Coupling of CH$_3$OH and CO$_2$ with 2-cyanopyridine for enhanced yields of dimethyl carbonate over ZnO–CeO$_2$ catalyst

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Abstract. The present work is aimed to produce dimethyl carbonate by coupling of CH$_3$OH and CO$_2$ with 2-cyanopyridine over ZnO–CeO$_2$ catalysts prepared by co-precipitation method. These catalysts were characterized by XRD, TEM, UV-Vis DRS, BET surface area, CO$_2$ and NH$_3$-TPD techniques and applied for the titled reaction. Among the investigated catalysts 10ZnO–90CeO$_2$ catalyst with CeO$_2$ crystallite size 8.0 nm exhibited 96% conversion of methanol with 99% selectivity to dimethyl carbonate. The superior catalytic activity is a unified effect of crystalline size of CeO$_2$ and presence of an optimum number of acidic and basic sites. This protocol offers enhanced conversion of methanol with the simultaneous conversion of 2-cyanopyridine into 2-picolinamide by removing water molecules formed in the reaction.

Keywords. Dimethyl carbonate; methanol; carbon dioxide; 2-cyano pyridine; acid-base property.

1. Introduction

Dimethyl carbonate (DMC) has been considered as a green chemical because it is projected as the substituent for toxic and corrosive chemicals like dimethyl sulfate and phosgene which are used as carbonylation and methylation agents respectively in organic synthesis.$^1$ Apart from that, DMC is a good solvent and a fuel additive. Because of its high dielectric constant, DMC is used as an electrolyte in lithium batteries.$^2$ The existence of high amount of oxygen in DMC and its low toxic and biodegradable nature makes it as a suitable replacement of methyl tert.butyl ether (MTBE), a gasoline oxygenate. It also acts as a promising octane booster.$^3,4$ Among the greenhouse gases, CO$_2$ is the main contributor. So, the utilization of CO$_2$ is very important. Availability of CO$_2$ in surplus quantity at cheap cost, hence it can be utilized as a precursor for synthesis of various chemicals and chemical intermediates.$^5$ Dimethyl carbonate (DMC) is one such an important chemical derived from CO$_2$.

There are so many routes to synthesize dimethyl carbonate. Among these, the production of DMC by combining methanol and carbon dioxide on a proper catalyst (Scheme 1) has been represented as a green chemical process.$^6$ Because of the thermodynamic constraints, the reaction between methanol and CO$_2$ results in low yields of DMC. However, higher pressure and instant removal of water produced by employing suitable dehydrating agents can shift the equilibrium towards products side.$^7$ However CO$_2$ is kinetically inert and thermodynamically stable. Hence, CO$_2$ activation is the key problem in its conversion to DMC.$^8$ The reaction between CH$_3$OH and CO$_2$ is slightly exothermic, with the heat of reaction of 23 kJ/mol. Hence to reach a higher amount of DMC yields, a lower reaction temperature is preferable. The low yields of DMC due to the generation of H$_2$O as a by-product.$^9$

Currently, CeO$_2$, ZrO$_2$, CeO$_2$–ZrO$_2$, K$_2$CO$_3$, Cu-Ni/SBA-15, Nb$_2$O$_5$/CeO$_2$, Cu-Ni/graphite, metal tetra alkoxydes, H$_3$PW$_{12}$O$_{40}$/ZrO$_2$ are some of the major catalyst compositions for DMC synthesis. Among the heterogeneous catalysts, ZrO$_2$-based and CeO$_2$-based catalysts exhibit highest activities. Ki et al., reported that CeO$_2$-ZnO catalysts are active in the synthesis of DMC from methanol and CO$_2$. However, the conversion of methanol in their study is limited to 1% only and also there are no results regarding the
influence of reaction temperature, pressure on the synthesis of DMC from methanol and CO$_2$. Since the synthesis of DMC from methanol and CO$_2$ is equilibrium controlled reaction, the removal of water is pre-requisite for the enhanced yield of DMC. Under pressurized reaction conditions, the mechanical removal of water is so difficult that the addition of dehydrating agent which doesn’t disturb the targeted reaction is desirable. In this context, the addition of 2-cyanopyridine to the reaction would be an added advantage where 2-cyanopyridine converted to 2-picolinamide (an industrially interested chemical) by consuming the water molecules. Here some extent of methanol is reacted with 2-picolinamide to form methyl picolinate as described in Scheme 4.

