Thermally decomposed mesoporous Nickel Iron hydrotalcite: An active solid-base catalyst for solvent-free Knoevenagel condensation

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A B S T R A C T

Thermal decomposition of co-precipitated Ni–Fe–HT materials led to the formation a mesoporous Ni–Fe–HT catalyst and we have demonstrated here its active role as solid and active catalyst for the Knoevenagel condensation reaction of various aldehydes with active methylene compounds (R=CH2-CN, where R=CN or CO2Et). High product yields are obtained at moderate temperature under solvent-free conditions and the catalyst can be easily separated from the reaction mixture, simply by filtration and reused several times without a significant loss of its activity. Since these mesoporous metal oxides derived from the NiFe hydrotalcites, their basicity mediated abstraction of the acidic protons from the active methylene compounds was responsible for their catalytic activity under solvent-free conditions.

1. Introduction

The Knoevenagel condensation of aldehydes with active methylene compounds is one of the most important carbon—carbon bond formation methodologies in synthetic organic chemistry. It has been commonly employed in the synthesis of numerous specialty chemicals and chemical intermediates, such as carbocyclic as well as heterocyclic compounds of biological significance, calcium antagonists, polymers, coumarin derivatives, cosmetics, perfumes and pharmaceuticals [1–5]. The condensation reaction is generally catalyzed by bases, acids or catalysts containing both acidic and basic active sites [3]. A number of acid–base reagents, such as ethylene diamine [6], dimethyl amino pyridine [7], potassium fluoride and sodium nitrate mixture [8] and surfactants [9] have been reported for the condensation. Most of these reagents are used under homogeneous conditions or in the presence of excess solvent, leading to the generation of large volumes of waste.

A few methods, using stoichiometric or catalytic amounts of Lewis acids, such as SmI3 [10], CuCl2 [11], ZnCl2 [12], LaCl3 [13], and triphenylphosphane (TPP) [14] under solvent-free conditions have also been reported for the Knoevenagel condensation. However, the use of strong acid catalysts causes polymerization and/or demands aqueous workup for the catalyst separation. Particularly, the use of stoichiometric amounts of Lewis acids causes waste disposal problem. Generally, Lewis acid catalysts are highly moisture sensitive thereby demanding moisture-free reaction conditions and also cannot be reused in the reaction.

Recently a few methods using easily separable and reusable solid acid/base catalysts, such as sulfated zirconia [15], hydrotalcite [16–19], zeolites [20] and calcite/flourite [21] have been reported for the condensation. Use of ionic liquids [22] and α-amino acid (L-Lysine) [23] for the condensation was also suggested. However, most of the catalysts suffer from limitations, such as use of undesirable solvents and/or harsh reaction conditions. These drawbacks have negative impact on the environment. Therefore, it is of both scientific and practical interest to develop an environmentally benign and moisture-insensitive catalyst which shows high activity for the Knoevenagel condensation under mild reaction conditions. Recently some of the solid-base catalysts obtained from corresponding LDH precursors have also been reported for the Knoevenagel/aldol condensation [24–29]. Base catalyzed Knoevenagel condensation reactions attracted a lot of attention in the recent past [30–32], due to its advantages over the solid acid catalysts. Most of these catalysts have been used to catalyze the Knoevenagel condensation in the presence of solvents. In addition, the catalytic activity of thermally decomposed hydrotalcite/layered double hydroxides was not explored for these condensation reactions. These mixed metal oxides derived from hydrotalcite like

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materials can act as bases to absorb the strongly acidic protons from an active methylene bearing organic compound, which generate carbamions in a solvent free conditions.

