

Article

Enhancing DMC Production from CO₂: Tuning Oxygen Vacancies and In Situ Water Removal

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Abstract: The direct synthesis of dimethyl carbonate (DMC) from methanol and CO₂ presents an attractive route to turn abundant CO₂ into value-added chemicals. However, insufficient DMC yields arise due to the inert nature of CO₂ and the limitations of reaction equilibrium. Oxygen vacancies are known to facilitate CO₂ activation and improve catalytic performance. In this work, we have demonstrated that tuning oxygen vacancies in catalysts and implementing in situ water removal can enable highly efficient DMC production from CO₂. Ce_xZr_yO₂ nanorods with abundant oxygen vacancies were synthesized via a hydrothermal method. In liquid-phase DMC synthesis, the Ce₁₀Zr₁O₂ nanorods exhibited a 1.7- and 1.4-times higher DMC yield compared to CeO₂ nanoparticles and undoped CeO₂ nanorods, respectively. Zr doping yielded a CeZr solid solution with increased oxygen vacancies, promoting CO₂ adsorption and activation. In addition, adding 2-cyanopyridine as an organic dehydrating agent achieved an outstanding 87% methanol conversion and >99% DMC selectivity by shifting the reaction equilibrium to the desired product. Moreover, mixing CeO₂ nanoparticles with hydrophobic fumed SiO₂ in gas-phase DMC synthesis led to a doubling of DMC yield. This significant increase was attributed to the faster diffusion of water molecules away from the catalyst surface, facilitated by the hydrophobic SiO₂. This study illustrates an effective dual strategy of enhancing oxygen vacancies and implementing in situ water removal to boost DMC production from CO₂. The strategy can also be applied to other reactions impacted by water accumulation.

Keywords: DMC synthesis; CeZr solid solution; CeO₂ nanorods; oxygen vacancies; dehydrating agent



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1. Introduction

Carbon dioxide (CO₂) is the primary greenhouse gas driving climate change from human activities, and an effective climate change mitigation approach involves carbon capture and utilization (CCU) methodologies that transform CO₂ into value-added fuels or chemicals [1,2]. A promising CCU strategy is to convert CO₂ into organic carbonates, like dimethyl carbonate (DMC), which capitalizes on CO₂'s nontoxicity, availability, and low cost [3]. DMC has garnered substantial interest as a versatile chemical intermediate and fuel additive with an environmentally benign profile. In fuel blends, DMC can function as an oxygenate to improve combustion efficiency, substituting for the toxic gasoline additive methyl tert-butyl ether (MTBE) [4]. Additionally, DMC readily biodegrades in the atmosphere without producing toxic or corrosive byproducts, overcoming critical concerns around traditional alkylating agents like dimethyl sulfate and phosgene used for chemical syntheses [5]. These properties have motivated the exploration of DMC as a “green” chemical for a wide range of applications from nontoxic solvents in pharmaceuticals and coatings to electrolytes for lithium metal batteries [6–9]. With surging global demands for cleaner fuels and sustainable chemicals, as well as increasingly stringent environmental

regulations, DMC exhibits strong potential to replace conventional hazardous reagents across a breadth of technology sectors moving forward.

Traditional DMC synthesis procedures involve multiple steps, relying on the inherent hazards of a methanol and phosgene reaction scheme, while also necessitating carbon monoxide as an intermediate compound [10]. In contrast, direct DMC production from CO₂ and methanol in a single-step reaction offers a promising alternative. This route replaces phosgene with the comparatively benign and abundant CO₂ reactant, mitigating issues related to safety, environmental impact, and process complexity that burden conventional DMC processes. Additionally, the development of effective processes to facilitate this phosgene-free DMC production route would concurrently provide a valuable CO₂ utilization pathway to make constructive use of this major greenhouse gas emission, aligning with critical climate change mitigation strategies. While the direct synthesis of DMC from CO₂ and methanol is promising, there remain technological obstacles to overcome insufficient DMC yield and selectivity. This reaction ($2\text{CH}_3\text{OH} + \text{CO}_2 \rightleftharpoons (\text{CH}_3\text{O})_2\text{CO} + \text{H}_2\text{O}$, $\Delta G = +26 \text{ kJ/mol}$) is not spontaneous due to the thermodynamic limitations and the inert property of CO₂ [11]. An efficient catalyst will be the key to this reaction. Consequently, designing and developing highly efficient catalysts to overcome the barrier of reaction energy is vitally important. Various catalysts, including CeO₂ [12–14], ZrO₂ [15], Cu–Ni alloys [16–18], and CeO₂–ZrO₂ [10,14] composites, have been investigated for direct DMC synthesis in order to enhance catalytic performance. Among these candidates, CeO₂-based catalysts have demonstrated the highest activity among common oxide catalysts. For instance, Ma et al. compared the performance of CeO₂ and ZrO₂ in DMC synthesis and found that CeO₂ (5.34 mmol_{DMC}/g_{cat}) exhibited superior activity in DMC synthesis compared to ZrO₂ (0.21 mmol_{DMC}/g_{cat}) [15]. Through comprehensive characterization, the authors proposed that the different performances arose from divergent reaction mechanisms on each surface. Monodentate methyl carbonate reacted with methanol on ZrO₂, while on CeO₂, methanol reacted with adsorbed CO₂ to form an activated carbomethoxy intermediate. These active sites for CO₂ adsorption are key factors influencing the efficacy of CO₂ activation on catalyst surfaces. The high activity of CeO₂ catalysts may derive from the abundant oxygen vacancies in CeO₂, which can facilitate CO₂ adsorption and activation.

