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# Direct dimethyl carbonate synthesis from CO<sub>2</sub> and methanol over a flower-like CeO<sub>2</sub> catalyst with 2-cyanopyridine as a dehydrating agent in continuous packed-bed reactor

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A flower-like CeO<sub>2</sub> catalyst was successfully synthesized using an acrylamide graft copolymerized on glucose under hydrothermal conditions and used for the direct synthesis of dimethyl carbonate (DMC) from CO<sub>2</sub> and CH<sub>3</sub>OH in a packed-bed reactor with 2-cyanopyridine as a dehydrating agent. The synthesized flower-like CeO<sub>2</sub> exhibited both basicity and acidity properties with values of 300 μmol g<sup>-1</sup> and 80 μmol g<sup>-1</sup>, respectively, according to CO<sub>2</sub>-TPD and NH<sub>3</sub>-TPD results. The effect of reaction parameters such as reaction temperature, feed ratio, catalyst quantity, and operating pressure on the DMC production over the flower-like CeO<sub>2</sub> catalyst was investigated. The optimum conditions were found to be a temperature of 120 °C, catalyst weight of 1.0 g, CH<sub>3</sub>OH : CO<sub>2</sub> ratio of 1 : 1, and pressure of 30 bar, which provided the highest CH<sub>3</sub>OH conversion, DMC selectivity, and DMC yield of 86.6%, 99.3%, and 86.0%, respectively. Furthermore, no changes were observed in the structure, morphology, and particle size of the flower-like CeO<sub>2</sub> catalyst after the DMC synthesis reaction, indicating that the synthesized catalyst was resistant to the reaction test under such optimum reaction conditions.

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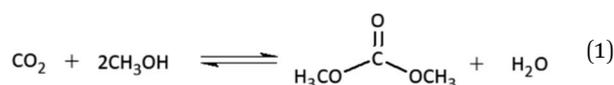
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## 1. Introduction

Climate change is a major issue caused by increasing carbon dioxide (CO<sub>2</sub>) emissions into the atmosphere, and significant attention is being paid globally to reducing these emissions by converting CO<sub>2</sub> into value-added fuels or chemicals. The conversion of CO<sub>2</sub> to dimethyl carbonate (DMC) has received a lot of attention because DMC is an environmentally friendly and low toxicity chemical. DMC stands out as a remarkably versatile molecule with multifaceted chemical reactivity and serves as an exemplary green chemical methylating agent and solvent, finding wide application across various industries. It is also one of the green chemicals that is the raw material to produce electrolytes used in lithium-ion batteries due to its high dielectric constant and potential gasoline additives due to its

high oxygen content and good blending properties as compared to methyl *tert*-butyl ether (MTBE).<sup>1,2</sup> Traditionally, DMC has been produced by several methods such as the phosgenation of methanol<sup>3</sup> and the oxidative carbonylation of methanol.<sup>4</sup> However, both procedures have significant disadvantages, such as the high toxicity of phosgene and the utilization of hazardous CO. As a result, the direct synthesis of DMC from methanol (CH<sub>3</sub>OH) and CO<sub>2</sub> (reaction (1)) is considered one of the most promising ways to effectively utilize carbon resources and reduce greenhouse gas emissions, yielding just water as a byproduct.



Direct DMC synthesis from CH<sub>3</sub>OH and CO<sub>2</sub> is considered a green and sustainable route; however, it typically yields low amounts of DMC due to thermodynamic limitations (ΔG = +26 kJ mol<sup>-1</sup>), DMC hydrolysis, and catalyst deactivation. Water removal from the reaction system is expected to shift the reaction equilibrium toward DMC synthesis resulting in enhanced DMC yield. Therefore, the catalytic activity can be boosted by water removal using several dehydrating strategies including

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dehydration of methanol before the reaction,<sup>5</sup> the use of organic molecules<sup>6</sup> or inorganic (zeolite) materials<sup>7</sup> as a dehydrating agent, and the use of a membrane reactor.<sup>8</sup> Several studies have reported the use of different dehydrating agents such as  $\text{CH}_3\text{I}$ ,<sup>9</sup> butylene oxide,<sup>10</sup> acetonitrile,<sup>11</sup> and 2-cyanopyridine<sup>12–16</sup> for water removal from the DMC synthesis reaction. Honda and co-workers<sup>16</sup> examined the use of various dehydrating agents for direct DMC synthesis from  $\text{CH}_3\text{OH}$  and  $\text{CO}_2$  using  $\text{CeO}_2$  catalyst in a batch system. They found that the use of 2-cyanopyridine as a dehydrating agent resulted in excellent catalytic activity. Moreover, 2-picolinamide product from the reaction between 2-cyanopyridine and water can be easily removed from the reaction mixture and recyclable back to 2-cyanopyridine by a dehydration reaction over a catalyst.

One of the challenges for researchers is to find suitable catalyst materials that could improve the catalytic activity for the synthesis of DMC. Generally, acid and basic sites are required for the synthesis of DMC from  $\text{CO}_2$  and  $\text{CH}_3\text{OH}$ .  $\text{CH}_3\text{OH}$  molecules are activated at both acid and basic sites, while  $\text{CO}_2$  molecules are adsorbed at the basic site of the catalyst. Therefore, the development of catalysts with high acidity and basicity properties are an interesting area that is currently being investigated.<sup>3,17</sup> So far, many studies on the direct DMC synthesis with homogeneous and heterogeneous catalysts have been published. However, homogeneous catalysts have many disadvantages such as being difficult to recycle, requiring the co-catalyst as a support to increase activity, which leads to high processing costs, as well as easily forming water as a side effect, which decomposes the catalyst and leads to deactivation.<sup>18,19</sup> Therefore, heterogeneous catalysts received more attention because they can overcome these disadvantages and exhibit higher stability compared to homogeneous catalysts. There are many types of metal oxides such as  $\text{CeO}_2$ ,  $\text{ZrO}_2$ ,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$  and  $\text{ZnO}$ <sup>20,21</sup> as well as some mixed metal oxides such as  $\text{CeO}_2$ – $\text{ZrO}_2$ ,  $\text{TiO}_2$ – $\text{CeO}_2$ ,  $\text{CeO}_2$ – $\text{ZnO}$ ,  $\text{ZrO}_2$ – $\text{MgO}$  and  $\text{MgO}$ – $\text{SiO}_2$ <sup>8,10,22–25</sup> have been reported as heterogeneous catalyst for the direct DMC synthesis. Among these catalysts, cerium oxide ( $\text{CeO}_2$ ) has gained a lot of attention and has become a favorable choice due to its acid–base properties, redox properties, suitable crystal structure, high oxygen storage capacity and high oxygen vacancies<sup>26–29</sup> which induce ability in  $\text{CO}_2$  adsorption and  $\text{CH}_3\text{OH}$  activation led to increased catalytic activity. P. Kumar *et al.*<sup>30</sup> investigated the synthesis of DMC from  $\text{CO}_2$  and  $\text{CH}_3\text{OH}$  over  $\text{CeO}_2$  catalyst using a molecular sieve as a dehydrating agent in a batch reactor. They found that the catalytic performance was correlated with the basic and acidic properties of the  $\text{CeO}_2$  catalyst, resulting in a DMC yield of 2.046 mmol DMC per g cat. at a reaction temperature of 120 °C, pressure of 150 bar, and reaction time of 4 h. D. Stoian *et al.*<sup>31</sup> studied the efficiency of the direct DMC synthesis from  $\text{CO}_2$  and  $\text{CH}_3\text{OH}$  over the  $\text{CeO}_2$  catalyst with the presence of 2-cyanopyridine as a dehydrating agent in both batch and continuous operations. They reported that high DMC yield was observed due to the right balance in basicity and acidity properties of  $\text{CeO}_2$  catalyst. Furthermore, it has been reported that  $\text{CeO}_2$  not only acts as an excellent catalyst in DMC synthesis but also in dehydration

reaction of dehydrating agent (2-cyanopyridine, 2-CP) to remove water byproduct in both batch and continuous operations.<sup>12,15</sup>

