Synthesis of 1,8-dioxo-octahydroxanthenes utilizing nanodiatomite@melamine-\(\text{SO}_3\text{H}\) as a novel heterogeneous catalyst under solvent-free conditions

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Abstract. A new heterogeneous catalyst, nanodiatomite@melamine-\(\text{SO}_3\text{H}\), was introduced for synthesizing 1,8-dioxo-octahydroxanthenes via multicomponent reactions of aldehydes and dimedone. The prepared catalyst was characterized by employing several techniques, including FT-IR, XRD, TGA, EDX, BET, SEM, and TEM. The products were obtained under solvent-free conditions, with high yields in short reaction times. The nanodiatomite@melamine-\(\text{SO}_3\text{H}\) was reused five times without substantial activity loss.

Keywords. Mesoporous; Diatomite; Xanthenes; Catalyst; Solvent-free.

1. Introduction

Nano-sized catalysts continue to be considered for many research areas because of their various chemical and physical features than bulk materials. More surface area is available to the reactant due to the smaller size of the particles. Therefore, the process accelerates because more reactions simultaneously occur.\(^1\)

In recent years, the modification of nanoparticle surfaces with desired features has attracted much attention.\(^2\) Diatomite is cheap and non-toxic support with high thermal and mechanical stability. So, it can be a promising candidate for catalyst designing.\(^3\) Also, diatomite-supported catalysts can be easily prepared by functionalizing diatomite surface hydroxyl groups with various functionalization agents. These heterogeneous catalysts are simply separated from the reaction mixture and may be used multiple times. These options make them favorable for industrial and academic applications.\(^4\)

In recent years, xanthenes have obtained a lot of interest because of their pharmaceutical and biological applications,\(^5\) such as anticancer,\(^6\) antiviral,\(^7\) and antibacterial activities.\(^8\) The other practical uses of these compounds are in fluorescent compounds to visualize biomolecules\(^9\) and their application in dyes.\(^10\) Due to the significance of xanthenes, many synthetic techniques of these compounds were reported, such as the intramolecular reaction of aldehydes with 2-naphthol\(^11\) and cyclodehydrations.\(^12\) Different catalysts were used to synthesize xanthenes, such as nano titania-supported aluminum phosphate,\(^13\) \([\text{H-NMP}]^+\,[\text{HSO}_4^-]\) as ionic liquid,\(^14\) \(p\)-toluene sulfonic acid,\(^15\) and Amberlyst-15.\(^16\) Still, these approaches have drawbacks, including long reaction times, using toxic solvents, low yield, time-consuming workup procedures, need for extra reagents/catalysts, and severe reaction conditions.\(^12\) As a result, a technique for synthesizing xanthene derivatives that is environmentally benign is in high demand.

In continued to our papers on synthesizing biologically active compounds using a heterogeneous catalyst,\(^17-21\) herein, we introduce a convenient procedure for synthesizing 1,8-dioxo-octahydroxanthenes by condensing dimedone with different aromatic aldehydes with nanodiatomite@melamine-\(\text{SO}_3\text{H}\) as catalyst (Scheme 1).
2. Experimental

2.1 Chemicals and apparatus

All compounds were acquired in high purity from Merck chemicals and utilized without purification. FT-IR spectra were taken on a Thermo Nicolet IMPACT-400 FT-IR Spectrometer. $^{13}$C-NMR and $^1$H-NMR spectra were taken on a Bruker DRX-400 spectrometer. XRD diffraction of the samples were determined by employing a Philips X’pert X-ray diffractometer at $2\theta = 10^\circ$ to $80^\circ$. The morphology of the samples was characterized using a KYKY EM-3200 SEM at an accelerating voltage of 100 kV using a Leo 912 AB Omega device. TGA of the samples was measured on a Linseis (STA PT 1600) thermogravimetric analyzer from room temperature to 800 $^\circ$C. The product’s purity was realized using TLC plates (Silica-gel polygram SIL G UV 254).

2.2 Catalyst preparation

2.2a Activation of nano diatomite: Diatomite was obtained from Semnan, Iran. It was converted to nanodiatomite powder using a ball mill and was dispersed in distilled water by magnetic stirring. The obtained nanodiatomite was activated five times by HCl (1 M) treatment to remove fines and impurities. After that, it was rinsed with deionized H$_2$O, filtered, and dried for 48 h at 70 $^\circ$C in a vacuum.