Prior reports have identified oxygen vacancies as active sites that promote CO₂ conversion reactions including methanation [19–22]. Additionally, studies have shown oxygen vacancies serve as Lewis acid centers, enabling CO₂ hydrogenation reactions [23]. Lewis acid sites are often associated with oxygen vacancies and are commonly found in metal oxides, such as In₂O₃ and CeO₂ [24]. Lewis acid sites are coordinatively unsaturated metal cations, and adjacent unobstructed lattice oxygen serves as a Lewis basic site. This is a typical situation on the (110) surface of CeO₂. Proposed mechanisms indicate that oxygen vacancies stabilize adsorbed intermediates and final products through interactions with the oxygen atoms of activated CO₂ molecules. The abundance and accessibility of surface oxygen vacancies are thereby directly correlated with CO₂ activation capacity and subsequent conversion performance of catalytic materials [23].

Moreover, creating additional vacancies in CeO₂ through doping with metal oxides like ZrO₂, Y₂O₃, and TiO₂ can enhance catalytic performance. For example, Li et al. doped 5% Y₂O₃ into CeO₂, increasing DMC yield to 15 mmol_{DMC}/g_{cat}, 1.4 times increase over undoped CeO₂ [25]. In situ spectroscopic analysis revealed that the Y-doped CeO₂ effectively suppressed undesired triple-bonded methoxy species formation while promoting beneficial bidentate carbonate and bridged methoxy intermediates, thereby improving catalytic activity. In another work, Liu et al. synthesized a series of CaO-promoted CeO₂ catalysts. Among the formulations tested, Ca_{1.5}Ce (the sample containing 1.5 wt.% of Ca) exhibited the maximum DMC yield of 2.47 mmol_{DMC}/g_{cat}, attributed to concurrent modulation of acid–base properties and augmentation of surface oxygen vacancies [26]. This dual-pronged promotion of active site generation and reactant activation pathways demonstrated the potential of tailored doping strategies to optimize DMC synthesis over CeO₂-based catalysts.

Tailoring CeO₂ morphology can also improve DMC synthesis by tuning oxygen vacancies. CeO₂ nanorods exhibit higher oxygen vacancy densities compared to cubic and octahedral morphologies, attributed to the exposure to reactive (110) and (100) facets that concentrate defects [27]. Capitalizing on this, Liu et al. prepared Zr-doped CeO₂ nanorods and observed 1.3- and 6.7-times higher DMC production activity compared to pure CeO₂ and ZrO₂ nanoparticles, respectively [23]. The enhancement directly correlated with surface oxygen vacancy levels, which was confirmed through characterization. Similar morphological effects were noted for other dopants, with Ti- [28] and Fe-doped [29] CeO₂ nanorods also conferring large catalytic activity increases for DMC synthesis compared to undoped counterparts. These findings highlighted the dual importance of tailored morphology and dopant selection in optimizing the oxygen vacancy landscape of CeO₂ for enhanced CO₂ conversion capability.

In addition to insufficient catalytic activity, equilibrium limitations hinder direct DMC synthesis from methanol and CO₂ [30–32]. Removing the concurrently produced H₂O during the synthesis can shift the equilibrium towards DMC based on Le Chatelier's principle [3]. However, conventional dehydration agents like molecular sieves are inefficient at high reaction temperatures, while others like P₂O₅ are too reactive for safe handling. Alternatively, catalytic hydration of organic compounds provides an alternative approach to eliminating water. This hydration process involves substantial free energy changes, transforming the organic reactants into more easily handled products while removing water. For instance, Tomishige et al. examined various dehydrating agents for direct methanol/CO₂ to DMC conversion over CeO₂ catalysts and they found 2-cyanopyridine (2-CP) gave the highest activity [33]. Importantly, 2-picolinamide can be recycled to 2-CP via catalytic dehydration. Recently, the same group reported mechanistic insights showing a consistent reaction pathway with and without the dehydrating agent [34]. They also demonstrated that the dehydration strategy worked for various alcohol substrates, not just methanol. Moreover, DMC synthesis has also been explored in the gas phase, which facilitates the desorption of the generated water from the catalyst surface. A comparative study by Aouissi et al. demonstrated higher DMC yield in gas-phase reactions due to the absence of water accumulation on the active sites [35]. Chen et al. later showed that bismuth-doped CeO₂ monoliths enabled effective water removal during gas-phase DMC synthesis, attributed to the porous support structure allowing vapor-phase diffusion. At optimal bismuth-doping levels, they obtained a methanol conversion of 20% for DMC synthesis [36].

The current work focused on achieving enhanced performance for the conversion of CO₂ to DMC, promoted by optimized CeO₂-based catalysts. A key research aim was to systematically elucidate how to fine-tune the abundance of associated oxygen vacancies by doping ZrO₂ into CeO₂ catalysts. Additionally, this study investigated the interaction of combining 2-CP with CeO₂-based catalysts, specifically regarding the dehydrating capabilities of 2-CP in mitigating water inhibition phenomena. A further experimental aim involved transitioning the CO₂ reaction system to the gas phase, hypothesizing that facilitating rapid water vapor removal would substantially improve equilibrium conversion toward DMC. This study provides insight into structure–performance relationships for optimized CO₂ conversion.

2. Materials and Methods

2.1. Catalyst Synthesis

CeO₂ nanoparticles (CeO₂ NPs) were fabricated by calcination of Ce(NO₃)₃·6H₂O at 600 °C, utilizing a heating ramp rate of 5 °C/min in a muffle furnace for 5 h under static air. CeO₂ nanorods (CeO₂ NRs) along with CeZr solid solution samples were synthesized, employing a hydrothermal technique [23]. Specially, ZrO(NO₃)₂·xH₂O and Ce(NO₃)₃·6H₂O of varying molar proportions were dissolved in 10 mL of deionized water with vigorous agitation until fully dissolved. Concurrently, 28.0 g of NaOH was dissolved in 70 mL of deionized water. Subsequently, the two solutions were combined and sustained under stir-

ring for 30 min. The resulting mixed slurry was transferred into a 100 mL Teflon autoclave and maintained at 100 °C for 24 h. After cooling the autoclave to ambient temperature, the precipitate was separated via centrifugation and washed alternately with deionized water and ethanol five times. The obtained product was dehydrated at 80 °C overnight, followed by calcination at 600 °C for 5 h in a muffle furnace to acquire the final products. The synthesized catalysts were denoted as $\text{Ce}_x\text{Zr}_y\text{O}_2$, where x and y signify the molar proportions of Ce and Zr, respectively. For illustration, $\text{Ce}_{10}\text{Zr}_1\text{O}_2$ represents a 10:1 molar ratio of Ce to Zr in the catalyst.