Recently, the synthesis of  $\text{CeO}_2$  catalyst with a special morphology such as nanorods,<sup>32</sup> nanotubes,<sup>33</sup> nanocubes,<sup>34</sup> nanoplates<sup>35</sup> and nanospheres<sup>36</sup> have received great attention. The different crystal facets exposed on the surface of  $\text{CeO}_2$  nanostructures were strongly controlled by their morphologies, resulting in differential properties that can influence the interaction between the  $\text{CeO}_2$  surface and the adsorbed reactants, as well as the catalytic performance. Wang *et al.*<sup>28</sup> investigated nano- $\text{CeO}_2$  catalysts with various morphologies (spindle, rod, cube, and octahedron) for the DMC synthesis from  $\text{CH}_3\text{OH}$  and  $\text{CO}_2$  and found that spindle-like  $\text{CeO}_2$  provided better catalytic efficiency than other morphologies because the spindle-like  $\text{CeO}_2$  displayed more active (111) planes and acid–base sites, resulting in higher DMC yield. Three dimensional (3D)  $\text{CeO}_2$  hierarchical structures, such as flower-like assembled from 1D or 2D structures, have a significant impact on performance improvements. It provided high active surface areas that facilitated surface reactions, high specific surface area and high surface-to-bulk ratio.<sup>37–39</sup> Moreover,  $\text{CeO}_2$  catalyst with flower-like morphology has been rarely reported for direct DMC synthesis reaction from  $\text{CH}_3\text{OH}$  and  $\text{CO}_2$ .

Therefore, this study is interested in synthesizing a flower-like  $\text{CeO}_2$  catalyst using a graft copolymerization reaction between acrylamide and glucose under hydrothermal treatments and applied for the direct synthesis of DMC from  $\text{CO}_2$  and  $\text{CH}_3\text{OH}$  reaction with 2-cyanopyridine as a desiccant in a continuous tubular packed-bed reactor. The synthesized catalyst was characterized by XRD, SEM, BET,  $\text{CO}_2$ -TPD,  $\text{O}_2$ -TPD and  $\text{NH}_3$ -TPD techniques. Furthermore, the effect of reaction parameters such as temperature, feed ( $\text{CH}_3\text{OH}:\text{CO}_2$ ) ratio, catalyst weight and pressure on catalytic performance for the DMC synthesis are also investigated.

## 2. Methodology

### 2.1. Catalyst preparation

A synthetic procedure is as follows: 3.6 g of glucose was dissolved in 180 mL of distilled water and stirred until completely dissolved at room temperature. 2.12 g of acrylamide and 4.34 g of cerium(III) nitrate hexahydrate were then added to the previous solution until became transparent. Subsequently, the pH of the solution was adjusted to 10–12 by adding 8–10 mL of 28–30% wt. ammonia solution and vigorously stirring. The solution was changed from a transparent solution to a viscous gel. After 5 h of continuous stirring, the brown gel was transferred to a hydrothermal bomb and stored in the oven at 180 °C for 72 h. The hydrothermal bomb was naturally cooled to room temperature. The brown suspension was washed three times with distilled water and once with ethanol using a centrifuge at 9000 rpm for 10 min before being dried overnight at 60 °C. Finally, the obtained suspension was calcined in two steps: first, at 600 °C for 12 h under Ar gas flow. Second, at 400 °C for 10 h with an air flow and a heating rate of 2 °C  $\text{min}^{-1}$ .



## 2.2. Catalyst characterization

The crystalline structure of the synthesized and spent catalysts were characterized using X-ray diffraction (XRD, Rigaku TTRAX III diffractometer) with Cu  $K_{\alpha}$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) at an accelerating voltage of 40 kV and current of 30 mA. The scanning range of  $2\theta$  was set from  $20^{\circ}$  to  $90^{\circ}$  with a step width of  $0.02^{\circ}$ . The morphology of the  $\text{CeO}_2$  samples was investigated using Thermo Scientific Phenom Pharos G2 Desktop Field Emission Gun-Scanning Electron Microscope (FEG-SEM) with an accelerating voltage of 10 kV. Textural properties of the synthesized catalyst were studied by nitrogen physisorption technique at  $-196^{\circ}\text{C}$  using Quantachrome Autosorb-1. Prior to the measurements, the sample was degassed in vacuum to clean the catalyst surface. The specific surface area was determined using the Brunauer–Emmett–Teller (BET) method. The basicity and acidity of the synthesized catalyst were characterized using  $\text{CO}_2$ - and  $\text{NH}_3$ -temperature programmed desorption (TPD), respectively. Before starting the TPD study, the catalyst sample was packed into a quartz reactor and first pretreated at  $150^{\circ}\text{C}$  for 1 h with a flow rate of  $100 \text{ mL min}^{-1}$  Argon gas (Ar) and then cooled to room temperature. After pretreatment, the sample was exposed to the corresponding gas mixtures at different temperatures. Individually,  $100 \text{ mL min}^{-1}$  of 5% vol.  $\text{CO}_2/\text{Ar}$  was fed at  $100^{\circ}\text{C}$  ( $\text{CO}_2$ -TPD) or  $50 \text{ mL min}^{-1}$  of 5% vol.  $\text{NH}_3/\text{Ar}$  was fed at  $50^{\circ}\text{C}$  ( $\text{NH}_3$ -TPD) to the system for 2 h, then cooled to room temperature by continuing the gas flow and left overnight. During the TPD process, the temperature was increased by  $5^{\circ}\text{C min}^{-1}$  from  $25$  to  $700^{\circ}\text{C}$  under Ar flow rate of  $100 \text{ mL min}^{-1}$ . The gas ( $\text{CO}_2$  or  $\text{NH}_3$ ) desorption profiles were measured using a real-time quadrupole mass spectrometer gas analyzer (GSD 320, OmniStar).  $\text{O}_2$ -temperature programmed desorption ( $\text{O}_2$ -TPD) was also measured on the above instrument. The sample (1.0 g) was first pretreated with  $100 \text{ mL min}^{-1}$  of 10%  $\text{O}_2/\text{Ar}$  at  $700^{\circ}\text{C}$  for 1 h and then cooled to ambient temperature. After that, the sample was flushed with Ar to eliminate excess/ physisorption of oxygen. The oxygen desorption amount was continuously monitored using an on-line mass spectrometer (GSD 320, OmniStar) in the presence of  $100 \text{ mL min}^{-1}$  of Ar, while the temperature was ramped up from room temperature to  $800^{\circ}\text{C}$  at a heating rate of  $5^{\circ}\text{C min}^{-1}$ .