2.2b Preparation of the chloro-functionalized nano diatomite (B, nanodiatomite@CH$_2$Cl): For the preparation of chloro-functionalized nano diatomite, activated diatomite (1 g) was added to a 3-chloropropyltrioxysilane (1.3 mL) solution in dry toluene (100 mL) and refluxed for 24 h. The resulting white solid was then filtered and rinsed many times with n-hexane and dried for 12 h at 90 $^\circ$C in a vacuum.

2.2c Grafting of 2,4,6-triamino-1,3,5-triazin on the functionalized nanodiatomite (C, nanodiatomite-CH$_2$NH$_2$): For the grafting of 2,4,6-triamino-1,3,5-triazin on the nanodiatomite@CH$_2$Cl, 2 g of 2,4,6-triamino-1,3,5-triazin was dispersed in 30 mL of ethanol. Then, 2 g of chloro-functionalized diatomite was added, and the reaction was refluxed for 24 h. The obtained solid was filtered and rinsed repeatedly with ethanol to remove the excess of 2,4,6-triamino-1,3,5-triazin. After that, it was dried under a vacuum for 24 h at 100 $^\circ$C.

2.2d Synthesis of nanodiatomite@melamine-SO$_3$H (D): Chlorosulfonic acid (8 mmol, 0.93 g) were added dropwise to a nanodiatomite-CH$_2$NH$_2$ (1 g) mixture in dry CH$_2$Cl$_2$ (30 mL), and this mixture was stirred at room temperature for 5 h. The obtained sample was filtered, washed with ethanol and H$_2$O, and dried under a vacuum. The acidic capacity was quantitatively determined by back acid-base titration and found that each gram of catalyst contains 6.33 mmol H$^+$ sites of diatomite-SO$_3$H.

2.2e Synthesis of xanthenes catalyzed with nanodiatomite@melamine-SO$_3$H: Under solvent-free conditions and for 10-15 min, nanodiatomite@melamine-SO$_3$H (0.02 g), dimedone (2 mmol), and aldehyde (1 mmol) were heated in an oil bath at 120 $^\circ$C, and the reaction progress was checked by TLC. Ethanol was added to the reaction after completion, and the nanodiatomite@melamine-SO$_3$H was then separated by filtration. The products were acquired by solvent evaporation with a rotary and recrystallized in ethanol to achieve greater purity.

![Scheme 1. Synthesis of xanthenes catalyzed by nanodiatomite@melamine-SO$_3$H.](image-url)
2.2f Selected spectral data: 9-(4-bromophenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (3q): IR (KBr)/\(\text{cm}^{-1}\) = 2954, 1600, 1625, 1468, 1362, 1197. 1H NMR (500 MHz, DMSO-d6): \(\delta = 7.44\) (d, 2H, \(J = 6.4\) Hz, Ph), 7.14 (d, H, \(J = 6.4\) Hz, Ph), 4.49 (s, 1H, CH pyran), 2.50 (d, 4H, \(J = 16.4\) Hz, CH2), 2.26 (d, 4H, \(J = 16.4\) Hz, CH2), 1.04 (s, 6H, CH3), 0.91 (s, 6H, CH3) ppm. 13C NMR (125 MHz, DMSO-d6): \(\delta = 27.5, 29.6, 31.8, 32.2, 40.2, 50.1, 114.3, 119.7, 130.8, 131.2, 144.1, 163.5, 196.5\).

3,3,6,6-tetramethyl-9-(3,4,5-trimethoxyphenyl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (3k): IR (KBr)/\(\text{cm}^{-1}\) = 2954, 1668, 1625, 1461, 1357, 1128. 1H NMR (500 MHz, DMSO-d6): \(\delta = 6.42\) (s, 2H, Ph), 4.50 (s, 1H, CH pyran), 3.70 (s, 6H, CH3O), 3.60 (s, 3H, CH3O), 2.52 (d, 4H, \(J = 16.0\) Hz, CH2), 2.12 (d, 2H, \(J = 16.0\) Hz, CH2), 2.07 (d, 2H, \(J = 16.4\) Hz, CH2), 1.05 (s, 6H, CH3), 0.95 (s, 6H, CH3) ppm. 13C NMR (125 MHz, DMSO-d6): \(\delta = 39.3, 39.5, 39.7, 39.9, 40.2, 40.4, 40.6, 50.5, 56.2, 60.3, 105.8, 114.7, 136.3, 140.3, 152.8, 163.5, 196.6\).