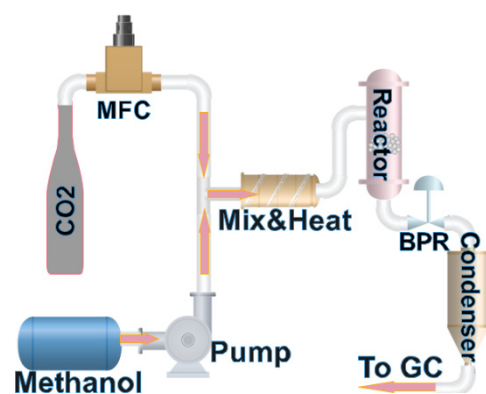
2.2. Catalyst Characterizations

Determination of the specific surface area was conducted utilizing a Quantachrome Nova 4000e surface analyzer (Quantachrome, Boynton Beach, FL, USA) through nitrogen adsorption/desorption at liquid nitrogen temperature (−196 °C). The sample was degassed at 250 °C for 4 h before analysis. Estimation of the surface areas of the catalysts was performed via the Brunauer–Emmett–Teller (BET) technique. Powder X-ray diffraction (XRD) was implemented using a PANalytical X'Pert Pro multifunctional diffractometer (Malvern PANalytical Ltd., Almelo, The Netherlands) equipped with $\text{CuK}\alpha$ radiation at a wavelength of 1.5406 Å and scanning rate of 3°/min, operated at 40 kV and 40 mA. The interplanar spacing values were calculated using the Bragg's equation from the (1 1 1) plane of the samples. Observation of the morphologies of the obtained catalysts was carried out by transmission electron microscopy (TEM) using a FEI Tecnai F20 instrument (FEI, Eindhoven, The Netherlands). Raman spectra were acquired with a Horiba Jobin Yvon Aramis 8902 (Horiba, Kyoto, Japan) utilizing a 632.8 nm HeNe 17 mW laser, 15 min collection time, and 5 repetitions for averaging. The integrated peak areas for the Raman peaks at 460 cm^{-1} and 600 cm^{-1} were determined using LabSpec 5 (Version 1-004) data analysis software. The peak fitting tool enables the deconvolution of overlapping features for accurate evaluation of individual Raman peak intensities and quantitative determination of relative mode abundances. Hydrogen temperature-programmed reduction (H_2 -TPR) was executed utilizing a Micrometrics AutoChemTM II 2920 (Micrometrics, Norcross, GA, USA) equipped with a thermal conductivity detector (TCD) with temperature ramping from 100 °C to 900 °C at 10 °C/min and a gas stream containing 10% H_2 /90% Ar at a flow of 50 mL/min passed through the powder sample (~100 mg) packed in a U-shaped quartz tube. NH_3 temperature-programmed desorption (NH_3 -TPD) was performed utilizing the same instrument. Prior to analysis, 100 mg of the sample underwent in situ pretreatment with 50 mL/min helium at 200 °C for 1 h. After cooling to 50 °C, NH_3 adsorption occurred by 50 mL/min exposure for 1 h duration. Subsequently, the system was purged with 50 mL/min helium for 2 h to eliminate residual gases. For TPD analysis, the temperature was ramped from 50 to 600 °C at 10 °C/min, with the effluent gas composition continuously monitored by TCD. By employing the calibration relating peak areas to acid site quantities, the amount of acidity was able to be determined from the experimentally measured peak areas. Temperature-programmed desorption of CO_2 (CO_2 -TPD) was conducted in a quartz tube reactor coupled to a QMS200 mass spectrometer (Stanford Research System, Sunnyvale, CA, USA) for gas analysis. Prior to analysis, 100 mg of catalyst sample underwent in situ pretreatment at 200 °C for 1 h duration under flowing helium (50 mL/min). The system was subsequently cooled to 50 °C, followed by CO_2 adsorption for 1 h with 50 mL/min CO_2 exposure. Residual gases were then removed by a 2 h 50 mL/min helium purge. For TPD, the temperature was ramped from 50 °C to 600 °C at 10 °C/min, with the effluent gas composition continuously monitoring $m/z = 44$ to track the evolution of desorbed CO_2 . Deconvolution of TPD profiles was performed utilizing the peak analyzer tool in Origin 2021 (Version 9.8) software. The resulting multi-peak model fits for the TPD profiles' displayed R-squared values exceeding 0.97.

2.3. Catalytic Performance Evaluation

The synthesis of DMC in the liquid phase was performed in an autoclave reactor with continuous agitation of the slurry. In a typical experiment, 0.1 g of the synthesized

catalyst was loaded into an autoclave reactor, along with 12 g of methanol as the reactant. Prior to the reaction, the reactor was purged multiple times with CO₂ to displace the air, followed by pressurization to 3 MPa with CO₂ at ambient temperature. The reaction temperature and pressure within the reactor were elevated to 140 °C to conduct the reaction for 3 h, after which the system was cooled down to room temperature. To quantify the yield of DMC, n-butanol was incorporated as an internal standard into the mixture, and analysis of the products was carried out by gas chromatography (GC). It was observed that DMC was the sole product generated in the catalytic reactions in this study, with no other byproducts detected, excluding a small quantity of water. Subsequently, we examined the influence of water elimination by adding various amounts of 2-CP as a dehydrating agent. The gas-phase DMC synthesis was conducted in a fixed-bed reactor. CO₂ flow was regulated by a mass flow controller (MFC), while methanol was delivered via a high-pressure Teledyne Pharma 500X pump (Teledyne ISCO, Lincoln, NE, USA). Prior to reactor entry, the methanol/CO₂ feed mixture underwent preheating to 180 °C. The reaction pressure was modulated using a back pressure regulator (BPR). Post-reactor products and unreacted methanol were condensed for collection and subsequent analysis by GC. A simplified schematic diagram of the experimental gas-phase DMC synthesis setup is provided in Scheme 1.