## 2.3. Catalytic performance test

The catalytic activity of the  $\text{CeO}_2$  catalyst for the synthesis of DMC from  $\text{CH}_3\text{OH}$  and  $\text{CO}_2$  were evaluated by using a continuous tubular packed-bed reactor. The schematic for the DMC synthesis is shown in Fig. 1. One gram of catalyst was packed inside a stainless-steel tube between a thin layer of quartz wool (I.D. = 10 mm, O.D. = 13 mm). The heater temperature is measured by a K-type thermocouple located along the wall of the reactor near the catalyst bed and the system pressure is determined by a pressure gauge and controlled by a back pressure regulator (BPR). 2-Cyanopyridine (2-CP) as a dehydrator was dissolved in  $\text{CH}_3\text{OH}$  at a stoichiometric molar ratio (2-CP :  $\text{CH}_3\text{OH} = 1 : 2$ ).<sup>12</sup> In the experiment, gaseous  $\text{CO}_2$  was introduced into the reactor through a mass flow regulator to increase the pressure of the system to the desired reaction

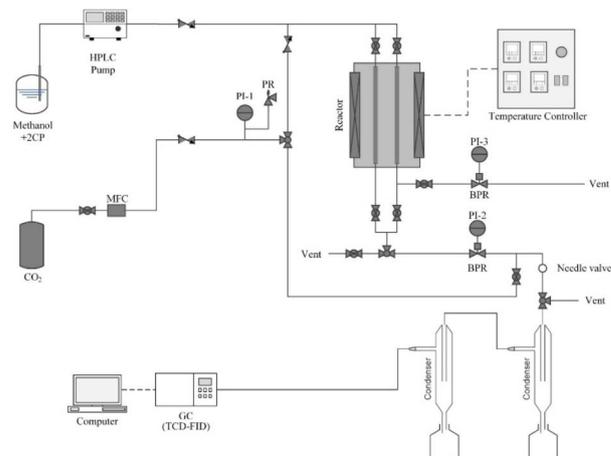


Fig. 1 Schematic illustration of the reaction system for direct synthesis of dimethyl carbonate.

pressure. The molar feed ( $\text{CH}_3\text{OH}:\text{CO}_2$ ) ratio was adjusted differently (1:2, 1:1, and 2:1). Separation of products is divided into two steps using 2-stage condensers. The first step captures the unwanted substance with a high boiling point (2-CP, 2-picolinamide) and the other captures the desired product substance (DMC,  $\text{CH}_3\text{OH}$ ). The gas and liquid products analysis were performed by gas chromatography (Shimadzu GC-2014, FID-TCD detector).

## 3. Results and discussion

### 3.1. Catalyst characterizations

**3.1.1. Structural analysis.** The X-ray diffraction patterns of the flower-like  $\text{CeO}_2$  catalyst before and after the reaction testing are shown in Fig. 2. The fluorite structure of  $\text{CeO}_2$  (PDF No. 01-075-8371) was presented as a major crystalline phase in the flower-like  $\text{CeO}_2$  catalyst before the reaction at  $2\theta$  of 28.5, 33.1, 47.5, 56.3, 59.1, 69.4, 76.7, 79.1, and  $88.4^{\circ}$ , corresponding to (111), (200), (220), (311), (222), (400), (331), (420), (422) planes, consistent with the literature.<sup>37–39</sup> It indicated that the calcination of the  $\text{Ce}(\text{OH})\text{CO}_3$  complex at  $400^{\circ}\text{C}$  under air flow resulted in a complete formation of the  $\text{CeO}_2$  structure. After

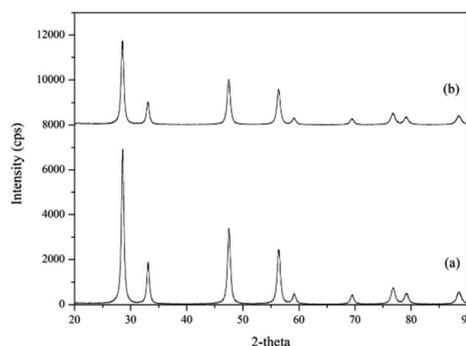


Fig. 2 XRD diffractograms of the flower-like  $\text{CeO}_2$  catalyst: (a) before and (b) after reaction.



reaction testing, the spent flower-like  $\text{CeO}_2$  catalyst was calcined again at  $400\text{ }^\circ\text{C}$  under air flow and then analyzed using XRD. The XRD patterns of the spent  $\text{CeO}_2$  structure remained unchanged. This confirmed that the  $\text{CeO}_2$  catalyst was resistant to the reaction test at the reaction temperature of  $120\text{ }^\circ\text{C}$  and reaction pressure of 10 bar. The crystallite sizes of  $\text{CeO}_2$  before and after the reaction can be determined using the Scherrer equation, obtaining values of 16.8 and 15.6 nm, respectively. These crystallite sizes were close to Z. Zongcheng *et al.*<sup>40</sup> who reported crystallite sizes of flower-like  $\text{CeO}_2$  of 15.6 nm.

**3.1.2. Morphology and particle size analysis.** The morphology and particle sizes of the synthesized flower-like  $\text{CeO}_2$  catalyst prepared by hydrothermal treatments and calcined at  $400\text{ }^\circ\text{C}$  (before reaction) and the spent flower-like  $\text{CeO}_2$  calcined at  $400\text{ }^\circ\text{C}$  (after reaction) were examined by SEM images as shown in Fig. 3 and 4, respectively. It was found that the synthesized flower-like  $\text{CeO}_2$  in Fig. 3 appeared as three-dimensional (3D) flower-like mesoporous microspheres with a diameter of 3–4  $\mu\text{m}$ . The microspheres consist of numerous petal-like plates with thickness of less than 100 nm connected to each other to form an open porous structure. Furthermore, there were no changes in the morphology and particle size of the spent flower-like  $\text{CeO}_2$  after reaction (Fig. 4) when compared to the catalyst before the reaction (Fig. 3). This indicated that the flower-like shape of the  $\text{CeO}_2$  catalyst was resistant to the

reaction test at the reaction temperature of  $120\text{ }^\circ\text{C}$  and reaction pressure of 30 bar, which was consistent with the XRD data.

Different morphologies of  $\text{CeO}_2$  expose distinct crystal facets on the surface, resulting in varied surface properties such as particle size, surface area, and acid–base sites, as well as differing catalytic activities. The cubic fluorite structure of  $\text{CeO}_2$ , as confirmed by XRD results, typically comprises three crystal facets: (100), (110), and (111). The surface properties of  $\text{CeO}_2$  vary depending on these exposed facets, which have distinct oxygen vacancy formation energies, leading to varying quantities of oxygen vacancies or defects on different planes.<sup>41,42</sup> The synthesis of  $\text{CeO}_2$  with different morphologies or exposed facets is influenced by the preparation conditions employed. For instance, polycrystalline  $\text{CeO}_2$  can be prepared by the thermal decomposition of cerium nitrate,<sup>43</sup> which mainly terminates with the (111) surface while octahedra, rods, and cubes morphologies can be synthesized by hydrothermal synthesis.<sup>44</sup> The octahedra, sheets, spheres and spindle-like morphologies also expose the (111) plane while cubes expose the (100) plane and the rods consist of the (110) and (100) surfaces.<sup>28,45–47</sup> From Fig. 3 and 4, the flower-like structure of the  $\text{CeO}_2$  catalyst was formed by numerous nanosheets, indicating that the observed flower-like  $\text{CeO}_2$  exposed the (111) surface plane. Z. Zongcheng *et al.*<sup>40</sup> used HR-TEM to analyze the crystal facets of the flower-like  $\text{CeO}_2$  and found lattice spacings corresponding to the (111) planes of  $\text{CeO}_2$  which were consistent with Q. Wang *et al.*<sup>48</sup>

**3.1.3. Porosity analysis.** The  $\text{N}_2$  adsorption–desorption isotherm as shown in Fig. 5 was used to characterize the porous properties of the synthesized flower-like  $\text{CeO}_2$  catalyst. The synthesized catalyst exhibited a type-IV isotherm with a hysteresis loop, attributed to capillary condensation in the mesopores, indicating the presence of a mesoporous structure in the flower-like  $\text{CeO}_2$  catalyst, which was consistent with the SEM data. The appeared hysteresis loop related to the mesoporous with tapered plate pore type with four opening sides (Fig. 5, inset). The flower-like  $\text{CeO}_2$  catalyst had a specific BET surface area of  $26.06\text{ m}^2\text{ g}^{-1}$ . The total pore volume and average pore diameter were  $0.122\text{ m}^3\text{ g}^{-1}$  and  $93.61\text{ \AA}$ , respectively.