With these preliminary understandings, the present work has been undertaken to (i) apply ZnO-CeO$_2$ mixed oxide catalysts for the synthesis of dimethyl carbonate with high yield by coupling methanol and CO$_2$ reaction with the hydration of 2-cyanopyridine (Schemes 1, 2, 3) and optimizing reaction parameters for the best yield (ii) to establish a correlation between the catalytic activity and the characterization results.

The synthesis of DMC from methanol and CO$_2$ requires a catalyst with acidic and basic sites. The mechanism for the synthesis of DMC from CH$_3$OH and CO$_2$ over the acid-base catalyst is shown in Scheme 5.

Both the basic sites and acidic sites play a key role in the activation of methanol to methoxy species and methyl species respectively. Basic sites adsorb CO$_2$ and adsorbed CO$_2$ attacks on methoxy group to get methoxy carbonate anion. The reaction between methoxy carbonate anion with methyl species results in the formation of DMC.

$$2\text{CH}_3\text{OH} + \text{CO}_2 \rightleftharpoons \text{O} = \text{C} - \text{O} + \text{H}_2\text{O}$$

Scheme 1. Direct synthesis of DMC from CO$_2$ and methanol.

$$\text{N} - \text{CN} + \text{H}_2\text{O} \rightarrow \text{N} - \text{CO} - \text{NH}_2$$

Scheme 2. Hydration of 2-cyanopyridine to 2-picolinamide.

$$2\text{CH}_3\text{OH} + \text{CO}_2 + \text{N} - \text{CN} \rightarrow \text{O} = \text{C} - \text{O} + \text{N} - \text{CO} - \text{NH}_2$$

Scheme 3. Coupling of methanol and 2-cyanopyridine.

2. Experimental

2.1 Catalyst preparation

ZnO-CeO$_2$ mixed oxide catalysts were prepared by the co-precipitation method. In a typical procedure, an aqueous solution of (NH$_4$)$_2$Ce(NO$_3$)$_6$ and Zn(NO$_3$)$_2$ was co-precipitated with (5%) aqueous NH$_4$OH solution at pH maintained at around 9–9.5. The resulting precipitate after ageing for 24 h was subsequently filtered with deionized water, washed several times until the pH of the filtrate become neutral. The resulting solid was dried in an oven at 100°C for 12 h followed by calcination at 773 K for 5 h in static air. In the same manner, pure CeO$_2$ and ZnO were prepared by precipitation method. Finally, obtained catalysts named as (a) pure CeO$_2$ (b) 10wt%ZnO-90wt%CeO$_2$ (c) 30wt%ZnO-70wt%CeO$_2$ (d) 50wt%ZnO-50wt%CeO$_2$ (e) 70wt%ZnO-30wt%CeO$_2$ (f) 90wt%ZnO-10wt%CeO$_2$ (g) Pure ZnO.

2.2 Catalyst characterization

The X-ray powder diffraction (XRD) patterns of the CeO$_2$ samples were recorded on Ultima-IV X-ray diffractometer (M/s. Rigaku Corporation, Japan) with Cu Ka radiation operated at 40 kV and 20 mA. The diffraction patterns were recorded in the 2$\theta$ range of 10–80$\degree$ at a scan rate of 4$\degree$/min. The average crystallite size (D) was calculated using the Scherrer equation:

$$D = \frac{k \lambda}{\beta \cos \theta}$$

Where $\lambda$ is X-ray wavelength, K constant of proportionality taken as 0.94, $\beta$ is the full width at half maximum of the maximum intensity peak and $\theta$ is the diffraction angle. The BET surface areas of all catalysts were determined by nitrogen adsorption on an Autosorb Instrument (M/s. Quantachrome, USA). UV-Vis diffused reflectance spectra was recorded on a UV Win Lab spectrometer (M/s. Perkin Elmher, Germany) with an integrating sphere reflectance accessory in a range of 200–800 nm. The acidic and basic strengths of the samples were obtained by subjecting the catalyst sample
Scheme 5. Mechanism for the synthesis of DMC from CH₃OH and CO₂ over acid-base catalyst.¹⁶