Scheme 1. Gas-phase synthesis of DMC from methanol and CO₂. The arrows indicate the flow directions.

In this work, the DMC yield was defined as follows:

$$\text{DMC yield} = n_{\text{DMC}}(\text{mmol}) / m_{\text{cat}}(\text{g}),$$

where n stands for the mole numbers of DMC and m stands for the mass of the catalysts.

3. Results and Discussion

3.1. Material Characterizations

XRD was used to investigate the crystal structure of the prepared catalysts. CeO₂ has a fluorite structure in which Ce⁴⁺ is surrounded by eight equivalent O^{2−} ions forming the corner of a cube, with each O^{2−} coordinated to four Ce⁴⁺ ions [37,38]. The XRD patterns in Figure 1 exhibit characteristic CeO₂ diffraction peaks at 2θ values of 28.5°, 33.1°, 47.5°, 56.3°, and 69.4°, corresponding to the (111), (200), (220), (311), and (400) crystallographic planes, respectively [23]. Lattice parameters for the CeO₂ and Ce₁₀Zr₁O₂ nanorods, summarized in Table 1, were 5.40 Å and 5.36 Å, respectively. The comparative contraction in lattice parameters accompanying Zr incorporation was attributable to the replacement of Ce⁴⁺ ions (ionic radius 0.97 Å) with the smaller Zr⁴⁺ ions (ionic radius 0.84 Å) on CeO₂ lattice sites. Consequently, the Zr⁴⁺ substitution gave rise to solid solution formation and an associated reduction in the (220) interplanar spacing from 3.125 Å to 3.118 Å. The smaller Zr⁴⁺, in comparison with Ce⁴⁺, prefers a 7-fold coordination, in contrast to the 8-fold coordination of the fluorite cation, resulting in a driving force to form oxygen vacancies associated with structural relaxation through a reduction of the smaller Ce⁴⁺ to the bigger Ce³⁺ [39]. The introduction of the oxygen vacancies and the accompanying Ce³⁺ ions led

to a distortion of local symmetry. This caused the change in the Ce–O bond length (lattice distortion) and the overall lattice parameter [38]. The shrinking of the lattice lowered the energy barrier for Ce^{4+} reduction and thus enhanced the overall reducibility of CeO_2 [10,40]. These structural characterization results confirmed the successful isovalent substitution of Zr^{4+} into the CeO_2 host lattice. For the phase composition, the CeZr solid solution phase diagram has been extensively studied by Yashima et al. [41,42]. Based on their research, a cubic, fluorite-type phase c is formed (Fm3m) for Ce mole percentages above 85% under 1000 °C, while a monoclinic phase (group P21/c) is present for Ce mole percentages below 10%. In our case, a cubic phase can be expected since the mole percentage of Ce is greater than 85%, which is also consistent with the XRD results.

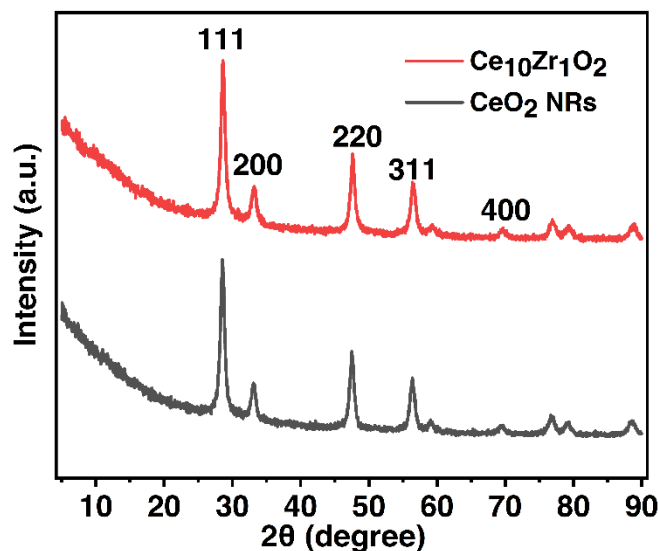


Figure 1. XRD patterns of CeO_2 NRs and $\text{Ce}_{10}\text{Zr}_1\text{O}_2$ NRs.

Table 1. Interplanar spacing, lattice parameters, and specific surface area of the catalysts.

Sample IDs	2θ	Interplanar Spacing (Å)	Lattice Parameter	S_{BET} (m^2/g)
CeO_2 NRs	28.73	3.105	5.405	71
$\text{Ce}_{10}\text{Zr}_1\text{O}_2$ NRs	28.61	3.117	5.362	102

Raman spectroscopy was adopted to study oxygen vacancies in CeO_2 -based catalysts. The Raman spectra of CeO_2 NPs, CeO_2 NRs, and $\text{Ce}_{10}\text{Zr}_1\text{O}_2$ NRs in Figure 2 exhibit two predominant peaks. The peak centered at 460 cm^{-1} corresponds to the F2g symmetric stretching mode of the Ce–O bond, corresponding well to the cubic phase [37,43]. Additionally, a broad peak at approximately 600 cm^{-1} (Figure 2 insets) can be assigned to the defect-induced D band, attributed to oxygen vacancies generated by the presence of Ce^{3+} ions [23,26]. The relative intensity ratio between these peaks, I_{600}/I_{460} , provides an indication of comparative oxygen vacancies. For instance, Cao et al. used I_{600}/I_{460} values to indicate the concentration of oxygen vacancies for different morphologies of $\text{MnO}_x/\text{ZrO}_2\text{--CeO}_2$. They found that the nanorod shape exhibited the highest oxygen vacancies [44]. Similarly, Wei et al. used I_{600}/I_{460} values to indicate the amount of oxygen vacancies in different shapes of CeO_2 catalysts. They found the amount of oxygen vacancies followed the trend: nanorod > nano-octa > nanocube > nanoparticle [45]. In our case, as shown in Figure 3, the I_{600}/I_{460} ratio was substantially lower for the CeO_2 NPs compared to that of the CeO_2 NRs. Moreover, the incorporation of Zr into the CeO_2 NRs further increased the I_{600}/I_{460} ratio, suggesting an elevation in oxygen vacancies.