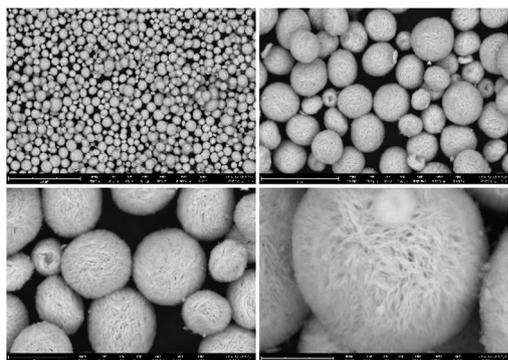


Fig. 3 SEM image of the synthesized flower-like  $\text{CeO}_2$  catalyst (before reaction).

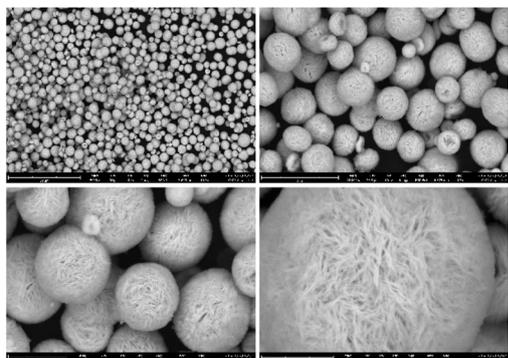


Fig. 4 SEM image of the spent flower-like  $\text{CeO}_2$  catalyst (after reaction).

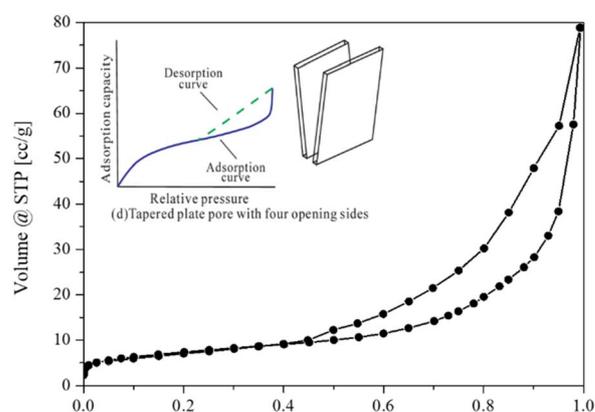


Fig. 5  $\text{N}_2$  adsorption–desorption isotherm of the flower-like  $\text{CeO}_2$  catalyst and isotherm for tapered plate pore with four opening sides (inset).<sup>49</sup>



**3.1.4. Possible mechanism of the flower-like CeO<sub>2</sub> microspheres formation.** The flower-like CeO<sub>2</sub> microspheres were produced by calcining a flower-like Ce(OH)CO<sub>3</sub> microspheres twice.<sup>50,51</sup> The initial step was calcination at 600 °C for 12 h under inert gas to decompose Ce(OH)CO<sub>3</sub>, followed by calcination at 400 °C for 10 h under air environment to oxidize Ce<sub>2</sub>O<sub>3</sub> into CeO<sub>2</sub> structure, as described in eqn (2) and (3). The flower-like Ce(OH)CO<sub>3</sub> microspheres were synthesized *via* acrylamide graft copolymerization on glucose, with cerium(III) nitrate hexahydrate as a Cerium source. Under basic conditions, cerium salts precipitated to generate cerium hydroxide [Ce(H<sub>2</sub>O)<sub>x</sub>(OH)<sub>y</sub>], and acrylamide could be graft-copolymerized onto glucose to form graft-copolymers.<sup>50</sup> Nevertheless, in the hydrothermal process, these graft copolymers were easily decomposed, yielding many various N-containing organic molecules. As a result, a plausible formation mechanism is proposed: the created N-containing organic molecules interacted with [Ce(H<sub>2</sub>O)<sub>x</sub>(OH)<sub>y</sub>] particles to form Ce(OH)CO<sub>3</sub>-N-R hybrids, which subsequently self-assemble to form the flower-like Ce(OH)CO<sub>3</sub> microspheres.<sup>51</sup>



**3.1.5. Basicity, acidity and oxygen vacancies analysis.** It has been reported that acid and basic sites presented on the surface of the catalysts have been identified as active sites for DMC synthesis from CH<sub>3</sub>OH and CO<sub>2</sub>. The CO<sub>2</sub>-TPD profile as shown in Fig. 6 showed the interaction between adsorbate (gaseous CO<sub>2</sub>) and absorbent (flower-like CeO<sub>2</sub>) in the temperature ranges of 25–700 °C. At 100–200 °C, which is the optimum temperature for DMC synthesis, CO<sub>2</sub> was desorbed at low temperature and considered as weak basic site. This had a significant effect on DMC production. The calculated amount of basic site on the flower-like CeO<sub>2</sub> catalyst surface was 300 μmol g<sup>-1</sup>. The NH<sub>3</sub>-TPD profile of the flower-like CeO<sub>2</sub> catalyst in the temperature ranges of 25–700 °C is shown in Fig. 7. The desorbed NH<sub>3</sub> from the surface of the flower-like CeO<sub>2</sub> catalyst occurred in a wide peak ranging from 40 to 700 °C, corresponding to the weak, medium and strong acid site, with a total

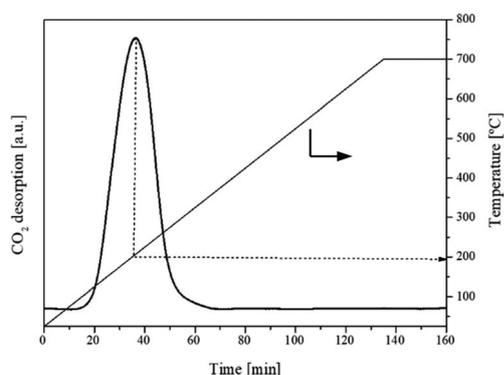


Fig. 6 CO<sub>2</sub>-TPD profile of the flower-like CeO<sub>2</sub> catalyst.

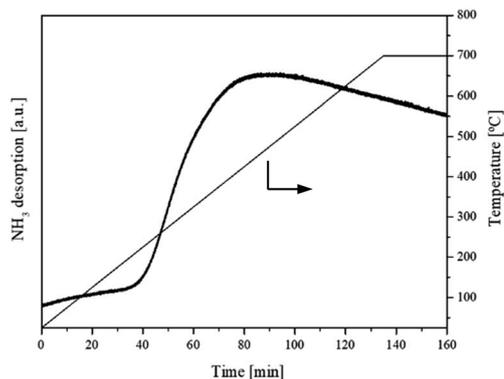


Fig. 7 NH<sub>3</sub>-TPD profile of the flower-like CeO<sub>2</sub> catalyst.