In this communication, we report a simple and effective greener protocol for the Knoevenagel condensation of aromatic aldehydes with active methylene compounds using thermally decomposed Ni–Fe–HT at 600 °C as a highly efficient catalyst in the absence of solvent (Scheme 1). The catalyst was thermally decomposed to form a mesoporous metal oxide form, which has larger pore diameter suitable for the condensation reactions involving larger molecules. The catalyst showed high activity in the reaction under mild conditions and, moreover, it is insensitive to moisture in the reaction mixture. It can be easily separated from the reaction mixture, simply by filtration, and reused several times without significant loss of activity. The same catalysts showed less conversion, when the same reaction was carried out in the presence of solvent. Moreover, basic catalysts comprising Nickel and Iron have not been studied for Knoevenagel condensation reactions and the present work was carried out to screen their catalytic activity for the afore-mentioned reaction.

2. Experimental

2.1. Catalyst preparation and characterization

The solid catalyst used in the present work was obtained by calcining the Ni–Fe layered hydroxide (hydrotalcite like). The synthetic protocol followed here to obtain Ni–Fe–HT catalyst, was slightly modified from the general method of preparing layered hydroxide structures, which was reported earlier by us [33–35]. These Ni–Fe–HT materials were synthesized by hydrolyzing the solution containing Nickel(II) nitrate (3 mmol) and Iron(III) nitrate (1 mmol) by drop-wise addition of aqueous mixture containing potassium hydroxide/potassium carbonate mixture. As-synthesized hydrotalcite material was filtered and washed with deionized water to ensure complete removal of free ions. Subsequently this material was kept for drying under air and after complete drying; this Ni–Fe–HT material was calcined at 600 °C for 4 h under static air. This material was used as a catalyst for the Knoevenagel condensation reaction without any further treatment and termed as Ni–Fe–HT hereafter.

Nitrogen adsorption/desorption isotherms, BET surface area, pore diameter and pore volume were acquired at 77.25 K using Micromeritics ASAP 2010 instrument. Thermogravimetric data (TGA) were acquired using a Perkin Elmer TGA-7 from 35 °C to 700 °C with a heating rate of 20 °C per minute under the flow of nitrogen. XRD of these materials was carried out using Bruker D8 X-Ray Diffraction system operating at a voltage of 40 kV and current of 40 mA with Cu Ka radiation. XPS measurements were obtained with a Thermo K-5 Alpha XPS instrument at a pressure better than $1 \times 10^{-9}$ torr with core levels aligned with C 1s binding energy of 285 eV.

2.2. Catalytic reactions

The catalytic Knoevenagel condensation reaction was carried out in a magnetically stirred round bottom flask (capacity: 25 cm$^3$) at the following reaction conditions: reaction mixture = 2.5 mmol aldehyde + 3 mmol active methylene compound + catalyst (0.05 g); bath temperature = 80 °C and reaction time = 4–10 h. The reaction was monitored by TLC. After completion of the reaction, the catalyst was separated by filtration and the filtrate was treated with water, followed by extraction with ethyl acetate to give the crude product, which was subsequently purified by column chromatography on silica gel, using petroleum ether/ethyl acetate as eluent. The catalyst was further washed with acetone, dried and reused. The reaction product was isolated by column chromatography and was confirmed by its NMR spectra by comparing with that of known product. All the products were known organic compounds.

3. Results and discussion

3.1. Catalyst formation and characterization

Under alkaline conditions, hydrolyzing the divalent and trivalent metal precursors generally led to the formation of hydrotalcite like structures. In the present case, hydrolysis of Nickel nitrate and Iron nitrate resulted in their formation of their layered hydroxide. Calcination of this material at 600 °C led to the formation of their mixed metal oxide and making their structure porous due to the dehydroxylation and condensation of hydroxyl groups. Therefore powder X-Ray Diffraction of the dried material (a) and calcined material (b) was carried out in order to see the structural changes and their diffraction patterns are given in Fig. 1. The as synthesized Ni–Fe catalyst prior to calcination exhibits broader Bragg reflections at lower 2θ values and diffraction peaks observed at 11.6, 23.2 and 34.7 correspond to the layered Nickel Iron hydroxide structures such as hydrotalcite. The other notable diffraction peak observed as doublet at 2θ values at 60.3 and 61.5 and these values correspond to Fe$_2$O$_3$ phase and no peaks correspond to Ni(OH)$_2$ phases was observed despite being the fact that the initial mole concentration of nickel was three times higher than iron concentration. This might be probably due to the formation of an amorphous phase of Ni(OH)$_2$. Interestingly, the as-synthesized catalyst after calcination underwent significant structural changes and it was clearly reflected in their XRD patterns, as it is seen in Fig. 1 (red). Complete absence of small angle diffraction peaks (2θ ~ 11.6, 23.2 and 34.7) after calcination, clearly indicated that the layered hydroxide (hydrotalcite like structure) structure was totally decomposed. After calcination, most intense diffraction peaks appeared at 2θ value at 43.6, which corresponds to the (220) plane