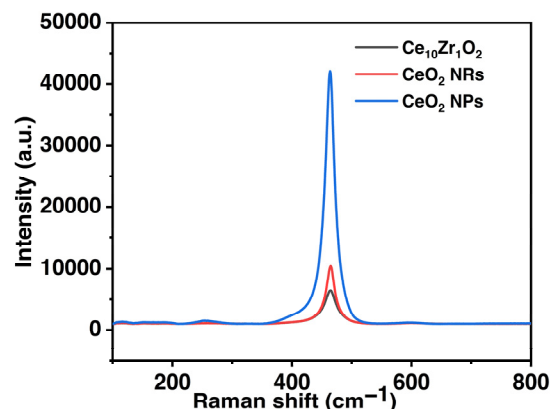


Figure 2. Raman spectra of CeO₂ NPs, CeO₂ NRs, and Ce₁₀Zr₁O₂ NRs. Inset is the zoom in of the 550–650 cm^{−1} range.

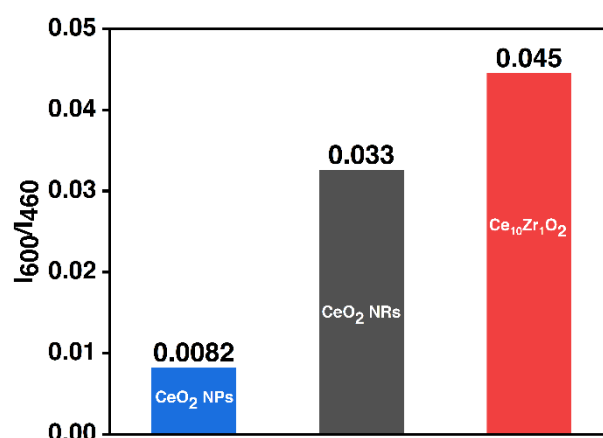


Figure 3. The I_{600}/I_{460} values of CeO₂ NPs, CeO₂ NRs, and Ce₁₀Zr₁O₂ NRs.

H₂-TPR was used to investigate the reducibility and surface species of the samples, with the resulting profiles presented in Figure 4. All tested samples exhibited two reduction peaks at around 500 °C (low temperature) and 800 °C (high temperature), respectively. Reduction temperature is influenced by the metal–oxygen bond energy. Thus, it is widely acknowledged that the low-temperature region is assigned to oxygen vacancies, while the high-temperature region is ascribed to interior lattice oxygen in bulk CeO₂ [46,47]. Generally, oxygen vacancies are more easily reduced, providing increased opportunities to serve as active sites. Therefore, the low-temperature region of the TPR profiles (below 600 °C) warrants additional attention. In this low-temperature region, CeO₂ NRs are more easily reduced than CeO₂ NPs, with reduction beginning at 282 °C and 320 °C, respectively. This reduction temperature shift indicated that CeO₂ NRs possessed increased reducible oxygen vacancies relative to CeO₂ NPs, aligning with the previous literature report [48]. With the addition of Zr to CeO₂ NRs, the initiation of reduction of Ce₁₀Zr₁O₂ NRs occurred at 248 °C, approximately 70 °C lower than that for CeO₂ NPs. Furthermore, the reduction peak temperature for Ce₁₀Zr₁O₂ NRs was around 30 °C lower than that for CeO₂ NPs. Ce₁₀Zr₁O₂ NRs were more easily reduced, indicating a higher level of oxygen vacancies, thus aligning with the Raman spectroscopic results. The lower reduction temperature indicated that Ce₁₀Zr₁O₂ NRs were more easily involved in the catalytic reaction at a lower temperature and hence exhibited better catalytic activity [49]. For the reduction of bulk CeO₂, the reduction peak temperature was lowered from 814 °C for CeO₂ NPs to 781 °C for CeO₂ NRs, which indicates that the reductivity of CeO₂ nanomaterials highly depended on the morphology [50,51]. However, when Zr was doped to CeO₂ NRs, the reduction peak temperature increased from 781 °C to 795 °C, which is inconsistent with previous reports [52,53]. Previous research showed that the addition of ZrO₂ to CeO₂ to form a solid solution could enhance the reducibility of the Ce⁴⁺ ion in the bulk material [53]. The

underlying reason for the higher reduction peak temperature observed after Zr doping remains unclear currently. One possible explanation is that the bulk reduction is nearly independent of the surface reduction for nonoriented CeO₂ nanomaterials [54]. Further study is required to elucidate the contradictory behaviors of bulk versus surface reduction profiles.

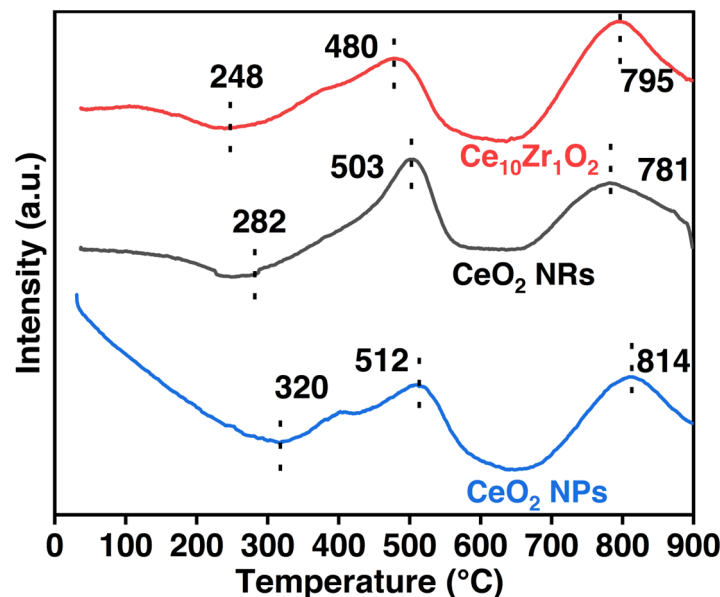


Figure 4. H₂-TPR profiles of CeO₂ NPs, CeO₂ NRs, and Ce₁₀Zr₁O₂ NRs.