NH<sub>3</sub> quantity of 80 μmol g<sup>-1</sup>. As a result, it can be confirmed that CeO<sub>2</sub> catalysts have both basic and acidic sites, allowing them to behave as bifunctional acid–base catalysts. The CeO<sub>2</sub> catalyst surface consists of three types of surface-active sites that coexist on its surface, including (i) oxygen vacancies as redox sites, (ii) coordinately unsaturated Ce cations near the oxygen vacancies as Lewis's acid sites, and (iii) nearby oxygen ions as Lewis's basic sites.<sup>27</sup> The presence of oxygen vacancies within the flower-like CeO<sub>2</sub> catalyst was investigated using the O<sub>2</sub>-TPD technique, as shown in Fig. 8. The O<sub>2</sub>-TPD profile of the catalyst exhibited two desorption peaks at 400–600 °C and 600–800 °C. The lower temperature peak (400–600 °C) is attributed to desorbed oxygen that adsorbed on oxygen vacancies, which readily desorb from the surface. The higher temperature peak (600–800 °C) could be assigned to oxygen within the bulk lattice of the catalyst.<sup>52</sup>

### 3.2. Catalytic behavior

As described earlier, 2-cyanopyridine (2-CP), dissolved in CH<sub>3</sub>OH at a 2-CP:CH<sub>3</sub>OH molar ratio of 1:2, was utilized as a dehydrator to remove water from the reaction system and push the reaction equilibrium towards DMC synthesis. The hydration of 2-cyanopyridine gives 2-picolinamide (2-PA) product (eqn (4)), which is also catalyzed by the CeO<sub>2</sub> catalyst. The produced 2-picolinamide can be readily desorbed from the catalyst surface, easily removed from the reaction mixture and

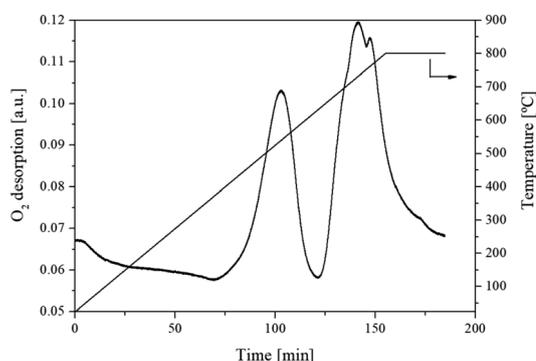
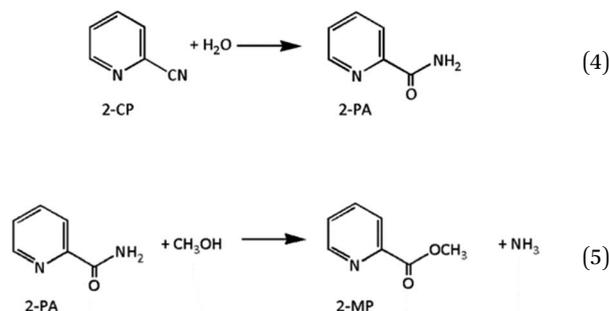


Fig. 8 O<sub>2</sub>-TPD profile of the flower-like CeO<sub>2</sub> catalyst.

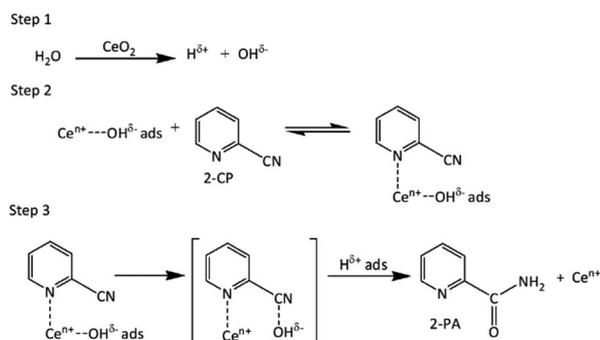


dehydrated to obtain 2-cyanopyridine. However, the generated 2-picolinamide can interact with  $\text{CH}_3\text{OH}$  to produce methyl picolinate (2-MP) and ammonia by-products, as shown in eqn (5).<sup>14</sup>

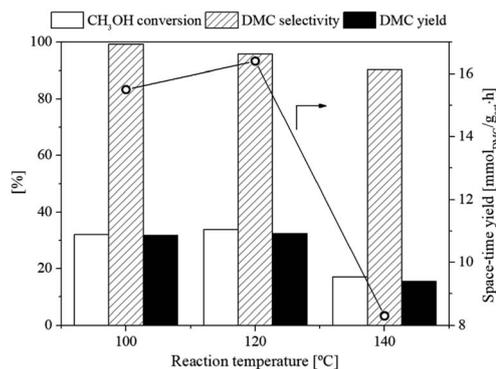


Tamura *et al.*<sup>13</sup> proposed a possible reaction mechanism of 2-cyanopyridine hydration by  $\text{CeO}_2$  catalyst which can be also used to described in this work as shown in Scheme 1. The hydration occurs by dissociating  $\text{H}_2\text{O}$  to produce  $\text{H}^{\delta+}$  and  $\text{OH}^{\delta-}$  ions on the surface of  $\text{CeO}_2$  catalyst (step 1). In step 2, nitrile and  $\text{Ce}-\text{OH}^{\delta-}$  are in equilibrium with the nitrile -  $\text{Ce}-\text{OH}^{\delta-}$  adsorption complex. In step 3,  $\text{OH}^{\delta-}$  and  $\text{H}^{\delta+}$  on the  $\text{CeO}_2$  surface were attached to the cyano group of 2-CP, forming an amide (2-PA). In addition, the effects of reaction parameters such as temperature (3.2.1), feed ratio ( $\text{CH}_3\text{OH}:\text{CO}_2$ ) (3.2.2), catalyst amount (3.2.3) and pressure (3.3.4) on the DMC production over the flower-like  $\text{CeO}_2$  catalyst were investigated to optimize the reaction conditions.

**3.2.1. Effect of reaction temperature.** The influence of reaction temperature on the catalytic activity of the flower-like  $\text{CeO}_2$  catalyst was investigated at various temperatures ranging from 100 to 140 °C (Fig. 9) while the reaction pressure, molar feed ratio and catalyst weight were 10 bar, 1 : 1 and 1.0 g, respectively. The results showed that the  $\text{CH}_3\text{OH}$  conversion, space-time yield of DMC and DMC yield increased from 32.0 to 33.9%, 15.5 to 16.4  $\text{mmol g}^{-1} \text{h}$  and 31.8 to 32.4%, respectively, when the reaction temperature increased from 100 to 120 °C. This increase in DMC yield and  $\text{CH}_3\text{OH}$  conversion means that reactant molecules have higher kinetic energy at higher temperatures, allowing more molecules to pass the activation



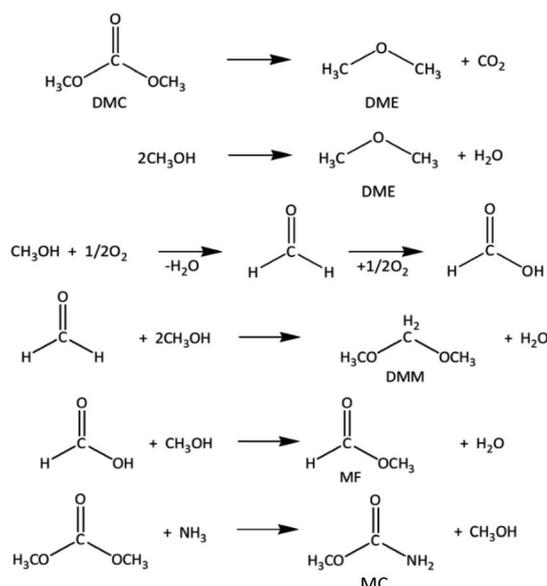
**Scheme 1** Proposed reaction mechanism for the 2-cyanopyridine (2-CP) hydrolysis to form 2-picolinamide (2-PA) over the  $\text{CeO}_2$  catalyst during the DMC synthesis from  $\text{CH}_3\text{OH}$  and  $\text{CO}_2$ .<sup>13</sup>