3. Results and Discussion

3.1 Sample characterization

Diatomite is a natural porous mineral for the immobilization of organocatalysts with unique properties such as thermal and mechanical stability and chemical inertness. In the present study, nanodiatomite was converted to nanodiatomite@melamine-SO3H via three-step pathways. As shown in Scheme 2 in the first step, the functionalization of nano diatomite occurred using 3-chloropropyltriethoxysilane to produce nanodiatomite-CH2Cl. In the next step, the immobilized nanodiatomite-CH2-NH2 was obtained by reacting 2,4,6-triamino-1,3,5-triazin with chloro functionalized nanodiatomite. Finally, amino-functionalized diatomite was reacted with chlorosulfonic acid to afford nanodiatomite@melamine-SO3H. The nanodiatomite@melamine-SO3H was characterized by several methods like FT-IR, TGA, XRD, EDX, SEM, and TEM analysis.
3.2 FT-IR spectra

FT-IR is a good method to prove the structure of inorganic and organic compounds. FT-IR spectra of different synthesized functionalized diatomites are shown in Figure 1. In all of these functionalized diatomites, the surface hydroxyl groups show two signals around 3600 and 1600 cm\(^{-1}\) linked to the stretching and bending vibrations. The signals at 1038 and 794 cm\(^{-1}\) are asymmetric and symmetric stretching of Si–O–Si bonds. Also, a band around 470 cm\(^{-1}\) is the bending vibration of Si–O–Si. FT-IR spectra of the nanodiatomite-CH\(_2\)Cl exhibit a vibration at 2957 cm\(^{-1}\) associated with the stretching of C–H bands of CH\(_2\)Cl. The C–Cl vibration frequency is observed at 698 cm\(^{-1}\) (Figure 1B). In the FT-IR spectra of the nanodiatomite-CH\(_2\)NH\(_2\), the NH\(_2\) groups show two bands at 3416 and 3466 cm\(^{-1}\) that belong to the N–H stretching of nanodiatomite-CH\(_2\)NH\(_2\). This vibration confirms the replacement of Cl with 2,4,6-triamino-1,3,5-triazin (Figure 1C). In the nanodiatomite-melamine-SO\(_3\)H, the presence of the SO\(_3\)H was established by a broad band at 3100-3600 cm\(^{-1}\) (Figure 1D).
3.3 X-ray diffraction

XRD is employed to obtain detailed information regarding the physical features and crystalline structure of the compounds.\(^{31}\) The XRD peaks of diatomite and functionalized ones agree with reference patterns, which show that the surface of diatomite did not change after a three-step modification (Figure 2). The XRD patterns clearly showed seven reflection peaks. A wide signal around 22° is related to the amorphous silicon dioxide form of diatomite, the peaks at 20 values of 21°, 26°, and 50° peaks are related to the crystal planes of the quartz, and the peak around 35° is related to the Fe\(_2\)O\(_3\). The nanocatalyst average crystallite size was determined at about 75 nm according to the Debye-Scherrer equation (\(D = k\lambda/\beta\cos\theta\)),\(^{32}\) where \(k\) is a constant, \(\lambda\) is the Cu-K\(_{\alpha}\) wavelength (1.54 Å), \(\beta\) is FWHM (full-width at half-maximum), and \(\theta\) is Bragg’s angle.\(^ {32}\)

3.4 TGA measurements

The thermal stability of the diatomite and its functionalized derivatives were analyzed by the TGA method (Figure 3). The first weight loss under 200 °C in all samples corresponds to removing water or solvent from the catalyst structure.\(^ {33,34}\) The second weight loss between 200 and 300 °C is linked to the supported sulfonic acid decomposition from the catalyst. Another weight loss at 300-600 °C may be related to removing organic groups grafted onto the nanodiatomite structure. The last loss of weight was attributed to decomposing of nanodiatomite at 600 °C.

3.5 EDX spectroscopy

The elements in the nanodiatomite@melamine-SO\(_3\)H structure and other samples were characterized by the EDX spectrum. Based on the EDX elemental analysis, the catalyst structure exhibited O, Si, C, N, and Cl elements in the material framework (Figure 4).

Also, elemental mapping analysis of the nanodiatomite@melamine-SO\(_3\)H was carried out to investigate the elements that are present in the catalyst structure. As was shown in Figure 5, the peaks of carbon, nitrogen, sulfur, silicon, and oxygen supported the presence of these elements in the catalyst.