CO₂-TPD and NH₃-TPD techniques were utilized to further characterize the surface acid–base properties of CeO₂ NPs, CeO₂ NRs, and Ce₁₀Zr₁O₂ NRs. The CO₂-TPD profiles of CeO₂ NPs, CeO₂ NRs, and Ce₁₀Zr₁O₂ NRs are displayed in Figure 5a. Based on the CO₂ desorption temperature range, the basic sites could be classified as weak (50–200 °C), moderate (200–400 °C), and strong (400–600 °C). The CeO₂ NPs and CeO₂ NRs exhibited only weak basic sites. In contrast, an additional asymmetric peak spanning 200–600 °C was observed for the Ce₁₀Zr₁O₂ NRs. As shown in Figure 5c, this asymmetric peak could be deconvoluted into two Gaussian peaks, representing the presence of moderate and strong basic sites. Given that the reaction was conducted at 140 °C, the focus was on the density of low-temperature weak basic sites. Thus, the area under the curve from 50 to 200 °C was integrated and normalized to a value of 1 for the CeO₂ NPs as a baseline for comparison. The relative density of basic sites was determined to be 1.81 and 2.40 for CeO₂ NRs and Ce₁₀Zr₁O₂ NRs, respectively. Consequently, the Ce₁₀Zr₁O₂ NRs exhibited the highest basic site density, aligning with its superior DMC yield, compared to CeO₂ NRs and CeO₂ NPs.

The NH₃-TPD profiles of CeO₂ NPs, CeO₂ NRs, and Ce₁₀Zr₁O₂ NRs are provided in Figure 5b, and the deconvolution of the NH₃-TPD profile of Ce₁₀Zr₁O₂ NRs is shown in Figure 5d. Similarly, the analysis concentrated on the low-temperature acid sites. The amount of NH₃ desorbed was 0.044, 0.076, and 0.15 mmol/g for the CeO₂ NPs, CeO₂ NRs, and Ce₁₀Zr₁O₂ NRs, respectively. Thus, the Ce₁₀Zr₁O₂ NRs possessed the greatest acid site density, attributed to the oxygen vacancies functioning as Lewis acid sites. Acid–basic site pairs present on the surfaces of ZrO₂, CeO₂, and CeO₂-ZrO₂ catalysts have been identified as active sites for DMC synthesis [55–57]. Therefore, the marked enhancement in both acid and basic sites explains the superior DMC yield achieved by the Ce₁₀Zr₁O₂ NRs.

TEM was utilized to investigate the morphologies of the synthesized catalysts. TEM analysis of CeO₂ and Ce₁₀Zr₁O₂ NRs is presented in Figure 6. The CeO₂ NRs exhibited average dimensions of ~11 nm diameter by ~140 nm length, while the Ce₁₀Zr₁O₂ NRs displayed reduced mean dimensions of ~8 nm diameter by ~50 nm length. High-resolution TEM imaging elucidated the crystallographic characteristics of both NR samples, with measured lattice spacings of 0.31 nm and 0.27 nm indexing to the (111) and (200) planes

of the fluorite CeO_2 structure (JCPDS 34-0394), respectively [23]. Energy dispersive X-ray spectroscopy (EDS) elemental mapping of the $\text{Ce}_{10}\text{Zr}_1\text{O}_2$ NRs demonstrated the uniform spatial distribution of the incorporated Zr dopant atoms.

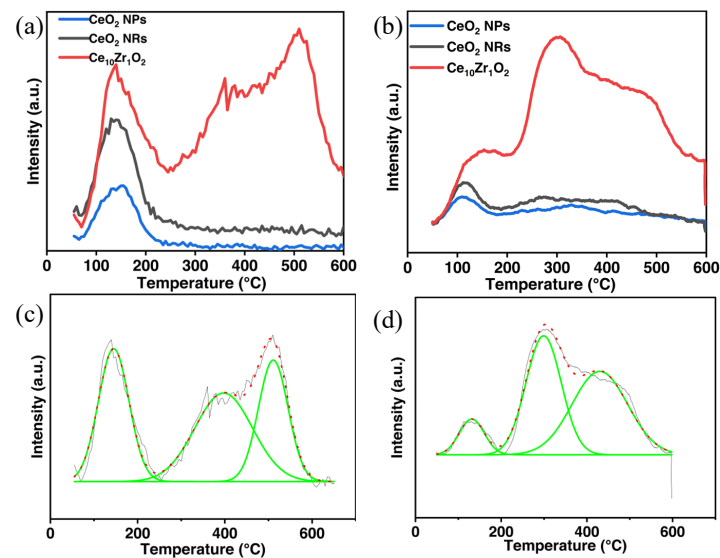


Figure 5. (a) CO_2 -TPD and (b) NH_3 -TPD profiles of CeO_2 NPs, CeO_2 NRs, and $\text{Ce}_{10}\text{Zr}_1\text{O}_2$ NRs, (c) deconvolution of CO_2 -TPD profile of $\text{Ce}_{10}\text{Zr}_1\text{O}_2$ NRs, and (d) deconvolution of NH_3 -TPD profile of $\text{Ce}_{10}\text{Zr}_1\text{O}_2$ NRs. The dots represent the original data points, the green line illustrates the peaks that have been fitted, and the cumulative peak fit is depicted by the grey line.