**Fig. 9** Effect of reaction temperature on  $\text{CH}_3\text{OH}$  conversion, DMC selectivity, and DMC yield of the flower-like  $\text{CeO}_2$  catalyst using 2-CP as dehydrating agent (10 bar,  $\text{CH}_3\text{OH}:\text{CO}_2 = 1:1$ ).

energy barrier and produce the products. On the contrary, the  $\text{CH}_3\text{OH}$  conversion, DMC selectivity, and DMC yield declined dramatically with further increasing operating temperature. This was primarily due to the decrease in  $\text{CO}_2$  adsorption on the catalyst surface, as well as the increased rates of the side reactions to produce by-products such as dimethyl ether (DME) from DMC decomposition and  $\text{CH}_3\text{OH}$  dehydration, dimethoxymethane (DMM) from the reaction of  $\text{CH}_3\text{OH}$  with formaldehyde (HCHO), and methyl formate (MF) from the interaction between  $\text{CH}_3\text{OH}$  and formic acid (HCOOH) at high reaction temperatures<sup>14,53,54</sup> as shown in Scheme 2. Moreover, methyl carbamate (MC) was also formed at such high temperatures from the reaction between ammonia (from reaction (5)) and DMC.<sup>14</sup> The optimal temperature for this reaction is therefore reported at 120 °C.

**3.2.2. Effect of feed ( $\text{CH}_3\text{OH}:\text{CO}_2$ ) ratio.** The impact of the initial molar ratio ( $\text{CH}_3\text{OH}:\text{CO}_2$ ) on the  $\text{CH}_3\text{OH}$  conversion,



**Scheme 2** Reaction of possible by-products formation during the direct synthesis of DMC from  $\text{CH}_3\text{OH}$  and  $\text{CO}_2$  at high temperatures.<sup>14,53,54</sup>



DMC selectivity, and DMC yield with different feed ratios of 1 : 2, 1 : 1, and 2 : 1 was investigated. The operating temperature of 120 °C, catalyst weight of 1.0 g and pressure of 10 bar were used for this experiment. The result shown in Fig. 10 revealed that the feed ratio of 1 : 1 provided the best performance with the CH<sub>3</sub>OH conversion, DMC selectivity, and DMC yield of 33.9, 95.8, and 32.4%, respectively. The molar ratios of 2 : 1 and 1 : 2 showed relatively lower performances possibly due to the too-high (ratio of 2 : 1) and too-low (ratio of 1 : 2) of CH<sub>3</sub>OH concentrations reduced the reaction rate because the active sites were covered with CH<sub>3</sub>OH (ratio of 2 : 1) or CO<sub>2</sub> (ratio of 1 : 2) and thus could not be accessed by another reactant in those active sites. Furthermore, the by-product DME was also produced from the CH<sub>3</sub>OH dehydration reaction at the molar ratio of 2 : 1.

**3.2.3. Effect of catalyst weight.** The influence of catalyst amount on the catalytic performance of the flower-like CeO<sub>2</sub> catalyst for the DMC synthesis from CH<sub>3</sub>OH and CO<sub>2</sub> was investigated using catalyst amounts varied at 0.5 and 1.0 g. The other experimental conditions including an operating temperature of 120 °C, a pressure of 10 bar, and a feed ratio (CH<sub>3</sub>OH : CO<sub>2</sub>) of 1 : 1 were chosen for this study. The results of this investigation are displayed in Fig. 11. The CH<sub>3</sub>OH conversion, DMC selectivity, and DMC yield increased from 19.3 to 33.9%, 94.6 to 95.8%, and 18.2 to 32.4%, respectively, when the catalyst amount increased from 0.5 to 1.0 g. The observed enhancement can be described as an increase in the concentration of active sites with increasing catalyst dosage. The impact of the catalyst weight of more than 1.0 g was not examined in this work; however, excess catalyst amounts have been reported to be inefficient because of excessive active centers or mass transfer limitations that promoted the side reaction formation, resulting in significantly reduced DMC yield.<sup>55,56</sup>

**3.2.4. Effect of reaction pressure.** The influence of operating pressure on the catalytic performance of the flower-like CeO<sub>2</sub> catalyst for the DMC production from CH<sub>3</sub>OH and CO<sub>2</sub> was investigated. Fig. 12 illustrates the CH<sub>3</sub>OH conversion, DMC selectivity, DMC yield and space-time yield at different reaction pressures (10, 20 and 30 bar), with the reaction temperature of 120 °C, molar feed ratio of 1 : 1 and the catalyst amount of 1.0 g. The results revealed that increasing operating

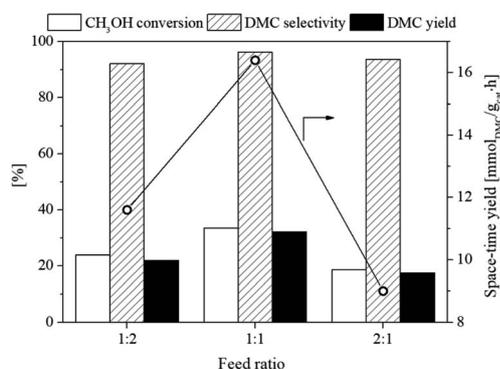


Fig. 10 Effect of feed ratio (CH<sub>3</sub>OH : CO<sub>2</sub>) on CH<sub>3</sub>OH conversion, DMC selectivity, and DMC yield of the flower-like CeO<sub>2</sub> catalyst using 2-CP as dehydrating agent (10 bar, 120 °C).

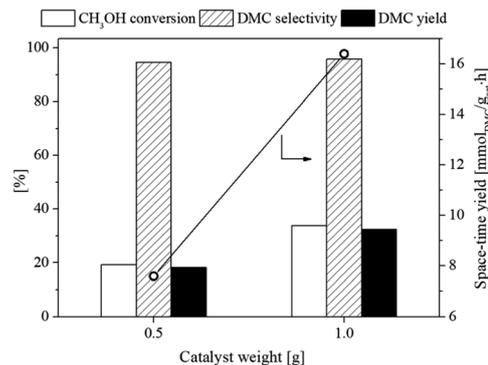


Fig. 11 Effect of catalyst contents on CH<sub>3</sub>OH conversion, DMC selectivity, and DMC yield of the flower-like CeO<sub>2</sub> catalyst using 2-CP as dehydrating agent (10 bar, 120 °C, CH<sub>3</sub>OH : CO<sub>2</sub> = 1 : 1).

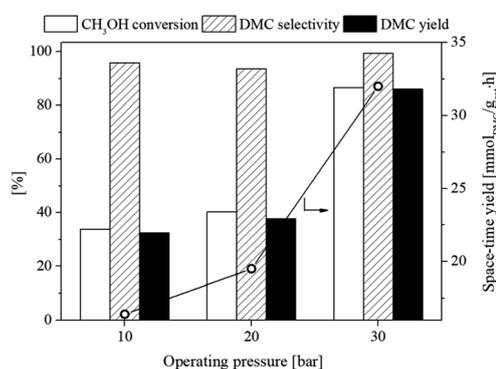


Fig. 12 Effect of operating pressure on CH<sub>3</sub>OH conversion, DMC selectivity, and DMC yield of the flower-like CeO<sub>2</sub> catalyst using 2-CP as dehydrating agent (120 °C, CH<sub>3</sub>OH : CO<sub>2</sub> = 1 : 1).