\[
\begin{align*}
\text{CH}_3\text{OH} & \quad \rightarrow \quad \text{CH}_3\text{O}^- + \text{H}^+ \quad \text{(Over basic sites)} \\
\text{CO}_2 & \quad \rightarrow \quad \text{CO}_2^* \quad \text{(Over basic sites)} \\
\text{CH}_3\text{O}^- + \text{CO}_2^* & \quad \rightarrow \quad \text{CH}_3\text{CO}_2^- \quad \text{(Over basic sites)} \\
\text{CH}_3\text{OH} & \quad \rightarrow \quad \text{CH}_3^+ + \text{OH}^- \quad \text{(Over acidic sites)} \\
\text{CH}_3\text{O}_2^- + \text{CH}_3^+ & \quad \rightarrow \quad \text{CH}_3\text{O}^-\text{C}^-\text{OCH}_3 \\
\text{(From basic sites)} \quad & \quad \text{(From acidic sites)}
\end{align*}
\]

3. Results and Discussion

3.1 X-ray diffraction analysis

Figure 1 shows the XRD patterns of (a) ZnO (b) 90Z-10C (c) 30Z-70C (d) 50Z-50C (e) 70Z-30C (f) 10Z-90C (g) CeO₂ catalysts. CeO₂ exhibited diffraction peaks due to the fluorite phase, while ZnO showed the characteristic diffraction peaks for the wurtzite phase. In the XRD patterns of ZnO-CeO₂ catalysts, the diffraction peaks at 2θ values of 31.7, 34.4, 36.2 and 63° correspond to ZnO and the diffraction peaks at 2θ values of 28.7 and 33.2° corresponds to CeO₂. Furthermore, a mixed-phase of CeO₂ and ZnO was observed with 2θ values of 47.6 and 56.4°, which are in good agreement with the reported results.¹⁶ The crystalline size of CeO₂ in ZnO-CeO₂ catalysts & BET surface area of catalysts are
Table 1. Textural features of CeO$_2$, ZnO and ZnO-CeO$_2$ catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Crystallite size (nm)$^a$</th>
<th>Surface area (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO$_2$</td>
<td>7.1</td>
<td>76.0</td>
</tr>
<tr>
<td>10Z-90C</td>
<td>8.0</td>
<td>71.2</td>
</tr>
<tr>
<td>30Z-70C</td>
<td>10.2</td>
<td>60.8</td>
</tr>
<tr>
<td>50Z-50C</td>
<td>11.4</td>
<td>48.2</td>
</tr>
<tr>
<td>70Z-30C</td>
<td>18.6</td>
<td>37.2</td>
</tr>
<tr>
<td>90Z-10C</td>
<td>25.2</td>
<td>23.4</td>
</tr>
<tr>
<td>ZnO</td>
<td>54.2</td>
<td>8.9</td>
</tr>
</tbody>
</table>

$^a$Crystallite sizes of CeO$_2$ are measured using Scherrer equation from (111) plane at $2\theta = 33.7^\circ$ and for pure ZnO from the diffraction peak at $2\theta = 36.2^\circ$.

Table 2. Band gap energies calculated from Tauc Plot method.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO$_2$</td>
<td>2.74</td>
</tr>
<tr>
<td>10Z-90C</td>
<td>2.81</td>
</tr>
<tr>
<td>30Z-70C</td>
<td>2.82</td>
</tr>
<tr>
<td>50Z-50C</td>
<td>2.85</td>
</tr>
<tr>
<td>70Z-30C</td>
<td>2.94</td>
</tr>
<tr>
<td>ZnO</td>
<td>3.11</td>
</tr>
</tbody>
</table>

illustrated in Table 1. In the XRD patterns of ZnO-CeO$_2$ catalysts, up to 50 wt % loading of ZnO, there are no significant peaks representing ZnO. Hence, the ZnO over CeO$_2$ exists either in amorphous form or in crystalline form with below the detection limit of the instrument. However, at higher loadings of ZnO on CeO$_2$ surface, high intense ZnO peaks were observed due to high crystalline nature of ZnO. Moreover higher ZnO loading is not good to well disperse on the surface of CeO$_2$. As well as the mutual interface between Ce and Zn oxide particles results in an increase in the surface areas with decreased crystalline sizes in the catalysts.

