Chapter 5

Synthesis of MgO by hydrothermal and solvothermal methods and their application for Claisen-Schmidt condensation reaction
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Synthesis of MgO precursors through different routes has been a fascinating field of catalysis due to the possibility of getting structurally diverse MgO morphologies and excellent basic properties, which can catalyze a good number of base catalyzed organic reactions [1-4]. Besides, MgO has been used in numerous applications such as filler in paints and superconductors [5], modifier [6], catalyst support [7], fertilizers [8], lubricating oils [9] and wastewater treatment [10]. Physico-chemical properties of this class of materials are highly governed by their particle sizes, surface area, crystallinity as well as morphologies which can be well achieved by altering the particle arrangements through various synthesis strategies [11-13]. Among a varieties of synthetic routes [14-18], hydrothermal and solvothermal routes have been widely used in the recent years and found successful in getting varied morphologies [19-22]. However, synthesis of MgO having newer design and improved catalytic activities is still challenge for chemists. It has been found that MgO can effectively catalyze organic reactions such as Aldol condensation, Knoevenagel condensation and Claisen-Schmidt condensation under optimized reaction conditions [23-25]. Among these, the Claisen-Schmidt condensation reaction generally requires elevated reaction temperature and strong base to give the desired product in high yield. Therefore, this reaction is commonly carried out with variety of promoted MgO catalysts and MgO catalysts having various shapes and sizes at high temperatures to obtain the products in high yield and selectivity [26]. However, catalytic activities of these materials are governed by the effect of shape, size, basic properties as well as surface properties which are not yet fully understood. This has inspired us to synthesize MgO precursors via hydrothermal and solvothermal routes and check their morphological features and catalytic activities for Claisen-Schmidt condensation reaction.

In this section, we have described the synthesis of MgO precursors from nitrate salts of magnesium in presence of three bases namely, urea, NaOH and Na₂CO₃ by
hydrothermal and solvothermal methods. Complete characterizations of these materials were done through XRD, FTIR, SEM and N\textsubscript{2} adsorption-desorption measurement methods. Catalytic applications for Claisen-Schmidt condensation reaction was performed under classical heating conditions and described herein. We have also described the effect of ratio of base versus magnesium salt and effect of three bases namely NaOH, Urea and Na\textsubscript{2}CO\textsubscript{3} upon growth of particles, phase obtained, crystallinity and their particle sizes. We have observed that the amount of magnesium salt and the base in the mixture has crucial role over the crystal growth. This section also illustrates the basic properties of the as synthesized MgO precursors, calcined MgO and their catalytic activities towards Claisen-Schmidt condensation reaction. The detailed study of effect of solvents, effect of catalysts, reaction time and temperatures on yield was investigated and explained herein. The complete Characterization methods of the materials have been described in Chapter 2.

