscript{12}O\textsubscript{19} is synthesized, characterized and its catalytic activity is investigated toward the Betti reaction.

Experimental

Materials and methods

The used chemical substances were purchased from Merck Company. An Electrothermal 9200 apparatus was applied for measuring melting points through the capillary tube method. Fourier-transform (FT)-Infrared (IR) Bruker Tensor 27 instrument and KBr disks were used for preparing IR spectra. \textit{H} NMR (250 MHz) and 13C NMR (62.5 MHz) spectra were obtained by the use of a Bruker DPX NMR instrument and tetramethylsilane (TMS) as internal standard in CDCl\textsubscript{3}. A 5973/6890 network mass selective detector (Agilent) was applied for gas chromatography-mass spectrometry (GC-Mass) analyses. The X-ray powder diffraction (XRD) pattern of the prepared SrFe\textsubscript{12}O\textsubscript{19} nanoparticles was collected by a Philips X’pert MPD diffractometer using Cu K\textsubscript{a} radiation (\(\lambda = 0.15478\) nm). The scanning electron microscopy (SEM) image was taken with SEM (MV2300).

Preparation of SrFe\textsubscript{12}O\textsubscript{19} nanoparticles

Fe(NO\textsubscript{3})\textsubscript{3}-9H\textsubscript{2}O and Sr(NO\textsubscript{3})\textsubscript{3} salts (the ratio of Fe to Sr was 10:1) were dissolved in a minimum amount of deionized water (100 mL for 0.1 mole of Fe\textsuperscript{3+}) and stirred well on a hot plate at 60 °C.\textsuperscript{[20,21]} Then, citric acid was added to it in a proper molar ratio with metal nitrates and stirred vigorously. Afterward, the mixture was cooled down to ambient temperature. Subsequently, NH\textsubscript{4}OH was added dropwise until the pH was adjusted at 7. Then, n-
decyltrimethylammonium bromide as a cationic surfactant (the ratio of surfactant to strontium was 4:10) was added to it. After evaporation of the solvent, a fluffy powder was obtained upon ignition. The product was ground and calcined at 900 °C for 1 h.

**General procedure of Betti reaction**

The SrFe$_{12}$O$_{19}$ nanoparticles (0.02 g) was activated under reduced pressure at 100 °C and after cooling to ambient temperature, mixture of piperidine (1.1 mmol, 0.09 g) and aldehyde (1 mmol) was added to it. Then, the mixture was heated for about 5 min under reflux condition, subsequently, 2-naphthol was added to it and the reaction was continued at 120 °C and its completion was traced by TLC. The obtained crude product was dissolved in minimum amount of hot EtOH and then, SrFe$_{12}$O$_{19}$ MNPs was easily separated from the solution using an external magnet. The filtrate was cooled to gain the pure crystalline product. The separated SrFe$_{12}$O$_{19}$ MNPs was washed well with hot EtOH and dried. It can be reused without loss of significant catalytic activity.

**1 -((2,3-Dichlorophenyl)(piperidin-1-yl)methyl)naphthalen-2-ol (4h)**

FT-IR (KBr): $v_{\text{max}}$ = 3058, 2935, 2854, 2821, 1620, 1595, 1447 cm$^{-1}$. $^1$H NMR (250 MHz, DMSO-$_d_6$): $\delta_{\text{H}}$ = 1.47–1.72 (m, 6H, CH$_2$), 2.35 (t, 2H, CH$_2$), 2.59 (d, 1H, CH), 3.34 (d, 1H, CH$_2$), 5.88 (s, 1H, CH–N), 7.01–7.74 (m, 9H, Ar–H), 14.21 (s, 1H, Ar–OH). 13CNMR (62.5 MHz, DMSO-$_d_6$): $\delta_{\text{C}}$ = 23.98, 25.92, 26.38, 49.35, 54.86, 67.05, 115.57, 12.14, 121.15, 122.63, 126.84, 128.82, 129.19, 129.81, 130.09, 132.51, 133.04, 139.42, 156.55. MS (m/e): 385 [M$^+$$]$.