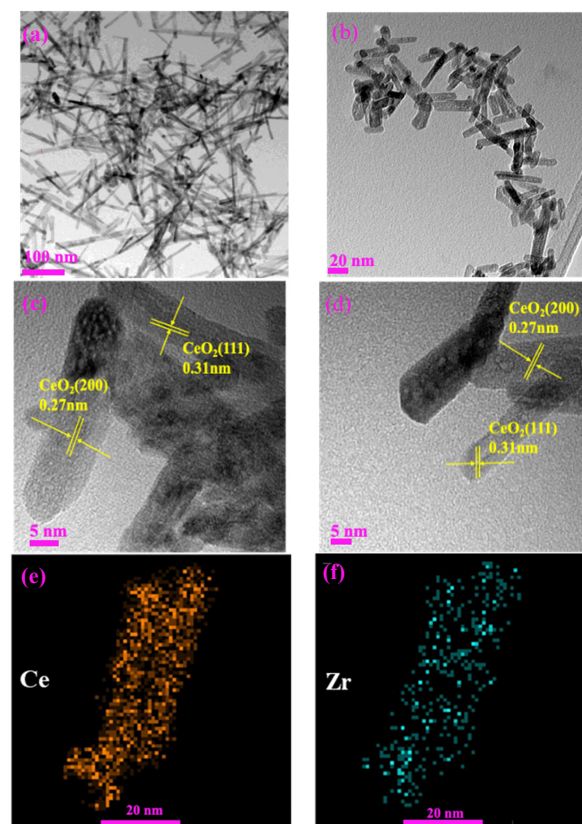


Figure 6. TEM images of (a) CeO_2 and (b) $\text{Ce}_{10}\text{Zr}_1\text{O}_2$ NRs, HRTEM images of (c) CeO_2 and (d) $\text{Ce}_{10}\text{Zr}_1\text{O}_2$ NRs, and EDS mapping of $\text{Ce}_{10}\text{Zr}_1\text{O}_2$ NRs: (e) Ce and (f) Zr.

3.2. Catalytic Performance in Liquid Phase

Figure 7 shows the catalytic performance of Ce-based catalysts. CeO₂ NRs showed a higher activity in DMC synthesis than CeO₂ NPs. With the addition of Zr to CeO₂ NRs, the DMC yield reached a maximum value of 11.19 mmol_{DMC}/g_{cat} for the catalyst with a Zr/Ce molar ratio at 1/10 and then decreased with further increasing of the Zr/Ce molar ratio. The activity of Ce₁₀Zr₁O₂ NRs was 1.7 and 1.4 times higher than that of CeO₂ NPs and pure CeO₂ NRs, respectively. This enhancement stemmed from increased oxygen vacancies caused by the formation of CeZr solid solution. The activity of the catalysts followed the following order: Ce₁₀Zr₁O₂ > Ce₁₀Zr_{0.5}O₂ > CeO₂ NRs > Ce₁₀Zr₂O₂ > CeO₂ NPs. Meanwhile, the methanol conversion trended similarly with a maximum of 0.6% achieved over the Ce₁₀Zr₁O₂ catalyst. It is well known that the nature of active sites for CO₂ adsorption strongly influences the efficiency of CO₂ activation. Surface oxygen vacancies can promote CO₂ adsorption and activation on catalyst surfaces. In recent years, substantial research efforts have focused on developing robust catalysts with tunable oxygen vacancies to improve CO₂ conversion efficiency [22,58,59]. Controlling the number and distribution of oxygen vacancies enables precise regulation of the adsorption and activation of reactants during CO₂ conversion. For instance, Wang et al. fabricated a large number of oxygen vacancies by reorganization and/or oxygen etching. Theoretical calculations pointed out that introducing oxygen vacancies significantly decreased the adsorption energy of the CeO₂ catalyst, increasing the DMC yield significantly [60]. Consistent with the above literature findings, CeO₂ NRs prepared in this study exhibited higher oxygen vacancies than NPs, as evidenced by Raman spectroscopy. Doping Zr into CeO₂ further increased the oxygen vacancies in CeO₂ NRs. In addition, increasing the initial pressure from 3 MPa to 5 MPa was found to boost both DMC yield and methanol conversion. For example, the DMC yield for Ce₁₀Zr₁O₂ increased from 11.19 to 12.98 mmol_{DMC}/g_{cat}, while the DMC yield for CeO₂ NRs increased from 8.22 to 9.52 mmol_{DMC}/g_{cat}. The improved performance under elevated pressure may originate from enhanced CO₂ solubility and mass transfer effects.

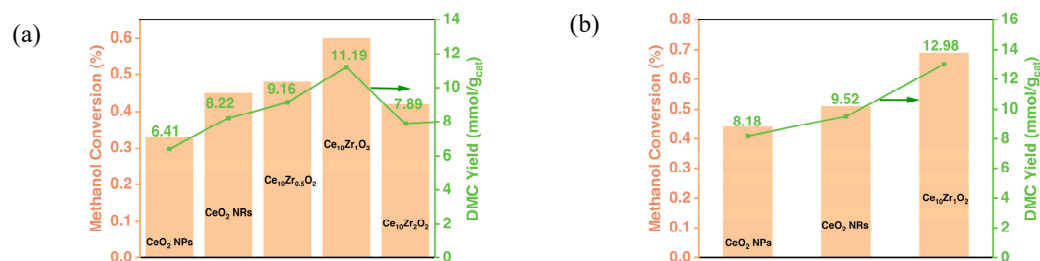


Figure 7. Catalytic performance of (a) CeO₂ NPs and Ce_xZr_yO₂ NRs under 3 MPa and 140 °C, and (b) CeO₂ NPs, CeO₂ NRs, and Ce₁₀Zr₁O₂ NRs under 5 MPa and 140 °C.