5.1 Results and discussion

5.1.1 Effect of synthesis parameters on morphologies

Initially, MgO precursors were synthesized through hydrothermal route by mixing base solution and Mg(NO\textsubscript{3})\textsubscript{2}.6H\textsubscript{2}O salt solution of water in three different molar proportions i.e. 0.1:1, 1:1 and 10:1 respectively at 120 °C for 6 h to understand the effect of ratio of base versus salt over the crystallization pattern of the precursors. The XRD pattern is presented in figure 5.1. Three bases namely urea, sodium hydroxide (NaOH) and sodium carbonate (Na\textsubscript{2}CO\textsubscript{3}) were used for the synthesis. It was observed that all the precursors were crystalline in nature where presence of the same basic environment leads to similar crystalline phases in the XRD pattern (MgO-U-0.1, MgO-U-1 and MgO-U-10; MgO-OH-1 and MgO-OH-10; MgO-CO-1 and MgO-CO-10). We have noticed that the precursors obtained from urea and Na\textsubscript{2}CO\textsubscript{3} form similar crystalline phases in the XRD and may be suggested for the formation of Magnesium Carbonate Hydroxide Hydrate like phase i.e. Mg\textsubscript{5}(CO\textsubscript{3})\textsubscript{4}(OH)\textsubscript{2}.(H\textsubscript{2}O)\textsubscript{4} (JCPDS Card Number-701177). On the other hand, precursor obtained from NaOH gives more crystalline and sharp diffraction lines that can be suggested for Mg(OH)\textsubscript{2} phase in the XRD pattern (JCPDS Card Number-860441). Again, ratio of salt versus base and time of crystallization has crucial effect over the
growth of crystalline phase. As the amount of base increases in the mixture, crystallinity of the precursors increases. It can be well explained from the samples synthesized in presence of urea as basic medium (figure 5.1). Increasing the ratio of urea versus salt from 0.1 to 10 in the mixture, crystal growth become more facile showing sharp and well defined diffraction lines in the XRD pattern. It shows that 10:1 ratio of base versus salt gives the highly crystalline phase. It is also observed that increase of hydrothermal treatment time from 6 h to 24 h, the intensity of the XRD peaks diminished (MgO24-U-10, figure 5.1). We have also observed similar dependence of basic environment on crystallization of MgO in case of NaOH and Na₂CO₃ environment. Crystallization becomes more facile on increasing NaOH and Na₂CO₃ in the mixture (Figure 5.1). This shows that the crystallization is highly dependent on the ratio of base versus salt and crystallization time.

![Figure 5.1: XRD pattern of MgO precursors synthesized under hydrothermal treatment for 6 h with different ratio of base versus salt; urea [MgO-U-10 (10:1), MgO-U-1 (1:1), MgO-U-0.1 (0.1:1), MgO24-U-10(10:1 for 24h)]; NaOH [MgO-OH-10 (10:1), MgO-OH-1 (1:1)] and Na₂CO₃ [MgO-CO-10 (10 :1), MgO-CO-1 (1:1)].]
The result of relative crystallinity (%) study from integration of XRD peaks at 2θ positions 9.7°, 13.75° and 38.8° are depicted in Figure 5.2. It again reveal that the highest crystallinity is obtained by the sample synthesized from 10:1 proportion of urea versus Mg(NO$_3$)$_2$.6H$_2$O salt. Therefore, synthesis of MgO through solvothermal route was carried out with 10:1 ratio of urea versus Mg(NO$_3$)$_2$.6H$_2$O salt with three different solvents namely ethanol, ethylene glycol and glycerol. The precursors were named as MgO-U-Et, MgO-U-EG and MgO-U-Gly for ethanol, ethylene glycol and glycerol respectively. It is observed that solvothermal synthesis using urea furnish similar type of XRD pattern as that of the hydrothermal methods (figure 5.3).

**Figure 5.2:** Relative crystallinity (%) of MgO precursors obtained from urea

**Figure 5.3:** XRD pattern of MgO precursors obtained via solvothermal route with ethanol (MgO-U-Et), ethylene glycol (MgO-U-EG) and glycerol (MgO-U-Gly)
However, intensities of the samples are low in comparison to hydrothermal route. Figure 5.4 compares the relative crystallinity of the precursors from solvothermal route to hydrothermal route which reveal that MgO-U-EG has the highest crystallinity among the three obtained through solvothermal route. This indicates slow and improper growth of the crystals obtained through this route.

**Figure 5.4:** Relative crystallinity (%) of MgO precursors obtained via solvothermal route

**Figure 5.5:** XRD pattern of MgO calcined at 500 °C
Following this, all the samples were calcined at 500 °C to obtain MgO phases (Figure 5.5). All the precursors converted into MgO phase showing sharp and distinct peaks at 2θ values 42.75° and 62.15° corresponding to MgO phase.