**1 -((3-Nitrophenyl)(piperidin-1-yl)methyl)naphthalen-2-ol (4i)**

FT-IR (KBr): $v_{\text{max}}$ = 3088, 2949, 2858, 2807, 1618, 1595, 1530 cm$^{-1}$. $^1$H NMR (250 MHz, DMSO-$_d_6$): $\delta_{\text{H}}$ = 1.24–2.60 (m, 9H, CH$_2$), 3.39 (bs, 1H, CH), 5.19 (s, 1H, CH–N), 7.15–8.07 (m, 9H, Ar–H), 8.40 (s, 1H, Ar–H), 13.62 (s, 1H, Ar–OH).

**Table 1. Optimizing the reaction condition for the preparation of compound 4a.**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Solvent</th>
<th>Condition</th>
<th>Time (h)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SrFe$<em>{12}$O$</em>{19}$</td>
<td>H$_2$O</td>
<td>Reflux</td>
<td>1</td>
<td>20</td>
</tr>
<tr>
<td>2</td>
<td>SrFe$<em>{12}$O$</em>{19}$</td>
<td>EtOH</td>
<td>Reflux</td>
<td>2</td>
<td>15</td>
</tr>
<tr>
<td>3</td>
<td>SrFe$<em>{12}$O$</em>{19}$</td>
<td>H$_2$O/EtOH</td>
<td>Reflux</td>
<td>3</td>
<td>15</td>
</tr>
<tr>
<td>4</td>
<td>SrFe$<em>{12}$O$</em>{19}$</td>
<td>–</td>
<td>r.t</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>5</td>
<td>SrFe$<em>{12}$O$</em>{19}$</td>
<td>–</td>
<td>100°C</td>
<td>1 min</td>
<td>30</td>
</tr>
<tr>
<td>6</td>
<td>SrFe$<em>{12}$O$</em>{19}$</td>
<td>–</td>
<td>120°C</td>
<td>15 min</td>
<td>90</td>
</tr>
<tr>
<td>7</td>
<td>–</td>
<td>–</td>
<td>120°C</td>
<td>N.R.</td>
<td>–</td>
</tr>
</tbody>
</table>

**Table 2. Synthesis of Betti products 4a–i in the presence of SrFe$_{12}$O$_{19}$ nanoparticles.**

<table>
<thead>
<tr>
<th>Entry</th>
<th>No.</th>
<th>R</th>
<th>Time (min)</th>
<th>Yield (%)</th>
<th>m.p.</th>
<th>m.p. [Ref.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4a</td>
<td>Cl</td>
<td>15</td>
<td>90</td>
<td>163–166</td>
<td>165–166 [22]</td>
</tr>
<tr>
<td>3</td>
<td>4c</td>
<td>4-OCH$_3$</td>
<td>15</td>
<td>85</td>
<td>120–123</td>
<td>134–136 [21]</td>
</tr>
<tr>
<td>5</td>
<td>4e</td>
<td>2-OCH$_3$</td>
<td>30</td>
<td>92</td>
<td>184–187</td>
<td>182–184 [21]</td>
</tr>
<tr>
<td>6</td>
<td>4f</td>
<td>4-F</td>
<td>15</td>
<td>95</td>
<td>157–160</td>
<td>152–153 [24]</td>
</tr>
<tr>
<td>7</td>
<td>4g</td>
<td>4-CH$_3$</td>
<td>15</td>
<td>88</td>
<td>142–146</td>
<td>145–147 [22]</td>
</tr>
<tr>
<td>8</td>
<td>4h</td>
<td>2,3-Cl</td>
<td>10</td>
<td>95</td>
<td>154–157</td>
<td>New</td>
</tr>
<tr>
<td>9</td>
<td>4i</td>
<td>3-NO$_2$</td>
<td>15</td>
<td>95</td>
<td>185–187</td>
<td>New</td>
</tr>
</tbody>
</table>

**Results and discussion**

**Application of SrFe$_{12}$O$_{19}$ nanoparticles in Betti reaction**

To study the catalytic activity of the SrFe$_{12}$O$_{19}$ MNPs, Betti reaction of piperidine, aromatic aldehydes and 2-naphthol was accomplished (Figure 1). Initially, the reaction conditions were optimized, thereby, 4-chlorobenzaldehyde 2a was selected for the reaction with piperidine 1 and 2-naphthol 3 and subjected to the mentioned conditions in Table 1 using a catalytic amount of SrFe$_{12}$O$_{19}$ as shown in Table 1, the reaction progress in the presence of solvents was not as well as the solvent free system. Therefore, among the tested conditions, solvent-free system at 120 °C provided the high yield of the product in the presence of SrFe$_{12}$O$_{19}$, within the shortest reaction time (15 min). Furthermore, the lack of progress in reaction without the catalyst (Entry 7, Table 1) emphasizes to this fact that the SrFe$_{12}$O$_{19}$ nanoparticles accelerate the reaction.