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1 For interpretation of color in Fig. 1, the reader is referred to the web version of this article.
of NiFe₂O₄ and (200) plane of NiO phase. The second major intense peak appeared at 63.2°, which was assigned to (440) NiFe₂O₄ and (220) plane of NiO phase. Moreover, it is clearly seen from the XRD data, there were moderate to smaller intense diffraction peaks observed at 2θ values 37.65, 57.66, 75.68, 79.54, 36.05, 57.66 and 30.65. All these diffraction peaks correspond very well with either cubic NiO or cubic NiFe₂O₄ phase. EDX analysis showed that atomic ratio of Ni and iron was found to be 2, instead of 3 based on the initial reactant concentration. Therefore the resultant material may be a combination of different phases such as mixed phase containing NiO:Fe₂O₃, single phase like NiFe₂O₄ or both these two phases co-exist together.

Fig. 2A shows the Thermo gravimetric data of as-synthesized Ni–Fe–HT (prior to calcination) and the derivative of thermogravimetric data (DTG). The TG data of the as-synthesized Ni–Fe material showed overall 31% weight loss; however DTG analysis showed two sharp major weight losses and another small weight loss. The smaller weight loss observed below 125 °C mainly attributed to the desorption of physically adsorbed/absorbed water present in the Ni–Fe–HT material. Since this material was obtained by hydrolyzing the Nickel and Iron precursors to form their layered hydroxides, these layered structures can trap lot of water molecules. The second major weight loss was centered at 190 °C, may be due to the loss of surface hydroxyl groups and carbonate groups. Third most intense weight loss was centered on 295 °C was attributed to the condensation of hydroxide groups to form the mixed metal oxide phase. These results were very well in agreement with the powder XRD-data of these materials, wherein calcined material and as-synthesized material have different diffraction peaks that correspond to different crystalline phases present in the catalyst. BET N₂ physisorption analysis of the calcined material was carried out to study the adsorption isotherms and average pore diameter and the results are shown in Fig. 2B. The total surface area of these materials estimated from the analysis was 36 m²/g. However the closer look at the adsorption isotherms clearly showed that these materials become mesoporous, which is evident from their type IV adsorption isotherm. The steepness in the capillary condensation regime clearly showed that these materials must be having very long open ended pores. BJH analysis of the average pore diameter estimation was given as inset in Fig. 2B. The average pore diameter of these materials was calculated to be 15.7 nm, and the pore volume of the materials was estimated to be 0.16 cm³/g. Such big pores are desirable for organic transformations that involve larger molecules.