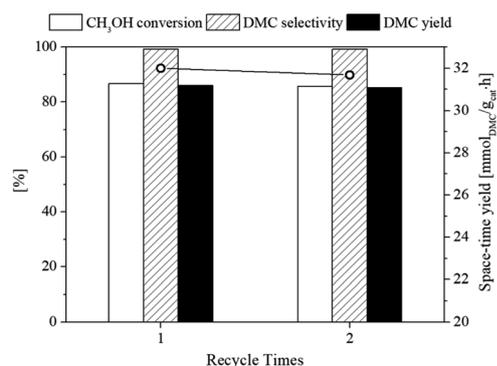
pressures from 10 to 30 bar improved CH<sub>3</sub>OH conversion, space-time yield of DMC and DMC yield from 33.9 to 86.6%, 16.4 to 32.0 mmol g<sup>-1</sup> h and 32.4 to 86.0%, respectively. This was mainly due to the ability of CH<sub>3</sub>OH and CO<sub>2</sub> molecules to fully adsorb on the active sites of the catalyst resulted in a shift in chemical equilibrium towards DMC production at high operating pressures.

The results exhibited that the reaction temperature of 120 °C, catalyst weight of 1.0 g, CH<sub>3</sub>OH : CO<sub>2</sub> ratio of 1 : 1 and operating pressure of 30 bar were the optimum conditions for the DMC synthesis using the flower-like CeO<sub>2</sub> catalyst, providing the highest CH<sub>3</sub>OH conversion, DMC selectivity, and DMC yield of 86.6%, 99.3%, and 86.0%, respectively. Many works from recent years reported CeO<sub>2</sub> with different morphologies as one of the best catalysts for DMC synthesis, as shown in Table 1.

**3.2.5. Recycling study.** The reusability of the catalyst is important for their practical application. As presented in Fig. 13, the fresh flower-like CeO<sub>2</sub> catalyst for the DMC synthesis from CO<sub>2</sub> and methanol with CH<sub>3</sub>OH : CO<sub>2</sub> molar ratio of 1 : 1 using 2-CP as dehydrating agent at temperature of 120 °C and pressure 30 bar displays CH<sub>3</sub>OH conversion, space-time yield of DMC and DMC yield of 86.6%, 32.0 mmol g<sup>-1</sup> h and 86.0%, respectively. Then, the used flower-like CeO<sub>2</sub> catalyst was calcined at 400 °C to remove impurity products and reactants

**Table 1** Comparison of catalytic activity of the present catalyst (flower-like CeO<sub>2</sub>) with the other reported catalysts in the direct DMC synthesis from CO<sub>2</sub> and CH<sub>3</sub>OH

Catalyst	Reaction conditions	DMC yield rate (mmol <sub>DMC</sub> g <sub>cat.</sub> <sup>-1</sup> h <sup>-1</sup> )	Ref.
Commercial CeO <sub>2</sub>	Fixed-bed reactor, 0.3 g catalyst, 2-CP: CH <sub>3</sub> OH = 1 : 2, CH <sub>3</sub> OH : CO <sub>2</sub> = 1 : 2.5, 30 bar CO <sub>2</sub> , 120 °C	11.1	12
CeO <sub>2</sub> (calcination of Ce(OH) <sub>4</sub> )	Autoclave reactor, 0.1 g catalyst, CH <sub>3</sub> OH : CO <sub>2</sub> = 192 : 200 mmol, 130 °C	1.8	58
Commercial CeO <sub>2</sub>	Autoclave reactor, 0.34 g catalyst, CH <sub>3</sub> OH : 2-CP = 2 : 1, 5 MPa CO <sub>2</sub> , 120 °C	23.3	16
Spherical-CeO <sub>2</sub>	Autoclave reactor, 0.17 g catalyst, 2-CP : CH <sub>3</sub> OH = 1 : 1, 5 MPa CO <sub>2</sub> , 110 °C	31.0	59
CeO <sub>2</sub> (calcination of Ce(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O)	Autoclave reactor, 1.0 g catalyst, 742 mmol	CeO <sub>2</sub> : 2.27	60
Nanorod-CeO <sub>2</sub>	CH <sub>3</sub> OH, 16 MPa CO <sub>2</sub> , 250 °C	Nanorod: 2.88	
Flower-CeO <sub>2</sub>		Flower: 3.11	
Commercial CeO <sub>2</sub>	Autoclave reactor, 0.34 g catalyst, CH <sub>3</sub> OH: 2-CP = 1 : 5, 5 MPa CO <sub>2</sub> , 120 °C	12.1	14
Spindle-CeO <sub>2</sub>	Autoclave reactor, 0.1 g catalyst, 2-CP :	Irregular: 79.0	57
Cube-CeO <sub>2</sub>	CH <sub>3</sub> OH = 1 : 2, 5 MPa CO <sub>2</sub> , 150 °C	Cube: 78.5	
Rods-CeO <sub>2</sub>		Rod: 95.5	
Irregular-CeO <sub>2</sub>		Spindle: 152.5	
Amorphous-CeO <sub>2</sub>	Autoclave reactor, 0.1 g catalyst, 15 mL	Amorphous: 116.9	15
Octahedron-CeO <sub>2</sub>	CH <sub>3</sub> OH, 50 mmol 2-CP, 5 MPa CO <sub>2</sub> , 140 °C	Rod: 126.2	
Rod-CeO <sub>2</sub>		Octahedron: 21.8	
Cube-CeO <sub>2</sub>		Cube: 3.2	
Octahedrons-CeO <sub>2</sub>	Autoclave reactor, 0.1 g catalyst, 15 mL	Octahedron: 0.35 × 10 <sup>-3</sup>	28
Rods-CeO <sub>2</sub>	CH <sub>3</sub> OH, 5 MPa CO <sub>2</sub> , 140 °C	Rod: 2.6 × 10 <sup>-3</sup>	
Cubes-CeO <sub>2</sub>		Cube: 1.7 × 10 <sup>-3</sup>	
Spindle-CeO <sub>2</sub>		Spindle: 4.0 × 10 <sup>-3</sup>	
Flower-CeO <sub>2</sub>	Packed-bed reactor, 1.0 g catalyst, 2-CP : CH <sub>3</sub> OH : CO <sub>2</sub> = 1 : 2 : 1, 30 bar CO <sub>2</sub> , 120 °C	32.0	This work

**Fig. 13** Recycling of the flower-like CeO<sub>2</sub> catalyst for the DMC synthesis using 2-CP as dehydrating agent (30 bar, 120 °C, CH<sub>3</sub>OH : CO<sub>2</sub> = 1 : 1).

on the catalyst surface before being put into the next reaction. The results showed that a significant loss of catalytic activity was not observed after two runs, indicating that the catalyst could be easily recovered.