3.2 BET surface analysis

The BET-surface areas of the pure ZnO, pure CeO$_2$ and ZnO/CeO$_2$ (10Z-90C, 30Z-70C, 50Z-50C, 70Z-30C and 90Z-10C) catalysts were shown in Table 1. Among all the synthesized catalysts, 10Z-90C, 30Z-70C were found to possess the highest BET surface area of 71.2 m$^2$/g, and 60.8 m$^2$/g respectively. With the increase in ZnO content from 10 wt% to 90 wt% the surface area of ZnO-CeO$_2$ catalysts decreases. It was majorly due to ceria species significantly facilitating enough space for the homogeneous dispersion of ZnO species accordingly high surface emerged in all catalysts. But high ZnO content in the catalysts play a negative role in view of the formation of agglomerated particles on the surface of the catalysts, which is responsible for less surface area and high crystalline size depicted in Table 1. It was further investigated from XRD patterns, high-intensity peaks observed in 90Z-10C catalyst rather than mild intensity peaks in the 10Z-90C catalyst. For that reason, 10Z-90C catalyst possesses the highest surface area of 71.2 m$^2$/g, whereas 90Z-10C presents the lowest surface area of only 23.4 m$^2$/g. Therefore, the highest surface area in the 10Z-90C catalyst was provided by uniform dispersion of zinc oxide particles on the surface of ceria species. It is noticed that there is a good correlation between the total adsorption capacity of CO$_2$, NH$_3$ and specific surface area of the catalysts.

3.3 UV-Vis-DRS studies

The UV-Vis DRS patterns of CeO$_2$ and ZnO-CeO$_2$ catalyst were depicted in Figure 2. From this study, it is found that a signal at 280 nm in the pattern of pure CeO$_2$ and ZnO-CeO$_2$ is due to the intrinsic character of CeO$_2$ while absorption edge at 413 nm in CeO$_2$ is blue-shifted for ZnO-CeO$_2$ mixed oxides which may be due to the presence of solid solution between Ce-O-Zn. The absorption bands at 256 and 296 nm are due to charge transfer transitions of O$^{2-} \rightarrow$ Ce$^{3+}$ and O$^{2-} \rightarrow$ Ce$^{4+}$.

Addition of CeO$_2$ to ZnO changes the absorption features indicating bands at 230, 280 and 340 nm in the UV region of the spectra due to localized transitions. Such narrow bands are reported in the spectra of ultrafine alignment of CeO$_2$ particles in SiO$_2$ and Al$_2$O$_3$ matrices. The bandgap energy from UV-Vis DRS spectra was calculated using the Tauc plot method and presented.
The band gap energy is increased from 2.74 eV to 2.94 eV with doping of ZnO to CeO2. It means, with a decrease in CeO2 content the band gap energy is increased. For pure ZnO, the band gap energy is 3.11 eV. The increase in band gap energies resulted in a decrease in surface oxygen vacancies.21

3.4 Transmission electron spectroscopy (TEM)

TEM studies were performed on 10Z-90C catalyst. The representative images were displayed in Figure 3. The HR-TEM and selected-area electron diffraction (SAED) patterns further confirmed the structure of the desired solid oxide materials. The HR-TEM image in Figure 3(a) clearly shows an interface between CeO2 and ZnO species. The d-spacing values were calculated on the basis of the HR-TEM image. The planes existed in SAED image are in correlation with peaks in XRD patterns in Figure 1, and reported studies.22,23 The calculated d-spacing values show that the ZnO species exhibited a hexagonal structure and that CeO2 exhibited a cubic structure which is close agreement with the XRD results.

3.5 Temperature programmed reduction studies

The redox properties of the ZnO-CeO2 catalysts were evaluated by temperature-programmed reduction (H2-TPR). Figure 4 depicts the H2-TPR profiles of the ZnO-CeO2 catalysts. As we know that cerium can exist as Ce3+ and Ce4+ ions while zinc exists as Zn2+ only. Thereby CeO2 has high oxygen storage capacity and possesses a larger number of oxygen vacancies.24 In case of pure CeO2 catalyst typically two reduction peaks are observed. The low-temperature peak is ascribed the most easily removable surface capping oxygen of CeO2, while the high-temperature signal is caused by the removal of bulk oxygen. The H2-TPR profiles of the mixed oxides ZnO-CeO2 catalysts show a main broad reduction in the region between 763–833 K with different Tmax values. For pure CeO2, two reduction peaks at around 853 and 923 K were observed, which ascribed to the reduction of surface and bulk oxygen of CeO2 respectively. It was interesting to note that two reduction peaks at 769 and 833 K of the ZnO-CeO2 mixed oxide shifted to lower temperatures extremely relative to those of pure CeO2. It was due to effective synergistic interface between ceria and zinc oxide species consequently exhibited higher catalytic activity than pure CeO2 and ZnO catalysts, which is reliable with the H2-TPR results.25 It is due to the beneficial interactions between ceria and zinc leads to facial reduction properties of mixed oxide catalyst rather than individual oxides. Moreover, some extent of ZnO particles might be inserted into the CeO2 lattice, these properties make the better catalytic activity.