In order to understand the chemical state of Ni, Fe and O in these materials, XPS analysis of these materials was carried out for as-synthesized and calcined NiFe catalyst. XPS spectra of Ni₂p (A&B), Fe 2p (C&D) and O1s (E&F) core levels obtained from the as-synthesized and calcined Ni–Fe–HT materials are shown in Fig. 3. Binding energy of Ni₂p 3/2 level (Fig. 3A) in the dried Cu–Fe–HT observed at 855.7 eV that corresponds to the Ni(OH)₂ species, which formed during the alkaline hydrolysis of Ni(II) nitrate. After calcination, the binding energy of Ni₂p 3/2 level shifted from 855.7 to 854.86 eV (Fig. 3B), which corresponds to the NiO phase. In addition, it was also observed another weak peak of Ni₂p 3/2 observed at 856.8 that corresponds to Ni₂O₃ phase. Both these results agree with the XRD results, which show the existence of NiO phase after calcination. In the case of iron, the binding energy of the Fe 2p 3/2 core level in the dried Ni–Fe–HT (Fig. 3C) material appeared at 711.7 eV, close to the binding energy value observed for iron hydroxides and iron oxyhydroxide species. However after calcination, this material showed two chemically different iron species (Fig. 3D). The first and intense iron species showed its
binding energy around 711.1 eV and the second and less intense species showed around 714.4 eV. The binding energy of the Fe 2p species appeared at 711.1 eV close to the Fe 2p level present in the Fe2O3 species. The other binding energy may be coming from the iron present in the mixed metal oxide phase. These results again prove the existence of NiO:Fe2O3 and NiFe2O4 phases. Analysis of O1s core level binding energies appeared in the case of dried Ni–Fe–HT material (Fig. 3E) showed 2 chemically different oxygen species. The binding energy values of the O1s levels observed at 532.1, and 533.4 eV was assigned to metal hydroxide and surface bound hydroxyl groups. The intensity of the metal hydroxide (531.2 eV) was found to be more intense than the metal oxide and supports the presence of hydrotalcite like structure. After calcination, it was observed that there are three chemically different oxygen species present and their O1s binding energies were observed at 530.1, 531.8 and 532.9 eV. The most intense binding energy O1s component observed at 530.1 eV was attributed to come from the metal oxides.

3.2. Knoevenagel condensation reactions

Ni–Fe–HT catalyzed condensation reaction between different aldehydes and active methylene compounds was investigated to study the potential of this ligand free Ni–Fe material in absence of any solvent. These results show the nature of different substituents present in both the substrates a strong influence of on the product yield. Results of the Knoevenagel condensation of benzaldehyde and substituted benzaldehyde with active methylene compounds (R—CH2—CN, where R=CN or CO2Et) (Scheme 1) at moderate temperature under solvent-free conditions have been presented in Table 1. The catalyst showed very high activity and selectivity and consequently high product yield in all the cases.

As shown in Table 1, aromatic aldehydes bearing electron-withdrawing groups such as 4-nitro- and 4-chloro-benzaldehyde (Table 1, entries 5 and 6, 12 and 13) as well as aldehydes bearing electron-donating groups such as 4-methoxy, 3-methoxy, 2-methoxy (Table 1, entries 2–4, 10 and 11) exhibited higher catalytic activity and gave the desired products in good to excellent yields. Furthermore, the steric effect does not have significant effect on the reaction time and yields (Table 1, entries 3 and 4 and 10 and 11). The substituted aromatic aldehydes readily condensed with malononitrile, while with ethyl cyanoacetate, the reaction is somewhat slower. This may be attributed to the fact that abstraction of a proton from the active methylene group of ethyl cyanoacetate is difficult due to lower acidity.

As can be seen from Table 1, all reactions proceeded selectively and only products of Knoevenagel adducts were obtained. The catalytic activity in the reaction, however, depends upon the substituent group present on the aromatic ring.