### 3.3. The relationship between the catalyst properties (crystal facet and acid–base sites) and the reaction mechanism

It has been reported that the morphology, crystal facet, and acid–base sites of the catalyst were a crucial factor in achieving

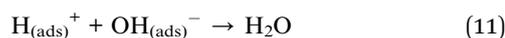
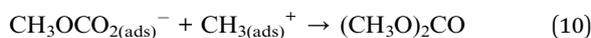
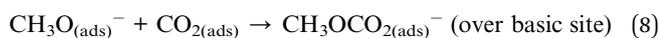
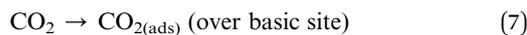
the highest catalytic activity for DMC synthesis. S. Wang *et al.*<sup>28</sup> and P. Unnikrishnan *et al.*<sup>57</sup> investigated the direct synthesis of DMC from methanol and CO<sub>2</sub> using various CeO<sub>2</sub> morphology catalysts. They observed that high DMC yields and methanol conversion were induced by the synergism between the exposed (111) plane, defect sites and acid–basic sites, which was controlled by CeO<sub>2</sub> shape. As mentioned in the morphology analysis section, the flower-like morphology of the synthesized CeO<sub>2</sub> catalyst indicated the (111).

Crystal facet, which was the most active plane for the DMC production from CO<sub>2</sub> and CH<sub>3</sub>OH. J. Jiang *et al.*<sup>61</sup> performed a comprehensive study on the catalytic mechanisms of the DMC synthesis from CO<sub>2</sub> and methanol on CeO<sub>2</sub> (111) and (110) surfaces. They found that the reaction pathways computed on the (111) and (110) surfaces exhibited high catalytic activity toward DMC synthesis. However, different rate-limiting steps were observed. The rate-determining step of the (111) surface was the regeneration of oxygen vacancy *via* the dehydration process, whereas that of the (110) surface was the esterification of monomethyl carbonate (reaction (10)). The rate-limiting step on the (111) facet can be accelerated more easily than the (110) plane by using a dehydrating agent to remove water from the active site (oxygen vacancy) of the catalyst. These results suggested that the (111) facet was more reactive for DMC synthesis than the (110) facet in the presence of a desiccant. S. Wang *et al.*<sup>28</sup> reported that spindle-like CeO<sub>2</sub> produced the highest



DMC yields, followed by nanorods and nanocubes morphologies, because the spindle-like with (111) facet contained a large specific surface area, amounts of acid–basic sites and number of defect sites than nanocubes (100) and nanorods [(111) and (100)], indicating that the crystal facet of (111) plane was the active factor for the DMC formation.

It is well-known that the acidity, basicity, and redox characteristics of CeO<sub>2</sub> catalyst promote the CH<sub>3</sub>OH activation and the CO<sub>2</sub> adsorption on its surface. The CO<sub>2</sub>-TPD and NH<sub>3</sub>-TPD results in Fig. 6 and 7 revealed that the synthesized flower-like CeO<sub>2</sub> displayed both basicity and acidity properties with amounts of 300 μmol g<sup>-1</sup> and 80 μmol g<sup>-1</sup>, respectively. It has been reported that both basic and acid sites activated CH<sub>3</sub>OH molecules, however only basic sites activated CO<sub>2</sub> molecules, which are critical steps in the direct synthesis of DMC from CH<sub>3</sub>OH and CO<sub>2</sub>. The reaction mechanism of the DMC synthesis from CH<sub>3</sub>OH and CO<sub>2</sub> is shown in the reaction (6)–(11).<sup>62</sup>



In the presence of the CeO<sub>2</sub> catalyst, CO<sub>2</sub> and CH<sub>3</sub>OH molecules are firstly adsorbed on its surface. CO<sub>2</sub> is adsorbed on the surface at the basic site without dissociation (CO<sub>2(ads)</sub>) while CH<sub>3</sub>OH is adsorbed and activated to form methoxide ions (CH<sub>3</sub>O<sub>(ads)</sub><sup>-</sup>) and hydrogen ions (H<sub>(ads)</sub><sup>+</sup>) at the basic site and to form methyl ions (CH<sub>3(ads)</sub><sup>+</sup>) and hydroxide ions (OH<sub>(ads)</sub><sup>-</sup>) at the acid site on the CeO<sub>2</sub> surface. The methoxide species interacts with adsorbed CO<sub>2</sub> to produce methoxycarbonyl ions (CH<sub>3</sub>OCO<sub>2(ads)</sub><sup>-</sup>). Finally, the methoxycarbonyl ions react with methyl ions to generate dimethyl carbonate ((CH<sub>3</sub>O)<sub>2</sub>CO, DMC), while hydrogen ions react with hydroxide ions to form water (H<sub>2</sub>O). Dimethyl carbonate and water products are desorbed from the catalyst surface, regenerating the active site. The produced H<sub>2</sub>O can be eliminated from the reaction mixture by adding a dehydrating agent (2-cyanopyridine, 2-CP) led to an increase in the DMC yield. According to the reaction mechanism, the acidity and basicity properties of the catalyst, as well as the appearance of the (111) crystal facet in the presence of a dehydrating agent, had a significant impact on the catalytic efficiency of the DMC synthesis from CO<sub>2</sub> and CH<sub>3</sub>OH.

## 4. Conclusions

In this study, the flower-like CeO<sub>2</sub> catalyst was successfully synthesized using graft copolymerization reaction between acrylamide and glucose under hydrothermal conditions. XRD and SEM results confirmed the complete formation of the

flower-like CeO<sub>2</sub> catalyst with the crystal facet of (111) plane. When compared with the spent flower-like CeO<sub>2</sub> after DCM synthesis reaction, there were no changes in the structure, morphology and particle size which indicated that the flower-like CeO<sub>2</sub> catalyst was resistant to the reaction test at reaction temperature of 120 °C and reaction pressure of 10 bar. Furthermore, the N<sub>2</sub> adsorption–desorption technique revealed a mesoporous structure in the flower-like CeO<sub>2</sub> catalyst, which was consistent with the SEM data, with a specific BET surface area of 26.06 m<sup>2</sup> g<sup>-1</sup>. The CO<sub>2</sub>-TPD and NH<sub>3</sub>-TPD results revealed that the synthesized flower-like CeO<sub>2</sub> displayed both basicity and acidity properties with amounts of 300 μmol g<sup>-1</sup> and 80 μmol g<sup>-1</sup>, respectively. The catalytic activity of the flower-like CeO<sub>2</sub> catalyst in producing DMC from CH<sub>3</sub>OH and CO<sub>2</sub> was investigated using continuous packed-bed reactor. 2-Cyanopyridine (2-CP) was utilized as a dehydrator to remove water from the reaction system and push the reaction equilibrium toward the DMC synthesis side. The effect of reaction parameters such as temperature, feed ratio, catalyst amount and pressure on DMC production over the flower-like CeO<sub>2</sub> catalyst was investigated. The results exhibited that the reaction temperature of 120 °C, catalyst weight of 1.0 g, CH<sub>3</sub>OH : CO<sub>2</sub> ratio of 1 : 1 and operating pressure of 30 bar were the optimum conditions for the DMC synthesis, providing the highest CH<sub>3</sub>OH conversion, DMC selectivity, and DMC yield of 86.6%, 99.3%, and 86.0%, respectively. The outstanding catalytic activity of the synthesized flower-like CeO<sub>2</sub> catalyst for the DMC synthesis was attributed to the synergistic effect of the exposed (111) crystal plane, basicity, and acidity properties on its surface. Therefore, the catalyst could be designed to possess a suitable shape, with a mainly exposed active (111) plane, a high surface area, and a large amount of defect, basic, and acid sites, to improve catalytic performance for DMC synthesis from CO<sub>2</sub> and CH<sub>3</sub>OH.

## Data availability

The data that support the findings of this study are available on request.

## Conflicts of interest

The authors confirm that there is no conflict of interest.

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