3.6 X-ray photoelectron spectroscopy studies

The XPS analysis spectrum is shown in Figure 5. The ZnO-CeO2 surface is composed of Zn, Ce, O, and C. The binding-energy values at 1021.61 eV and 1044.61 eV represent Zn 2p3/2 and Zn 2p1/2 in the ZnO-CeO2 mixed oxide catalyst as shown in Figure 5.23 The labels used in identifying Ce 3d XPS peaks were established by Burroughs et al.,26 where V and U indicate the spin-orbit coupling 3d5/2 and 3d3/2, respectively. The peaks corresponding to V, V′, V″, U, U′, U″ represent the
presence of Ce$^{4+}$, whereas the peaks $V_0$, $V'$, $U_0$, $U'$ represent Ce$^{3+}$ ions.\(^{27}\) As shown in the figure, the Ce 3d spectrum is integrated to subsequent peaks at about 881 ($V_0$), 882.3 (V), 888.9 (V$''$), 897.5 (V$'''$), 899 (U$_0$), 901.2 (U), 907.0(U$''$), and 918 eV (U$'''$). The primary peaks of 3d$_{5/2}$ and 3d$_{3/2}$ are located at 882.3 and 901.2 eV, respectively. The peak V$''$ is the satellite peak arising from ionization of Ce 3d$_{5/2}$, while the signals U$''$ and U$'''$ are accounting for ionization of Ce 3d$_{3/2}$.\(^{28}\) The satellite peak U$'''$ associated to the Ce 3d$_{3/2}$ is a characteristic aspect hinting to the presence of tetravalent Ce ions in ceria compounds which is in good agreement with literature reports.\(^{29}\)

3.7 Temperature programmed desorption (TPD) of NH$3$

Figure 6 shows the NH$_3$-TPD profiles of the catalysts. The synthesis of DMC from CH$_3$OH and CO$_2$ involves the activation of CH$_3$OH to CH$_3^+$ species on the acidic sites of the catalyst. So, higher acidity of the catalyst is helpful to get more yield of DMC. During the reaction, the decomposition of CH$_3$OH molecule is higher on 10Z-90C catalyst due to the higher amount of acidic sites present in ZnO along with a small fraction of acidic sites in CeO$_2$. Among these catalysts, 10Z-90C possesses a higher amount of acidic sites which could be responsible for the better catalytic performance with respect to higher production of DMC from CH$_3$OH and CO$_2$. The acidity of the catalysts increased as the content of CeO$_2$ increased, whereas the acidity decreased at an excessive amount of CeO$_2$ content. Cerium oxide is more

Figure 4. TPR patterns of (a) pure CeO$_2$, (b) 70Z-30C, (c) 50Z-50C, (d) 30Z-70C and (e) 10Z-90C.

Figure 5. XPS spectra of (a) Ce 3d in 10Z-90C, (b) Zn 2p in 10Z-90C and (c) Ce 3d in pure CeO$_2$ samples calcined at 773K.
Table 3. The total acidity and basicity of the catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Number of acidic sites (mmol/g)</th>
<th>Acidic site density ((\times10^{-2} \text{ mmol/m}^2))</th>
<th>Number of basic sites (mmol/g)</th>
<th>Basic site density ((\times10^{-2} \text{ mmol/m}^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO(_2)</td>
<td>0.56</td>
<td>0.73</td>
<td>1.497</td>
<td>1.96</td>
</tr>
<tr>
<td>10Z-90C</td>
<td>0.75</td>
<td>1.1</td>
<td>1.775</td>
<td>2.49</td>
</tr>
<tr>
<td>30Z-70C</td>
<td>0.59</td>
<td>1.0</td>
<td>1.635</td>
<td>2.68</td>
</tr>
<tr>
<td>50Z-50C</td>
<td>0.51</td>
<td>1.05</td>
<td>1.322</td>
<td>2.74</td>
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<tr>
<td>70Z-30C</td>
<td>0.47</td>
<td>1.26</td>
<td>1.183</td>
<td>3.18</td>
</tr>
<tr>
<td>90Z-10C</td>
<td>0.37</td>
<td>1.58</td>
<td>0.666</td>
<td>2.84</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.19</td>
<td>2.13</td>
<td>0.379</td>
<td>4.25</td>
</tr>
</tbody>
</table>