It is interesting to note that, apart from its high activity, the catalyst also showed excellent reusability without significant decrease in its activity (Table 1, entry 17). The observed increase
Table 1
Selective Knoevenagel reaction of different aldehydes with esters using thermally decomposed Ni–Fe–HT catalyst, under solvent-free conditions (reaction conditions: aldehyde = 2.5 mmol, esters = 3 mmol, catalyst = 0.05 g, bath temperature = 80 °C and reaction time = 4–10 h.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Aldehydes</th>
<th>Active methylene compound</th>
<th>Product</th>
<th>Reaction time (h)</th>
<th>Isolated product yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Benzaldehyde</td>
<td>Malononitrile</td>
<td><img src="image1" alt="Molecule" /></td>
<td>4</td>
<td>93</td>
</tr>
<tr>
<td>2</td>
<td>4-Methoxybenzaldehyde</td>
<td>Malononitrile</td>
<td><img src="image2" alt="Molecule" /></td>
<td>4</td>
<td>91</td>
</tr>
<tr>
<td>3</td>
<td>3-Methoxybenzaldehyde</td>
<td>Malononitrile</td>
<td><img src="image3" alt="Molecule" /></td>
<td>5</td>
<td>88</td>
</tr>
<tr>
<td>4</td>
<td>2-Methoxybenzaldehyde</td>
<td>Malononitrile</td>
<td><img src="image4" alt="Molecule" /></td>
<td>5</td>
<td>85</td>
</tr>
<tr>
<td>5</td>
<td>4-Chlorobenzaldehyde</td>
<td>Malononitrile</td>
<td><img src="image5" alt="Molecule" /></td>
<td>5</td>
<td>89</td>
</tr>
<tr>
<td>6</td>
<td>4-Nitrobenzaldehyde</td>
<td>Malononitrile</td>
<td><img src="image6" alt="Molecule" /></td>
<td>4</td>
<td>92</td>
</tr>
<tr>
<td>7</td>
<td>4-Hydroxybenzaldehyde</td>
<td>Malononitrile</td>
<td><img src="image7" alt="Molecule" /></td>
<td>5</td>
<td>89</td>
</tr>
<tr>
<td>8</td>
<td>Benzaldehyde</td>
<td>Ethylcyanoacetate</td>
<td><img src="image8" alt="Molecule" /></td>
<td>8</td>
<td>85</td>
</tr>
<tr>
<td>9</td>
<td>4-Methoxybenzaldehyde</td>
<td>Ethylcyanoacetate</td>
<td><img src="image9" alt="Molecule" /></td>
<td>8</td>
<td>90</td>
</tr>
<tr>
<td>10</td>
<td>3-Methoxybenzaldehyde</td>
<td>Ethylcyanoacetate</td>
<td><img src="image10" alt="Molecule" /></td>
<td>10</td>
<td>85</td>
</tr>
<tr>
<td>11</td>
<td>2-Methoxybenzaldehyde</td>
<td>Ethylcyanoacetate</td>
<td><img src="image11" alt="Molecule" /></td>
<td>8</td>
<td>80</td>
</tr>
</tbody>
</table>
in the reaction period for completing the reaction is expected because the recovered catalyst needs longer time to get further activation. The catalyst can be separated from the reaction mixture simply by filtration and reused several times in the reaction without a significant loss in its activity.

It may be noted that when the undecomposed Ni–Fe–HT was used as a catalyst in the reaction, much lower product yield was obtained in the reaction (Table 1, entry 15). The observed very high catalytic activity of the catalyst obtained from the thermal decomposition of Ni–Fe–HT may be attributed most probably to the uniformed distribution of Ni(II) and Fe(III) in the catalyst. This is consistent with the fact that when a catalyst prepared by thermal decomposition of mixed nitrates of Ni(II) and Fe(III) with Ni/Fe mole ratio of 3.0 was used in the reaction under similar conditions, a much lower product yield was observed (Table 1, entry 16).

It is also interesting to note that when the catalyst was exposed to moisture by storing it over water in a closed container at room temperature for 15 h, the product yield was not influenced significantly (Table 1, entry 18). This reveals that, unlike Lewis acid catalyst, the present catalyst is not at all sensitive to moisture and hence there is no need to dry the substrate or the catalyst before the reaction.

In order to optimize the reaction conditions, the reaction between benzaldehyde with malononitrile over the Ni–Fe–HT was carried out using different solvents (such as toluene, xylene, DMF and DMSO). The results are presented in Table 2. The product yields for the reaction in presence of toluene, p-xylene, DMF and DMSO as a solvent, are lower than that observed in the absence of any solvent. The observed lower activity of the catalyst in the presence of different solvents is mostly attributed to the competitive adsorption of the solvent molecules (which are at much higher concentration) on the catalyst surface and thereby occupying part of the active sites of the catalyst by the adsorbed solvent molecules.