Furthermore, to assess the generality and flexibility of this reaction, diverse Betti products 4a–i were produced productively under solvent-free condition. The obtained results, summarized in Table 2, were excellent in terms of the reaction times and products yields. The new products were characterized by Mass, FT-IR and NMR spectroscopy data. The plausible mechanism for the Betti reaction in the presence of SrFe$_{12}$O$_{19}$ MNPs is shown in Figure 2. Initially, SrFe$_{12}$O$_{19}$ MNPs acts as a Lewis acid catalyst to active the

![Figure 1](image_url)
carbonyl group of the aldehyde 2. Then, piperidine 1 attacks to the activated carbonyl group followed by dehydration to give intermediate 5. Afterwards, the 2-naphthol 3 is added to the intermediate 5 from its position-1 to produce 6. Furthermore, an aromatization is occurred which affords the desired product 4.

The recyclability of SrFe$_{12}$O$_{19}$ MNPs as the catalyst was also considered under the optimized conditions for the synthesis of compound 4a. In this regard, the reaction was performed in the first run for four times to recover about 0.07 g of SrFe$_{12}$O$_{19}$. Subsequently, the catalyst was washed with hot ethanol, dried and then reused. As shown in Table 3, within same time, the catalytic activity didn’t drop significantly from the first run to the second, which means SrFe$_{12}$O$_{19}$ MNPs is a recyclable catalyst.

Moreover, the published paper in related to the Betti reaction (according to the Figure 1) have been compared in Table 4. In comparison with the mentioned published methods, the use of SrFe$_{12}$O$_{19}$ MNPs shows several advantages such as very simple work-up, shorter reaction time, noncorrosiveness catalyst and excellent yields along with gaining the high pure products. The main advantage of current methodology is that the magnetic catalyst could be separated from the crude reaction mixture by the use of an external magnet (Figure 3).

![Figure 2. The suggested mechanism for Betti reaction in the presence of the SrFe$_{12}$O$_{19}$](image)

![Figure 3. Separated SrFe$_{12}$O$_{19}$ from the reaction mixture using an external magnet.](image)

![Figure 4. XRD pattern of SrFe$_{12}$O$_{19}$ nanoparticles.](image)

### Table 3. Reuse of SrFe$_{12}$O$_{19}$ MNPs for the synthesis of 4a.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Time (min)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15</td>
<td>90</td>
</tr>
<tr>
<td>2</td>
<td>15</td>
<td>83</td>
</tr>
</tbody>
</table>

### Table 4. Comparison of different conditions in the Betti reaction to obtain derivative 4b.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Solvent</th>
<th>Condition</th>
<th>Time (h)</th>
<th>Yield (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cu(OTf)$_2$-SiO$_2$</td>
<td>–</td>
<td>40 °C</td>
<td>45 min</td>
<td>92</td>
<td>[23]</td>
</tr>
<tr>
<td>2</td>
<td>–</td>
<td>MeCN</td>
<td>r.t</td>
<td>12</td>
<td>80</td>
<td>[24]</td>
</tr>
<tr>
<td>3</td>
<td>LiClO$_4$</td>
<td>Et$_2$O</td>
<td>r.t</td>
<td>1</td>
<td>65</td>
<td>[26]</td>
</tr>
<tr>
<td>4</td>
<td>–</td>
<td>EtOH</td>
<td>Reflux</td>
<td>12</td>
<td>90</td>
<td>[27]</td>
</tr>
<tr>
<td>5</td>
<td>Brønsted acidic ionic liquid catalyst</td>
<td>H$_2$O</td>
<td>r.t</td>
<td>4</td>
<td>91</td>
<td>[28]</td>
</tr>
<tr>
<td>6</td>
<td>Triton-x-100</td>
<td>H$_2$O</td>
<td>r.t</td>
<td>2.5</td>
<td>90</td>
<td>[29]</td>
</tr>
<tr>
<td>7</td>
<td>Nano-MgO</td>
<td>H$_2$O</td>
<td>r.t</td>
<td>3</td>
<td>90</td>
<td>[30]</td>
</tr>
<tr>
<td>8</td>
<td>Nano-SrFe$<em>{12}$O$</em>{19}$</td>
<td>–</td>
<td>120 °C</td>
<td>15 min</td>
<td>91</td>
<td>This work</td>
</tr>
</tbody>
</table>
Characterization of the SrFe$_{12}$O$_{19}$ nanoparticles

