Transesterification of propylene carbonate with methanol using Mg-Al-CO$_3$ hydrotalcite as solid base catalyst

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The catalytic activity of synthetic hydrotalcites of varying Mg/Al molar ratio from 2 to 5 has been investigated for the transesterification of propylene carbonate with methanol. The hydrotalcite with Mg/Al molar ratio of 5 at different calcination temperature has been characterized using FT-IR, P-XRD and surface area analyses. Under optimized conditions, the catalyst with Mg/Al molar ratio 5 shows highest propylene carbonate conversion (72 %) with 97 % dimethyl carbonate selectivity. The catalyst shows the highest TON (280 mmol DMC/g cat) ever reported with heterogeneous catalysts. A plausible reaction mechanism has been proposed based on the results obtained.

**Keywords**: Catalysts, Transesterification, Hydrotalcites, Carbonates, Magnesium, Aluminum

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Dimethyl carbonate (DMC) finds diversified applications in the chemical industries. Though one step synthesis of DMC from CO$_2$ and CH$_3$OH is attractive, yield is relatively low due to high thermodynamic stability and kinetic inertness of CO$_2$. Also, it leads to the deactivation of catalyst by water formed during the process. Recently, cyclo-addition of carbon dioxide to epoxides under ambient condition has been reported and needs more emphasis on the transesterification step (Scheme 1) to utilize CO$_2$ directly in a one pot synthesis.

Several researchers have reported the formation of DMC from cyclic carbonates using different catalysts. The equilibrium yield of DMC from propylene carbonate (PC) is found to be three times lower than that from ethylene carbonate (EC) in the presence of Na$_3$PO$_4$ as solid base catalyst. This has been explained in terms of steric factor though both the reactions have same activation energy (29 ± 2 kJ/mol).

Synthesis of dimethyl carbonate from ethylene carbonate at atmospheric pressure and dialkyl carbonates from cyclic carbonates at higher pressure have been reported using Mg-Al hydrotalcite as solid base catalyst. We have reported the synthesis of dimethyl carbonate from propylene carbonate and methanol using KF/Al$_2$O$_3$ as efficient base catalyst. Takagaki et al. have recently reported the synthesis of glycerol carbonate from glycerol and DMC using hydrotalcite. The ionic species from the catalyst were found to play an important role in overall reactivity of the reaction. The anion present in the hydrotalcite gallery plays an important role in determining the basic behavior of the materials calcined below the decomposition temperature. We have studied the effect of N,N'-dimethylformamide in cycloaddition reaction of carbon dioxide to propylene oxide (step I in Scheme 1) using Mg/Al hydrotalcite.

In the present study, we report the efficiency of Mg-Al-CO$_3$ hydrotalcite in transesterification of propylene carbonate with methanol in atmospheric pressure. The effect of calcination and reaction temperatures, reactant ratio and catalyst amount has also been studied.
Materials and Methods

Propylene carbonate (PC), ethylene carbonate (EC) and biphenyl were purchased from Acros Organics, Belgium. Dimethyl carbonate, propylene glycol, methanol, Mg(NO$_3$)$_2$·6H$_2$O, Al(NO$_3$)$_3$·9H$_2$O, Na$_2$CO$_3$, and NaOH were procured from SD Fine Chemicals, India. Methanol was dried using standard procedure and stored under activated molecular sieve 3A. Milli-pore deionized water was used for the synthesis of hydrotalcite catalyst.

Synthesis of the catalyst

The hydrotalcite samples with Mg/Al molar ratio varying from 2-5 were synthesized by co-precipitation method$^{19,20}$. The catalysts obtained were powdered, dried at 120 °C for 4 h and stored in a vacuum desiccator to avoid contamination by atmospheric moisture. The catalysts were coded as HT-X with X representing the molar ratio of Mg/Al salts used for synthesis. The catalyst (HT-5) was calcined separately at 200 °C and 450 °C for 4 h to evaluate the effect of calcination temperature on the title reaction.