3.6 SEM and TEM

The changes in the morphology and structure before and after surface modification can be observed by the SEM and TEM images.\(^ {35}\) Crystal structure and morphology of nanodiatomite, nanodiatomite-CH\(_2\)Cl, nanodiatomite-CH\(_2\)-NH\(_2\), and nanodiatomite@melamine-SO\(_3\)H were considered by both SEM and TEM techniques. The SEM image of nanodiatomite (Figure 6) demonstrated a porous structure and a typical disk topography layer structure. Furthermore, the particle size irregularity of nanodiatomite-CH\(_2\)-NH\(_2\) was observed in Figure 6C. The SEM image indicates that the average size of nanodiatomite@melamine-SO\(_3\)H is about 200 nm. In addition, particle size and morphology of nanodiatomite@melamine-SO\(_3\)H were determined utilizing a transmission electron microscope (TEM) (Figure 7). After treatment with sulfonic acid, an irregular surface layer was formed, that the nanodiatomite shell thickness was 80 nm.
3.7 Analysis of specific surface area and pore structure (BET)

The pore volume ($V_{\text{total}}$, cm$^3$/g), pore size (DBJH, nm), and specific surface area (SBET, m$^2$/g) of diatomite, and nanodiatomite@melamine-SO$_3$H are listed in Table 1 by using N$_2$ physisorption techniques at 77 K. As shown in Table 1, the specific surface area, pore volume and size of nanodiatomite@melamine-SO$_3$H are smaller than diatomite, this is mainly due to the reaction of APTES with the hydroxyl groups inside the diatomite pores, making the volume and size smaller, which suggests that the amino groups have been successfully modified to the surface of the diatomite. The specific surface area and average pore volume of diatomite are bigger than nanodiatomite@melamine-SO$_3$H, because it was cross-linked with diatomite to form some new pores.

A sorption systematic study of diatomite in comparison with the nanodiatomite@melamine-SO$_3$H was performed with nitrogen adsorption-desorption isotherms at 77 K. The results are shown in Figure 8.
Figure 6. SEM photographs of nanodiatomite (A), nanodiatomite-CH₂Cl (B), nanodiatomite-CH₂-NH₂ (C), and nanodiatomite@melamine-SO₃H (D).

Figure 7. TEM images of nanodiatomite@melamine-SO₃H.
According to the IUPAC classification, the diatomite exhibited a Type IV and V isotherm characteristic of mesoporous materials.

3.8 Nanodiatomite@melamine-SO₃H catalyzed synthesis of xanthene

The catalytic activity of the nanodiatomite@melamine-SO₃H was examined in the xanthene derivatives synthesis. In the first step, reaction conditions were optimized based on catalyst amounts, reaction time, temperature, and using different solvents. Therefore, the benzaldehyde (1 mmol) and dimedone (2 mmol) reaction were employed as a model. In terms of solvent, the reaction was accomplished under reflux (Table 2, entries 1-5) and solvent-free (Table 2, entry 6-14) conditions. The results showed that the reaction rate and the obtained yield were higher under solvent-free conditions. Also, under solvent conditions, the best yield was obtained in methanol after 15 min. Thereafter, the different temperature was checked, and it was found that the reactions at 120 °C led to the highest yield (Table 2, entries 6-9). In addition, the reaction was tested with different amounts of nanodiatomite@melamine-SO₃H (Table 2, entries 10-13). In this regard, 0.02 g of catalyst showed the highest reaction yields. The product was achieved in low yield after 4 h (Table 2, entry 14) in the absence of the nanodiatomite@melamine-SO₃H.

The dimedone reaction with different aldehydes was performed after conditions optimizing, and the findings are shown in Table 3. Aldehydes with EWG and EDG substituents reacted with dimedone in 10-15 min, and the product were obtained in proper yields. The EWG substituents slightly decrease the reaction yield, especially when they are at the ortho and meta positions of benzaldehyde.

A plausible reaction mechanism is illustrated in Scheme 3. In the first step, the nanodiatomite@melamine-SO₃H may activate the aldehyde and also facilitated the enolization of dimedone. The nucleophilic addition of enolized dimedone to the activated aldehyde produced the intermediate I after dehydration that catalyzed again by nanodiatomite@melamine-SO₃H. Michael addition of enolized dimedone to intermediate I lead to the intermediate II in the second step. The nanodiatomite@melamine-SO₃H can also improve the cyclization and dehydration rate in the last step.

Table 1. Surface area, pore volume, and pore size of diatomite and sulfonated catalyst.