The XRD pattern of the prepared SrFe$_{12}$O$_{19}$ MNPs is shown in Figure 4. The XRD pattern of SrFe$_{12}$O$_{19}$ crystal with a magnetoplumbite structure showed twelve characteristic peaks including $2\theta = 30.55^\circ$, $32.53^\circ$, $34.39^\circ$, $35.47^\circ$, $37.33^\circ$, $40.63^\circ$, $42.67^\circ$, $55.51^\circ$, $57.01^\circ$, $63.37^\circ$, $67.87^\circ$ and $72.85^\circ$ which can be indexed to the (110), (107), (114), (201), (203), (205), (206), (217), (304), (220), (2014) and (317) lattice planes, respectively. Comparing the XRD results with literature[31] demonstrates the successful formation of SrFe$_{12}$O$_{19}$ MNPs.

Furthermore, the SEM image (Figure 5-Left) of SrFe$_{12}$O$_{19}$ nanoparticles shows semi-spherical particles. The average particle size was calculated as 65 nm of diameter which is displayed in the particles size distribution curve in Figure 5-Right. The standard deviation for about 70 randomly selected particles was determined as 8.02.

The FT-IR spectrum of the SrFe$_{12}$O$_{19}$ nanoparticles is shown in Figure 6. The wide band around 3421 cm$^{-1}$ relates to the stretching vibration of OH stretching of the adsorbed water molecules, the OH group on the nanoparticles’ surface, and the carboxyl of citric acid. The spectrum displays very weak bands between 840 and 1077 cm$^{-1}$ which assign to the vibrations of nitrate groups (remaining from the initial reactant). The bands at 1456 and 859 cm$^{-1}$ are attributed to strontium carbonate. The sharp bands at 441, 551, 601 cm$^{-1}$ belong to the vibrations of Fe-O in the structure of SrFe$_{12}$O$_{19}$. All these observations are in accordance with the results obtained by Jean et al.[32] It is noteworthy to emphasize that the bands for nitrate (1350 cm$^{-1}$) and citric acid (1742 cm$^{-1}$) are weak because they were reduced and oxidized, respectively, during the combustion reaction. Moreover, citric acid not only is the better complexing agent, compared to the other routine organic acid such as oxalic acid,[33] but also can act as a fuel source.[20] In addition, it can be claimed that surfactant releases heat in the exothermic reaction which is sufficient to complete the combustion process, thus, it can be act as a fuel in addition to this fact that that surfactant in the gel makes the particle size of product much smaller.[21,34]

The hysteresis loops and magnetic properties of SrFe$_{12}$O$_{19}$ MNPs were examined by VSM at ambient temperature. As shown in Figure 7 the magnetic saturation of the compound is about 79 emu/g. According to the hysteresis loops, it was found that SrFe$_{12}$O$_{19}$ MNPs is a typical feature of ferromagnetic compound.

Figure 8 displays the N$_2$ adsorption–desorption isotherm of the SrFe$_{12}$O$_{19}$ MNPs. The observed isotherm is classified...
In conclusion, our work presents the synthesis of SrFe$_{12}$O$_{19}$ nanoparticles and its new application as a green magnetic Lewis acid catalyst for the synthesis of a-aminobenzylphenols through the solvent-free Betti reaction. The SrFe$_{12}$O$_{19}$ nanoparticles can be separated from the reaction mixture by the use of an external magnet and also are recyclable, which makes it as an eco-friendly catalyst.

Acknowledgments

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References