Characterization of the catalyst

Powder X-ray diffraction (P-XRD) patterns of the hydrotalcite samples were recorded with Phillips X’Pert MPD system equipped with XKR 900 reaction chamber, using Ni-filtered Cu-K$_\alpha$ radiation ($\lambda = 1.5405$ Å) over a 2θ range of 2–70°. The Fourier transform infrared (FT-IR) spectra of the hydrotalcite samples were recorded with Perkin–Elmer (Spectrum GX) FT-IR system using KBr pellets. The surface area was computed using N$_2$ adsorption data measured at 77 K on a Micromeritics, ASAP 2010 USA system. The BET isotherm model was used to calculate surface area while the HK model was used to calculate pore volume and pore radius. The samples were degassed at 120 °C for 4 h under vacuum (5 × 10$^{-2}$ mm Hg) prior to N$_2$ adsorption measurement. Hammett indicator method was used to determine the basic strength of the catalyst$^{31}$. Phenolphthalein (H ≥ 9.8), bromothymol (H ≥ 7.2) and methyl red (H ≥ 4.2) were used as indicators for different basic strengths. In a typical measurement, 50 mg of the catalyst in 5 mL dry methanol was stirred for 2 h under nitrogen atmosphere and the resultant solution was titrated against standard acid (0.02 mol/L benzene carboxylic acid in dry methanol) solution. The end points, i.e., pink to colorless with phenolphthalein indicator, blue to yellow with bromothymol and yellow to red with methyl red indicator, were measured separately and the results are given under three different strengths.

Catalytic reactions

In a typical catalytic experiment, the oven dried 25 mL round bottom flask was fed with 2.04 g (20 mmol) propylene carbonate, 6.4 g (200 mmol) methanol, 80 mg biphenyl (internal standard) and 50 mg catalyst. The reaction was carried out under N$_2$ atmosphere using N$_2$ filled balloon and long spiral condenser setup. The reaction setup was placed in a preheated oil bath (±2 °C temperature variation) and the reaction was initiated by stirring (500 rpm). After 4 h, the product mass was filtered to remove the catalyst and analyzed by gas chromatography (Shimadzu 17A) equipped with a flame ionization detector (FID). The products were further confirmed by GC–MS (Shimadzu GCMS, QP 2010); 5 % diphenyl- and 95 % dimethylsiloxane universal capillary column (60 m length, 0.25 mm diameter) was employed in both GC and GC-MS analyses. Propylene glycol was co-produced in all the reactions equimolar to the DMC formed and thus it has been exempted from the discussion. The conversion and selectivity were calculated using the following relationship in response to the internal standard:

% Conversion of PC = \[
\frac{\text{initial moles of PC} - \text{final moles of PC}}{\text{initial moles of PC}} \times 100
\]

% Selectivity of DMC = \[
\frac{\text{moles of DMC formed}}{\text{moles of PC reacted}} \times 100
\]

Results and Discussion

Catalyst characterization

The X-ray powder diffraction patterns of the synthesized samples with the reflection planes (003), (006), (012), (015), (018), (110), (113) and (116) matched perfectly with the literature report$^{22}$. No additional impurity phase was observed in any of the synthesized catalysts (see Supplementary Data). The basal spacing d(003) of HT-CO$_3$ at ~7.65 Å was in good agreement with the literature value and increased with decrease in the Al content (Table 1) as also reported by Miyata$^{23}$. The sample calcined at 200 °C showed decreased intensity of the HT peaks (003 and 006 reflections) and that at 450 °C showed the complete decomposition of HT phase into Mg-Al mixed oxide (Fig. 1). The intensity of 003 reflection of the reused catalyst after the 4th cycle was found to decrease as compared to the fresh catalyst, showing some crystallinity loss.
Table 1 – Physical characteristic values of HT samples with varying Mg/Al ratio

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>(d) spacing of (003) plane (Å)</th>
<th>BET surface area (m(^2)/g)</th>
<th>Pore vol. (cm(^3)/g)</th>
<th>Pore radius (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HT-2.0</td>
<td>7.60</td>
<td>86</td>
<td>0.45</td>
<td>10.6</td>
</tr>
<tr>
<td>HT-3.0</td>
<td>7.69</td>
<td>65</td>
<td>0.38</td>
<td>11.7</td>
</tr>
<tr>
<td>HT-4.0</td>
<td>7.92</td>
<td>90</td>
<td>0.39</td>
<td>8.6</td>
</tr>
<tr>
<td>HT-5.0</td>
<td>7.95</td>
<td>93</td>
<td>0.46</td>
<td>9.9</td>
</tr>
<tr>
<td>HT-5.0(^a)</td>
<td>7.55</td>
<td>82</td>
<td>0.40</td>
<td>9.6</td>
</tr>
<tr>
<td>HT-5.0(^b)</td>
<td>-</td>
<td>229</td>
<td>0.72</td>
<td>6.3</td>
</tr>
</tbody>
</table>

\(^a\)Calcined at 200 °C.
\(^b\)Calcined at 450 °C.

Fig. 2 — FT-IR profile of HT-5 catalyst [(a) as synthesized; (b) calcined at 200 °C; (c) after first cycle; (d) after fourth cycle].