**Figure 5.6:** SEM images of MgO precursors obtained by hydrothermal route
Figure 5.6 represents the SEM images of MgO precursors obtained by hydrothermal synthesis in presence of urea. Samples MgO-U-10 and MgO-U-0.1 contain non-homogeneous particle shapes and sizes and agglomerated leaf like particles. The morphologies were changed upon changing the basic environment. It is observed from Figure 5.6 that MgO-CO-10 sample (Na$_2$CO$_3$) shows similar particle arrangements as that of MgO-U-10 and MgO-U-0.1 which was also evident from XRD analysis (Figure 5.1). However, agglomeration of the particles in MgO-CO-10 is quite less in comparison to MgO-U-0.1 and thus shows leaf like particles with distinct phase. On the other hand, sample obtained from NaOH (MgO-OH-10) has uniform particle shapes and sizes and shows arrangement of homogeneous hexagonal leaf like particles in SEM images. Small and homogeneous particle size of this precursor is reflected from the XRD pattern of the sample showing distinct peaks (Figure 5.1).

![SEM images of MgO precursors obtained by solvothermal route](image)

**Figure 5.7:** SEM images of MgO precursors obtained by solvothermal route

The SEM images of the samples obtained through solvothermal synthesis shows amorphous sheets of structures with nonhomogeneous shapes (Figure 5.7). This has been
further confirmed by looking at the XRD pattern which showed less intense peaks in comparison to hydrothermal route. Therefore, it can be conferred that the presence of urea in the mixture does not favour particle growth to form definite shapes. On the other hand, NaOH as base favours the nucleation process to form uniform particles under hydrothermal method.

The surface area measurement of the calcined MgO samples showed varied specific area and pore volumes. It is observed from Table 5.1 that in MgO sample obtained from solvothermal route has larger surface area than that with hydrothermal route using the same basic environment i.e. urea. It may be due to smaller particle sizes of MgO obtained through solvothermal method. Among the studied oxides, BET area and pore volume of MgO obtained by using NaOH is the highest. This can be attributed to the small and uniform particles of this sample. We have also found comparable crystallite sizes of the precursors through hydrothermal and solvothermal route.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Sample</th>
<th>BET area (m² g⁻¹)</th>
<th>Pore volume (cm³ g⁻¹)</th>
<th>Pore diameter (Å)</th>
<th>Crystallite size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MgO-U-10</td>
<td>63</td>
<td>0.26</td>
<td>25</td>
<td>222</td>
</tr>
<tr>
<td>2</td>
<td>MgO-OH-10</td>
<td>283</td>
<td>0.46</td>
<td>37</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>MgO-CO-10</td>
<td>105</td>
<td>0.18</td>
<td>65</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>MgO-U-EG</td>
<td>208</td>
<td>0.46</td>
<td>41</td>
<td>269</td>
</tr>
<tr>
<td>5</td>
<td>MgO-U-Gly</td>
<td>217</td>
<td>0.50</td>
<td>36</td>
<td>275</td>
</tr>
</tbody>
</table>

The N₂-adsorption desorption isotherm of the calcined samples show type II isotherms according to the IUPAC classification. This type of isotherm is the characteristics of monolayer and multilayer adsorption in the samples. Again, we have observed that the samples MgO-U-EG, MgO-U-Gly and MgO-U-10, shows type A hysteresis loop according to “de Boer” [27] classification and characterize the presence of cylindrical pores. On the other hand, the samples MgO-OH-10 and MgO-CO-10 showed type C hysteresis loop characteristics of wedge shaped pores having open ends.
5.1.2 Catalytic reaction

To understand the relationship between the effect of morphologies and catalytic activity, Claisen-Schmidt condensation reaction was carried out with the prepared MgO samples calcined at 500 °C under solvent free condition (Scheme 5.1). For this purpose, 1mmol p-nitrobenzaldehyde, 1 mmol acetophenone and 35 mg MgO was taken in a round
bottomed flask and heated in an oil bath at 130° C with constant stirring. The results of catalytic reactions are presented in Table 5.2. We have seen that all the prepared MgO are active for this reaction and give respectable yields within 5-8 hours.