Figure 6. Temperature programmed desorption (TPD) patterns of NH\(_3\): (a) pure CeO\(_2\), (b) 10Z-90C, (c) 30Z-70C, (d) 50Z-50C, (e) 70Z-30C, (f) 90Z-10C and (g) pure ZnO.

Figure 7. Temperature programmed desorption (TPD) patterns of CO\(_2\): (a) pure ZnO, (b) 10Z-90C, (c) 70Z-30C, (d) pure CeO\(_2\), (e) 30Z-70C, (f) 50Z-50C and (g) 90Z-10C.

3.8 Temperature programmed desorption (TPD) of CO\(_2\)

Not only acidic sites but also basic sites of the catalyst can also play an important role in the synthesis of DMC. Basic sites of the catalyst are more accountable for the formation of methoxy carbonate through a reaction between methoxy species and CO\(_2\) molecules. Figure 7 shows the CO\(_2\)-TPD profiles of different catalysts. Among these catalysts, 10Zn-90C possesses more number of basic sites which could be useful in yielding better catalytic activity towards the synthesis of DMC from CH\(_3\)OH and CO\(_2\). The introduction of an appropriate amount of Ce into ZnO could increase the number of basic sites in the catalyst, whereas an excessive amount of Ce could lead to a decrease in the amount of basic sites. The reduction in the amount of basic sites may be due to the aggregation of CeO\(_2\) particles. It was reported that the CeO\(_2\) species were exhibited better O\(_2\) storage and releasing capacity which leads to adsorption of more number of CO\(_2\) molecules in view of higher number of methoxy carbonate molecule formation during the reaction. On 10Z-90C catalyst, we speculate that there could be better synergetic interactions between CeO\(_2\) and CO\(_2\) molecules which lead to the better conversion of CH\(_3\)OH molecules. Basicity of catalysts obtained from CO\(_2\)-TPD is described in Table 3. As can be seen from Scheme 5, both acidic and basic sites are major responsible for the better catalytic activity. Thus the amount of DMC obtained could be proportional to the high concentration of acidic and basic sites of basic oxide and therefore, a high amount of CeO\(_2\) in the catalyst may result in a decrease of ammonia adsorption. In the present study based on catalytic activity, we assumed that there might be the considerable synergetic interface between Lewis acidity of ZnO and Lewis basicity of CH\(_3\)OH. The amount of acidity of catalysts calculated from NH\(_3\)-TPD peak area is summarized in Table 3.
the catalysts. Based on Figures 6 and 7, DMC yields are typically dependent on more number of acidic and basic sites of the catalysts, which are close correlation with CO₂ and NH₃ TPD analysis shown in Figures 6 and 7. The surface acidic/basic site densities of the catalysts were calculated and presented in Table 3. The surface acidic site densities are increased from $0.73 \times 10^{-2}$ mmol/m² (for pure CeO₂) to $1.58 \times 10^{-2}$ mmol/m² (for 90Z-10C) with increase in ZnO loading. The surface basic site densities are also followed the same trend as surface acidic site density ($1.96 \times 10^{-2}$ mmol/m² (for pure CeO₂) to $2.84 \times 10^{-2}$ mmol/m² (for 90Z-10C)). These results indicate that, the incorporation of ZnO in CeO₂ enhances the available surface acidic and basic sites per unit surface area of the catalyst.