The BET surface, pore volume and pore radius values decreased on calcination at 200 °C as compared to those of the as synthesized catalyst. This may be due to the loss of interlayer water followed by decreased \(d\)-spacing of (003) plane (7.95 Å to 7.55 Å). On calcination at 450 °C, the catalyst completely lost its interlayer anions and surface hydroxyl groups resulting in the formation of Mg-Al mixed oxides. This resulted in increased surface area and pore volume but decreased pore radius.

The hydrotalcite samples were found to have different basicity at different basic strengths (Table 2). The basicity values in the basic strength between 7.2 and 9.8 increased with increase in Mg/Al ratio with as synthesized catalysts and decreased with calcination temperature of HT-5. The basicity of stronger basic sites (\(H \geq 9.8\)) decreased with increase in Mg/Al ratio and increased with calcination temperature of HT-5. The total number of basic sites presented in the calcined catalysts may not be the actual one, since the adsorption depends on the number of accessible sites which in turn depends on the pore size of the catalyst.

Screening of the catalyst

The catalytic activity of hydrotalcite samples dried at 120 °C was studied for the transesterification reaction and the data are given in Table 2. There was no conversion of propylene carbonate at the studied reaction temperature (130 °C) in the absence of catalyst. The conversion of PC increased with
increase in Mg/Al molar ratio reaching a maximum of 72.2 % with HT-5. The selectivity of DMC also increased with increase in Mg/Al molar ratio and reached a maximum of 97 % with HT-5. Considering the catalytic efficiency of the catalyst in terms of both conversion and selectivity, HT-5 was selected for further detailed investigations.

Effect of calcination temperature of the catalyst (HT-5)

The catalyst HT-5 dried at 120 °C showed higher activity as compared to the samples calcined at higher temperatures (Entries 5 and 6 in Table 2). The sample calcined at 200 °C resulted in 54.5 % conversion with 95.4 % selectivity. The drop in conversion (~18.5 %) may be due to the change in coordination of carbonate species from interlayer water to interlayer OH upon losing the interlayer water (Fig. 2). The presence of H-bonding between interlayer OH (Lewis basic sites) and carbonate ion gave selectivity greater than 95 %, while the absence of interlayer water brought the conversion down to 54.5 %. The presence of interlayer water was found to accelerate the activation of methanol via hydrogen bonded carbonate ion. The weak and medium basicity values of the hydrotalcite samples were matched well with the observed conversion of PC (Table 2). The sample calcined at 450 °C showed lower selectivity (76.1 %) of DMC. This might be due to the presence of high stronger basic sites (Brønsted basic sites) present in Mg-Al mixed oxide leading to the partial decomposition of PC. A similar lower selectivity has been observed with metal oxide catalyst in transesterification of ethylene carbonate with methanol. Watanabe et al. have reported that the ethylene carbonate gets activated at the edge of the HT layer during the synthesis of dimethyl carbonate. Based on this concept and the selectivity data obtained with the samples calcined at high temperature, one can say that PC can be activated at the surface of the catalyst and methanol by the hydrogen bonded carbonate ions present in the interlayer of the catalyst. Thus, the overall reactivity of Mg-Al-CO₃ hydrotalcite samples in this transesterification reaction was assigned to the surface basicity and carbonate coordination with interlayer water/OH.

Effect of temperature and amount of catalyst

The increase in temperature increased the formation of DMC and reached equilibrium at 130 °C within 4 h (Fig. 3a). Reaction temperature >130 °C resulted in lower selectivity of DMC, shifting the equilibrium back to the reactant side. Wei et al. have reported similar reversing of equilibrium at higher temperature. The cyclic carbonate with no sterically hindered methyl group, i.e., ethylene carbonate, attained optimum conversion (entry 11 in Table 3) at 80 °C in 4 h. This is in accordance with the difference in the frequency factor between EC→DMC and PC→DMC reaction as explained by Filippis et al.

The conversion of PC was significantly increased with increase in the reactant ratio up to 10 and was less significant beyond the ratio 10 (Fig. 3b). This might be due to the formation of methanol-DMC azeotrope which is subsequently involved in deciding the equilibrium shift. The variation of amount of catalyst shows that the conversion of PC increased with increase in amount of catalyst, keeping the selectivity greater than 97% (Fig. 4). Above 50 mg, the amount of catalyst was not significant in the optimum conversion (72 %) of 20 mmol PC.