![Scheme 5.1: Claisen-Schmidt condensation reaction catalyzed by MgO calcined at 500 °C](image)

**Table 5.2:** Effect of various MgO catalysts calcined at 500 °C

<table>
<thead>
<tr>
<th>Sl No</th>
<th>Catalyst</th>
<th>Time (h)</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MgO-U-10</td>
<td>8</td>
<td>78</td>
</tr>
<tr>
<td>2</td>
<td>MgO-OH-10</td>
<td>5</td>
<td>87</td>
</tr>
<tr>
<td>3</td>
<td>MgO-CO-10</td>
<td>8</td>
<td>67</td>
</tr>
<tr>
<td>5</td>
<td>Mg-U-EG</td>
<td>5</td>
<td>86</td>
</tr>
<tr>
<td>6</td>
<td>MgO-U-Gly</td>
<td>5</td>
<td>95</td>
</tr>
</tbody>
</table>

**Conditions:** Acetophenone = 1 mmol, p-nitrobenzaldehyde = 1 mmol, MgO = 35 mg, Temperature = 130 °C.

The reaction between acetophenone and p-nitrobenzaldehyde was faster with MgO obtained from NaOH base through hydrothermal method (MgO-OH-10) in comparison to the other two samples obtained via this route. This can be attributed to the well crystalline uniform MgO particles and high surface area. On the other hand, acetophenone conversion of 95 % was achieved from MgO obtained from glycerol base (MgO-U-Gly) in comparison to the other catalysts.

Therefore, the reaction was further carried out with MgO-U-Gly sample with a variety of aldehydes bearing electron withdrawing groups and electron donating groups (Table 5.3). We have observed that electron withdrawing substituents in aromatic ring
entries 1, 2 & 3, Table 5.3) react faster than that having electron donating substituents
(entry 5, Table 5.3) to give 91-95 % yield within 5-6 hours. The reaction with
naphthaldehyde was slow and showed 23 % yield within 8 hours. The reusability of the
catalyst was also tested for three repetitive cycles where the catalyst was found active to
give good yield of product within 8 hours (entry 7, table 5.3). However, the activity was
reduced gradually after each run. This may be due to loss of some MgO in each cycle or
deactivation of some active sites during the reaction.

Table 5.3 Claisen-Schmidt reaction with MgO at 130 °C.

<table>
<thead>
<tr>
<th>SL No</th>
<th>R</th>
<th>Time (h)</th>
<th>Yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Yield (%)&lt;sup&gt;d&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4-NO&lt;sub&gt;2&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;</td>
<td>5</td>
<td>95</td>
<td>97 (35)</td>
</tr>
<tr>
<td>2</td>
<td>3-NO&lt;sub&gt;2&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;</td>
<td>6</td>
<td>90</td>
<td>92 (35)</td>
</tr>
<tr>
<td>3</td>
<td>2-NO&lt;sub&gt;2&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;</td>
<td>5</td>
<td>91</td>
<td>89 (35)</td>
</tr>
<tr>
<td>4</td>
<td>4-CIC&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;</td>
<td>6</td>
<td>87</td>
<td>88 (40)</td>
</tr>
<tr>
<td>5</td>
<td>4-CH&lt;sub&gt;3&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;</td>
<td>8</td>
<td>68</td>
<td>79 (40)</td>
</tr>
<tr>
<td>6</td>
<td>1-Naphthyl</td>
<td>8</td>
<td>23</td>
<td>47 (40)</td>
</tr>
<tr>
<td>7</td>
<td>4-NO&lt;sub&gt;2&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;</td>
<td>8</td>
<td>82&lt;sup&gt;b&lt;/sup&gt;</td>
<td>73&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup>Isolated yields, <sup>b</sup>Second run, <sup>c</sup>Third run
<sup>d</sup>Reactions under microwave irradiation (Conditions: Acetophenone=1 mmol, aldehyde = 1 mmol,
MgO = 35 mg, solvent free, 490 Watt)

The scope of the catalysts was further checked by performing the reaction under
microwave irradiation condition (490 Watt). It is observed that the reaction time reduces
from hours to minutes under microwave condition to afford moderate to excellent yield
(47-97 %) within 40 minutes.

Thus, we have prepared an effective MgO catalyst of high surface area for
Claisen-Schmidt condensation reaction under classical heating as well as microwave
irradiation conditions.
5A.3: References