3.9 Activity studies

3.9a Effect of reaction temperature and pressure: Even though DMC synthesis is slightly exothermic, the high reaction temperature is needed for the activation of CH₃OH and CO₂. However, the activity decreases beyond 393 K due to considerable CO₂ and CH₃OH desorption. The selectivity to DMC also declines with an increase in temperature due to the decomposition of DMC (Figure 8 (a)). DME observed as a side product is due to the decomposition of dimethyl carbonate. It can also be obtained from MeOH via intermolecular dehydration in the presence of an acid-base catalyst at high temperature but this is very low when compared to the decomposition of DMC. The yield and selectivity of DMC increase with increasing pressure up to 40 bar (Figure 8 (b)). There is a decrease in the yield of DMC over 40 bar due to the dilution effect.

3.9b Effect of loading: The amount of formation of DMC over CeO₂, ZnO and ZnO-CeO₂ mixed oxide catalytic systems was shown in Figure 9. It is found that ZnO catalyst exhibited lower activity (14% CH₃OH conversion) than that of CeO₂ (84% conversion of CH₃OH) even though both catalysts are exhibited similar higher selectivity to DMC. Catalysts with 10 and 30% ZnO exhibited higher activity than that of CeO₂. Among these two, 10Z-90C exhibited higher activity (96% CH₃OH
conversion with 99% selectivity to DMC (Figure 9). Catalysts with higher ZnO content (>50%) showed lower activity when compared to bare CeO$_2$ because of high crystalline ZnO species existed on the surface of the CeO$_2$ leads to the mild surface area. CeO$_2$-ZnO mixed oxide catalysts with more number of acidic and basic sites in the moderate region (ranging from 573–773 K temperature) showed enhanced catalytic activity.

From Figure 10, it is clear that the crystalline size of CeO$_2$ and as well as ZnO have a profound effect in governing the yield of DMC. The crystalline sizes of CeO$_2$ in ZnO-CeO$_2$ are increased with the incorporation of ZnO in CeO$_2$ and vice versa. In general, the catalytic activity is decreased at high crystalline sizes of metal oxides. In the present case, the best catalytic activity is obtained over the 10Z-90C catalyst with CeO$_2$ crystalline size of 8.0 nm even though the crystalline size of pure CeO$_2$ is 7.1 nm. It indicates that the catalytic activity of the catalyst can’t be dependent alone on the crystalline size of CeO$_2$. In addition, the presence of surface acidic and basic sites is responsible for achieving the best yield of DMC. In particular, the optimum numbers of surface acidic and basic site densities along with small crystallites of CeO$_2$ are key contributors for the catalytic activity in the synthesis of DMC from CO$_2$ and methanol.

The reaction conditions for different catalysts used for the synthesis of DMC are reported in Table 4. Various catalysts have been reported for the synthesis of DMC from CO$_2$ and CH$_3$OH such as pure metal oxide, mixed metal oxides and bimetallic supported catalysts. Ahmed et al., reported 7.6% CH$_3$OH conversion and 87% DMC selectivity over Co$_{1.5}$PW$_{12}$O$_{40}$ catalyst. Over Cu-Ni/graphite, 10.2% CH$_3$OH conversion and 88% DMC selectivity were observed from the report of Bian et al. Yingjie et al., reported 5.3% CH$_3$OH conversion and 86% DMC selectivity over Cu-Fe/SiO$_2$ catalyst. Qinghai et al., reported 16.2% CH$_3$OH conversion and 100% DMC selectivity over CH$_3$OK catalyst. Over Ce-Zr/Graphene, 58% of CH$_3$OH conversion and 57% of DMC selectivity were reported by Rim et al. Over LG-HTO catalyst, 15.9% CH$_3$OH conversion and 99.9% DMC selectivity were observed from the report of Stoian et al. Zhongwei et al., reported 5.38% CH$_3$OH conversion and 83.1% DMC selectivity over Ti$_{0.04}$Ce$_{0.96}$O$_2$ catalyst. 63% CH$_3$OH conversion and 97% DMC selectivity over