### Table 2 – Effect of Mg/Al molar ratio on transesterification of PC with methanol. [React. cond.: Methanol/PC ratio 10:1 (mol/mol); Catalyst amt: 50 mg; Temp.: 130 °C; Time 4 h]

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conv. of PC (%)</th>
<th>Selectivity of DMC (%)</th>
<th>Basicity (µmol/gcat)</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>4.2&lt;śH≤7.2</td>
<td>7.2&lt;śH≤9.8</td>
</tr>
<tr>
<td>HT-2.0</td>
<td>61.3</td>
<td>90.2</td>
<td>44</td>
<td>126</td>
</tr>
<tr>
<td>HT-3.0</td>
<td>63.8</td>
<td>95.0</td>
<td>46</td>
<td>136</td>
</tr>
<tr>
<td>HT-4.0</td>
<td>67.8</td>
<td>97.9</td>
<td>42</td>
<td>159</td>
</tr>
<tr>
<td>HT-5.0</td>
<td>72.2</td>
<td>97.1</td>
<td>36</td>
<td>190</td>
</tr>
<tr>
<td>HT-5.0b</td>
<td>54.5</td>
<td>95.4</td>
<td>40</td>
<td>144</td>
</tr>
<tr>
<td>HT-5.0c</td>
<td>52.8</td>
<td>76.1</td>
<td>20</td>
<td>104</td>
</tr>
</tbody>
</table>

*Values are within ±5 % error limit.
*Calcined at 200 °C.
*Calcined at 450 °C.
Efficiency of the catalyst in terms of TON

The catalytic efficiency of Mg-Al-CO$_3$ used in this study was compared with the data for catalysts reported in literature$^{8,14,15,23}$ (Table 3). Since the basicity values are not available for the reported catalysts, TON (TON = mmol of product formed per gram catalyst) was employed as a unit of comparison. The efficiency of various heterogeneous catalysts on the title reaction was compared with the presently studied catalyst (Table 3). The TON obtained (280 mmol DMC/g$_{\text{cat}}$) was much higher than values reported in literature. The TON of Mg-Al mixed oxide (HT-5 calcined at 450 °C) was also comparably higher (160 mmol DMC/g$_{\text{cat}}$) than that of metal oxides reported in the literature$^{14,15,27}$.

Reusability of the catalyst HT-5

The catalyst once used in the fresh run was collected and thoroughly washed with methanol to remove the various adsorbed molecules such as internal standard, propylene carbonate propylene glycol, etc. The washed catalyst was dried at 120 °C for 4 h before use in the consecutive runs. The catalyst showed 60.5 % conversion of PC with 92.4 % DNC selectivity after the fourth cycle. This slight drop in activity (11.7 % in conversion and 4.7 % in selectivity) is due to the structural changes, i.e., loss in the crystallinity observed in the used catalyst as seen by the P-XRD (e in Fig. 1) and FT-IR studies (d in Fig. 2).

Plausible reaction mechanism

Based on the above results, a possible reaction mechanism is proposed (Scheme 2). In the first step, the H-bonded carbonate ions present in the basic gallery of the catalyst abstract proton from methanol.
forming methoxy species (CH$_3$O$^-$) and the Lewis acid site (active metal centre) present on the surface of HT interacts with carbonyl oxygen of PC to generate relatively charged carbonyl carbon. In the second step, the methoxy ions attack the carbonyl carbon of PC at the edge of the HT structure to produce DMC. Simultaneously, the relative positive charge is transferred into the gallery to release proton, which is subsequently involved in the formation of propylene glycol. The water molecule present in the gallery is proposed to be involved in easier activation of methanol followed by the proton transfer during simultaneous formation of DMC and PG. In the reaction with Mg-Al mixed oxide, both the reactants are to be activated on the surface of the catalyst where the transfer of methoxy species and proton is supposed to be slower due to the strong basic nature of the surface. This leads to the decomposition of PC into CO$_2$ and propylene oxide leading to decreased selectivity of DMC.

**Conclusions**

The hydrotalcite materials, Mg-Al-CO$_3$ with different Mg/Al molar ratio from 2-5 have been synthesized and characterized with FT-IR and P-XRD techniques. The catalyst HT-5 dried at 120 °C showed optimum activity at 130 °C. The catalyst calcined at 200 °C resulted in slightly lower conversion with nearly the same selectivity while that at 450 °C resulted in decreased conversion and selectivity. The increase in methanol to propylene carbonate ratio increased the conversion of propylene carbonate, shifting the equilibrium to the product side. The catalyst showed very high TON with moderate recyclability even after four cycles.

**Supplementary Data**
P-XRD patterns of HT samples of varying Mg/Al ratio may be obtained from the authors on request.

**Acknowledgement**
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**References**