<table>
<thead>
<tr>
<th>Name</th>
<th>Surface area² (m²/g)</th>
<th>Total pore volume² (cm³/g)</th>
<th>Pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diatomite</td>
<td>31.99</td>
<td>7.351</td>
<td>14.71</td>
</tr>
<tr>
<td>Catalyst</td>
<td>12.12</td>
<td>2.784</td>
<td>9.29</td>
</tr>
</tbody>
</table>

²The BET (Brunauer–Emmet–Teller) surface area
²The average pore diameter was obtained by using the BJH (Barrett, Joyner and Halenda) model.

Figure 8. Nitrogen adsorption–desorption isotherms of diatomite (A) and nanodiatomite@melamine-SO₃H (B).
Table 2. Reaction conditions optimization for the xanthene synthesis.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Catalyst (g)</th>
<th>Time (min)</th>
<th>Temperature (°C)</th>
<th>Yield (%)\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>EtOH</td>
<td>0.02</td>
<td>20</td>
<td>Reflux</td>
<td>80</td>
</tr>
<tr>
<td>2</td>
<td>MeOH</td>
<td>0.02</td>
<td>15</td>
<td>Reflux</td>
<td>82</td>
</tr>
<tr>
<td>3</td>
<td>H\textsubscript{2}O</td>
<td>0.02</td>
<td>60</td>
<td>Reflux</td>
<td>38</td>
</tr>
<tr>
<td>4</td>
<td>CH\textsubscript{3}CN</td>
<td>0.02</td>
<td>75</td>
<td>Reflux</td>
<td>65</td>
</tr>
<tr>
<td>5</td>
<td>THF</td>
<td>0.02</td>
<td>120</td>
<td>Reflux</td>
<td>25</td>
</tr>
<tr>
<td>6</td>
<td>Solvent-free</td>
<td>0.02</td>
<td>10</td>
<td>120</td>
<td>95</td>
</tr>
<tr>
<td>7</td>
<td>Solvent-free</td>
<td>0.02</td>
<td>10</td>
<td>90</td>
<td>75</td>
</tr>
<tr>
<td>8</td>
<td>Solvent-free</td>
<td>0.02</td>
<td>10</td>
<td>110</td>
<td>90</td>
</tr>
<tr>
<td>9</td>
<td>Solvent-free</td>
<td>0.02</td>
<td>10</td>
<td>130</td>
<td>95</td>
</tr>
<tr>
<td>10</td>
<td>Solvent-free</td>
<td>0.01</td>
<td>10</td>
<td>120</td>
<td>68</td>
</tr>
<tr>
<td>11</td>
<td>Solvent-free</td>
<td>0.03</td>
<td>10</td>
<td>120</td>
<td>95</td>
</tr>
<tr>
<td>12</td>
<td>Solvent-free</td>
<td>0.04</td>
<td>10</td>
<td>120</td>
<td>93</td>
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<tr>
<td>13</td>
<td>Solvent-free</td>
<td>0.05</td>
<td>10</td>
<td>120</td>
<td>90</td>
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<tr>
<td>14</td>
<td>Solvent-free</td>
<td>-</td>
<td>120</td>
<td>120</td>
<td>10</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Reaction conditions: benzaldehyde (1 mmol), dimedone (2 mmol), 10 min
\textsuperscript{b}Isolated yield

Table 3. Synthesis of xanthene derivatives using nanodiatomite@melamine-SO\textsubscript{3}H.\textsuperscript{a}

\begin{equation}
\begin{array}{cccc}
\text{Entry} & \text{Product no.} & \text{Aldehyde} & \text{Time (min)} & \text{Yield (%)}\textsuperscript{b} \\
1 & 3a & Benzaldehyde & 10 & 90 \\
2 & 3b & 4-Chlorobenzaldehyde & 10 & 90 \\
3 & 3c & 2-Chlorobenzaldehyde & 10 & 85 \\
4 & 3d & 2-Nitrobenzaldehyde & 15 & 83 \\
5 & 3e & 3-Nitrobenzaldehyde & 10 & 88 \\
6 & 3f & 4-Nitrobenzaldehyde & 15 & 80 \\
7 & 3g & 2,4-Dichlorobenzaldehyde & 10 & 82 \\
8 & 3h & 4-Methoxybenzaldehyde & 10 & 95 \\
9 & 3i & 2-Methoxybenzaldehyde & 10 & 90 \\
10 & 3j & 3,4-Dimethoxybenzaldehyde & 10 & 95 \\
11 & 3k & 3,4,5-Trimethoxybenzaldehyde & 10 & 92 \\
12 & 3l & 4-Methylbenzaldehyde & 10 & 92 \\
13 & 3m & 4-Formylbenzonitrile & 10 & 89 \\
14 & 3n & 2-Hydroxybenzaldehyde & 15 & 93 \\
15 & 3o & 4-Hydroxybenzaldehyde & 15 & 90 \\
16 & 3p & 5-Bromo-2-hydroxybenzaldehyde & 15 & 88 \\
17 & 3q & 4-Bromobenzaldehyde & 10 & 89 \\
\end{array}
\end{equation}