![Figure 10. Loading of ZnO against the crystalline size of CeO$_2$ and DMC yield.](image)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temperature (K)</th>
<th>Pressure (bar)</th>
<th>CH$_3$OH Conversion (%)</th>
<th>DMC Selectivity (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co$<em>{1.5}$PW$</em>{12}$O$_{40}$</td>
<td>473</td>
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<td>7.6</td>
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<tr>
<td>Cu-Ni/graphite</td>
<td>383</td>
<td>12</td>
<td>10.2</td>
<td>88</td>
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<tr>
<td>LG-HTO</td>
<td>403</td>
<td>-</td>
<td>15.9</td>
<td>99.9</td>
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<tr>
<td>Cu-Fe/SiO$_2$</td>
<td>393</td>
<td>12</td>
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<td>86</td>
<td>32</td>
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<tr>
<td>CH$_3$OK</td>
<td>353</td>
<td>73</td>
<td>16.2</td>
<td>100</td>
<td>33</td>
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<tr>
<td>Ce-Zr/Graphene</td>
<td>383</td>
<td>275</td>
<td>58</td>
<td>57</td>
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<tr>
<td>Ti$<em>{0.04}$Ce$</em>{0.96}$O$_2$</td>
<td>373</td>
<td>10</td>
<td>83.1</td>
<td>5.3</td>
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<tr>
<td>Ce$_2$-spindles</td>
<td>413</td>
<td>50</td>
<td>63</td>
<td>97</td>
<td>36</td>
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<tr>
<td>CeO$_2$</td>
<td>393</td>
<td>50</td>
<td>&lt;1</td>
<td>97</td>
<td>37</td>
</tr>
<tr>
<td>ZnO-CeO$_2$</td>
<td>443</td>
<td>70</td>
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<td>CeO$_2$-ZnO</td>
<td>393</td>
<td>40</td>
<td>2.7</td>
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<tr>
<td>*CeO$_2$-ZnO</td>
<td>393</td>
<td>40</td>
<td>96</td>
<td>99</td>
<td>This work</td>
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</table>

* With addition of 2-cyanopyridine.
CeO₂ spindles were reported by Unnikrishnan et al.\textsuperscript{37} Masayoshi \textit{et al.}, reported 97\% CH₃OH conversion and 99\% DMC selectivity over CeO₂ catalyst for 16 h.\textsuperscript{38}

In the present work, we report 96\% conversion of methanol with 99\% selectivity to DMC by coupling of methanol and CO₂ with 2-cyanopyridine. Since it is an equilibrium controlled reaction, removal of H₂O, the by-product is necessary to get better methanol conversion. We achieved this, by coupling of CH₃OH with 2-cyanopyridine which can be beneficial to get more DMC yield. Hence coupling with 2-cyanopyridine has been used and afforded good activity results.

4. Conclusions

In conclusion, ZnO–CeO₂ catalysts prepared by co-precipitation method were found to be active in the synthesis of dimethyl carbonate via coupling of CH₃OH and CO₂ with 2-cyanopyridine. UV-Vis DRS patterns evidenced the formation of Ce-O-Zn solid solution. The synergetic interaction between ZnO and CeO₂ had improved the quantity of acidic and basic sites. Among the series of catalysts, 10ZnO–90CeO₂ catalyst with CeO₂ crystallite size 8.0 nm and surface acid site density 1.1 x 10⁻² mmol/m² and surface basic site density 2.49 x 10⁻² mmol/m² delivered better results. Further, the addition of 2-cyanopyridine absorbed the formed water molecules during the reaction. Due to these unified effects, a maximum 95\% yield of dimethyl carbonate was achieved at 393K.

References

33. Yingjie Z, Shuanjin W, Min X, Dongmei H, Yixin L and Yuezhong M 2012 Novel Cu–Fe bimetal catalyst for the formation of dimethyl carbonate from carbon dioxide and methanol RSC Adv. 2 6831
34. Qinghai C, Chao J, Bin L, Hejin T and Yongkui S 2005 Structure of the active sites on H$_3$PO$_4$/ZrO$_2$ catalysts for dimethyl carbonate synthesis from methanol and carbon dioxide Catal. Lett. 103 225
36. Zhongwei F, Yunyun Z, Yuehong Y, Lizhen L, Min X, Dongmei H, Shuanjin W and Yuezhong M 2018 TiO$_2$-doped CeO$_2$ nanorod catalyst for direct conversion of CO$_2$ and CH$_3$OH to dimethyl carbonate: Catalytic performance and kinetic study ACS Omega 3 198
37. Unnikrishnan P and Srinivas D 2016 Direct synthesis of dimethyl carbonate from CO$_2$ and methanol over CeO$_2$ catalysts of different morphologies J. Chem. Sci. 128 6