Spectral data for a few products are given below. All the products of the condensation reaction are known compounds and the NMR data of the isolated product were compared with the earlier literature.

**Table 1** (continued)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Aldehydes</th>
<th>Active methylene compound</th>
<th>Product</th>
<th>Reaction time (h)</th>
<th>Isolated product yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>4-Chlorobenzaldehyde</td>
<td>Ethylcyanoacetate</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>10</td>
<td>80</td>
</tr>
<tr>
<td>13</td>
<td>4-Nitrobenzaldehyde</td>
<td>Ethylcyanoacetate</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>8</td>
<td>89</td>
</tr>
<tr>
<td>14</td>
<td>4-Hydroxybenzaldehyde</td>
<td>Ethylcyanoacetate</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>8</td>
<td>80</td>
</tr>
<tr>
<td>15</td>
<td>Benzaldehyde</td>
<td>Malononitrile</td>
<td><img src="image" alt="Chemical Structure" /></td>
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<td>62&lt;sup&gt;a&lt;/sup&gt;</td>
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<tr>
<td>16</td>
<td>Benzaldehyde</td>
<td>Malononitrile</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>4</td>
<td>68&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>17</td>
<td>Benzaldehyde</td>
<td>Malononitrile</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>5</td>
<td>91&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>18</td>
<td>Benzaldehyde</td>
<td>Malononitrile</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>4</td>
<td>92&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> Ni–Fe–HT without decomposition was used.

<sup>b</sup> Catalyst obtained from the decomposition of a mixture of Ni(II) nitrate and Fe(III) nitrate (with Ni/Fe mole ratio of 3.0) at 600 °C for 4 h.

<sup>c</sup> Fifth reuse of the catalyst.

<sup>d</sup> Catalyst exposed to atmospheric moisture.
4-methoxybenzylidene-malononitrile (Table 1, entry 2): 1H NMR (500 MHz, CDCl3): δ 7.55 (s, 1H), 3.84 (s, 3H), 7.86 (d, 2H), 6.95 (d, 2H).

3-methoxybenzylidene-malononitrile (Table 1, entry 3): 1H NMR (500 MHz, CDCl3): δ 7.70 (s, 1H), 7.50 (d, 2H), 7.82 (d, 2H).

Ethyl 2-cyano-3-phenylacrylate (Table 1, entry 8): 1H NMR (500 MHz, CDCl3): δ 1.40 (t, 3H), 4.39 (q, 2H), 7.40–7.60 (m, 1H), 7.35–7.44 (m, 3H), 7.55 (s, 1H), 3.84 (s, 3H), 7.86 (d, 2H).

Table 2

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Isolated product yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Toluene</td>
<td>40.0</td>
</tr>
<tr>
<td>2</td>
<td>p-Xylene</td>
<td>19.0</td>
</tr>
<tr>
<td>3</td>
<td>DMF</td>
<td>16.0</td>
</tr>
<tr>
<td>4</td>
<td>DMSO</td>
<td>20.5</td>
</tr>
<tr>
<td>5</td>
<td>Nil</td>
<td>93.0</td>
</tr>
</tbody>
</table>

DMF = dimethyl formamide; DMSO = dimethyl sulfoxide.

4. Conclusions

The thermally decomposed Ni–Fe–HT (Ni/Fe = 3) at 600 °C is a novel catalyst showing very high activity in the Knoevenagel condensation reaction of various aromatic aldehydes with active methylene compounds under solvent-free conditions and provides high product yields at moderate temperature. The catalyst is environmentally benign; it is easily separable and reusable without the significant loss of its activity. Moreover, it is moisture insensitive and hence does not demand moisture-free substrates and special precaution for its handling. The metallic elements (Ni and Fe) are uniformly distributed in the catalyst.

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