\textsuperscript{a}Reaction conditions: aldehyde (1 mmol), dimedone (2 mmol), catalyst (0.02 g), 120 °C, solvent-free
\textsuperscript{b}Isolated yield
The recyclability of the nanodiatomite@melamine-SO$_3$H catalyst in the xanthene derivatives synthesis was studied. The catalyst life cycle revealed a slight decrease in the total yield after cycles (Table 4).

Table 4. The recyclability of nanodiatomite@melamine-SO$_3$H for the xanthene 3a synthesis.$^a$

<table>
<thead>
<tr>
<th>Run</th>
<th>Cycle</th>
<th>Yield (%)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>95</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>90</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>86</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>80</td>
</tr>
</tbody>
</table>

$^a$Reaction conditions: benzaldehyde (1 mmol), dimethone (2 mmol), catalyst (0.02 g), 120 °C, solvent-free

$^b$Isolated yield
Table 5. The synthesis of 3a using different catalysts in comparison with nanodiatomite@melamine-SO$_3$H.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Time (min)</th>
<th>Reaction conditions</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H$<em>3$PW$</em>{12}$O$_{40}$/MCM-14</td>
<td>300</td>
<td>EtOH, Reflux</td>
<td>96</td>
</tr>
<tr>
<td>2</td>
<td>Cellulose sulfonic acid</td>
<td>300</td>
<td>Solvent-free, 110 °C</td>
<td>94</td>
</tr>
<tr>
<td>3</td>
<td>SmCl$_3$</td>
<td>540</td>
<td>Solvent-free, 120 °C</td>
<td>98</td>
</tr>
<tr>
<td>4</td>
<td>[Et$_3$N–SO$_3$H]Cl</td>
<td>60</td>
<td>Solvent-free, 80 °C</td>
<td>97</td>
</tr>
<tr>
<td>5</td>
<td>Amberlyst</td>
<td>300</td>
<td>Acetonitrile, Reflux</td>
<td>92</td>
</tr>
<tr>
<td>6</td>
<td>Ceric ammonium nitrate</td>
<td>35</td>
<td>2-Propanol, ultrasonic, 50 °C</td>
<td>98</td>
</tr>
<tr>
<td>7</td>
<td>SiCl$_4$</td>
<td>180</td>
<td>Dichloroethane, 70 °C</td>
<td>90</td>
</tr>
<tr>
<td>8</td>
<td>Sulfated zirconia</td>
<td>480</td>
<td>Ethanol, 70 °C</td>
<td>95</td>
</tr>
<tr>
<td>9</td>
<td>Nanodiatomite@melamine-SO$_3$H</td>
<td>10</td>
<td>Solvent-free, 120 °C</td>
<td>90</td>
</tr>
</tbody>
</table>

3.10 Comparison of the catalyst activity of nanodiatomite@melamine-SO$_3$H

The catalyst efficiency in the synthesis of xanthenes was evaluated with the different reported catalysts from the perspective of solvent, product yield, temperature, and reaction time. As shown in Table 5, most of the reactions were done in a solvent under reflux conditions and required a longer reaction time than nanodiatomite@melamine-SO$_3$H. Thus, nanodiatomite@melamine-SO$_3$H was one of the most efficient catalysts for synthesizing xanthene derivatives and can be considered an eco-friendly catalyst for further research.

4. Conclusions

In summary, the preparation of nanodiatomite@melamine-SO$_3$H as a novel heterogeneous catalyst was successfully developed in three steps under solvent-free conditions. The sample’s structure was defined through FT-IR, XRD, TGA, EDX, TEM, BET, and SEM. The nanodiatomite@melamine-SO$_3$H catalyst showed excellent catalytic activity in the xanthene synthesis, and pure products were achieved in short times with high yield. The good points of this methodology are ease of product isolation, the potential for catalyst recycling, catalyst efficiency, cleaner reaction profile, and the procedure agreement with the green chemistry.

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