Considering the complex feed composition in practical reaction environments, the performance of CeO₂ NPs pretreated in relevant atmospheres of H₂, CO₂, and CO was investigated. Specifically, CeO₂ NPs underwent pretreatment with air, H₂, H₂/CO₂ mixtures, and H₂/CO mixtures prior to evaluation. As can be seen in Figure 8, the DMC yield was enhanced to 8.39 mmol_{DMC}/g_{cat} when CeO₂ NPs were treated under a H₂/CO₂ (H₂:CO₂ = 3:1) mixture at 180 °C for 2 h at 2 MPa. However, DMC yield decreased to 6.97 mmol_{DMC}/g_{cat} when the gas was switched to a H₂/CO (H₂:CO = 2:1) mixture at 180 °C for 2 h at 2 MPa. Even worse, DMC yield decreased to 3.83 mmol_{DMC}/g_{cat} when the treatment was extended to 24 h using a H₂/CO (H₂:CO = 2:1) mixture at 180 °C at 2 MPa. Based on the above results, CO may diminish the catalytic performance of CeO₂ NPs. The inferior performance obtained upon H₂/CO treatment potentially correlates with the observed alteration in CeO₂ nanoparticle color. Upon exposure to H₂ or H₂/CO₂, the pale-yellow coloration of the CeO₂ nanoparticles immediately reverted to yellow after air exposure. However, treatment with H₂/CO for 2 h altered the appearance to gray. Subsequent air exposure slowly restored the yellow hue over 3 days. More prolonged 24 h H₂/CO exposure further changed the color to black, as depicted in Figure 9. Following

this reduction in a harsher environment, air exposure gradually recovered the original pale-yellow coloration, but 7 days were required for this change. The slower color change after harsh H_2/CO reduction suggests increased disruption and damage to the CeO_2 crystal lattice, necessitating longer periods under ambient conditions to reoxidize and regain structural integrity. Prior reports have investigated the color change in CeO_2 accompanying changes in the oxidation state and extent of reduction. Sohn et al. demonstrated that H_2 treatment induced a transformation of CeO_2 from pale yellow to various shades of grey and black, dependent on the degree of reduction [61]. While pure CeO_2 appears pale yellow due to $Ce(IV)-O(II)$ charge-transfer interactions [62], nonstoichiometric CeO_2 exhibits blue or near-black coloration [63]. Liu et al. attributed alterations in color and crystal surface morphology to arising from oxygen vacancy and Ce^{3+} species formation [64]. Notably, the fluorite CeO_2 lattice exhibited considerable tolerance to reduction without phase change, as evidenced under H_2 and H_2/CO_2 exposures. However, more intense reductive environments, as exemplified by H_2/CO treatment, may overwhelm this tolerance threshold and induce framework collapse. The degraded catalytic performance correlates with likely structural disruption, as indicated by the stark darkening of coloration. While moderate reduction preserves crystallinity, excessive reducing conditions provoke framework damage, underlying inferior activity.

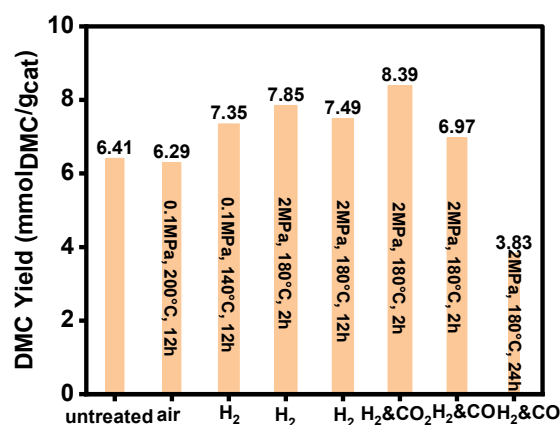


Figure 8. Catalytic performance of CeO_2 NPs treated by different gases.



Figure 9. Colors of CeO_2 NPs (a) treated for 2 h in the gas of H_2/CO (2 MPa, 180 °C) and (b) subsequently exposed to air for 3 days, (c) treated for 24 h in the gas of H_2/CO (2 MPa, 180 °C) and (d) subsequently exposed to air for 1 day.

The $Ce_{10}Zr_1O_2$ catalyst still exhibited low methanol conversion and DMC yield, constrained by thermodynamic equilibrium. Even under favorable high-pressure conditions

(ca. 40 MPa), the maximum achievable DMC yield is restricted to ~1%, as dictated by equilibrium constraints. However, according to Le Chatelier's principle, in situ water removal serves to shift the equilibrium toward enhanced product formation. Here, 2-CP was implemented as a dehydrating agent to actively eliminate water, considerably improving methanol conversion and DMC yields. As shown in Table 2, the addition of 1.04 g 2-CP increased methanol conversion over the CeO₂ NPs from 0.33% to 5.54%. Further elevating the catalyst and 2-CP levels to 0.3 g and 10.4 g, respectively, boosted methanol conversion to 72.52%, while raising DMC yields to 239 mmol_{DMC}/g_{cat}. Upon additional reaction pressure increase to 5 MPa, 87% methanol conversion, and 289.67 mmol_{DMC}/g_{cat} were attained. Therefore, removing water during the reaction is an effective approach to shift the equilibrium towards DMC formation. Various dehydrating agent strategies have been investigated for water removal. For example, inorganic agents like zeolites or MgSO₄ have been tested but exhibited insufficient dehydration capabilities at the required reaction temperatures [31]. Alternatively, catalytic hydration of organic compounds is a promising water removal technique. Different organic dehydrating agents, including acetonitrile and 2,2-dimethoxypropane, have been examined for DMC synthesis. Among these, 2-CP demonstrated the highest DMC yield because 2-CP possesses excellent hydration ability, and the resulting 2-picolinamide product readily desorbs from the catalyst surface [34]. In this work, implementing 2-CP as the dehydrating agent boosted DMC yields 45-fold, confirming the remarkable effectiveness of 2-CP for water removal and the consequent enhancement of catalyst activity. Despite its effectiveness at improving yields, 2-CP presents flammability and toxicity considerations for safe handling, as well as economic feasibility issues given current pricing exceeds that of DMC itself. Furthermore, the miscibility of 2-CP in the liquid-phase reaction medium would incur additional costs for catalyst separation and product purification. A more sustainable, scalable, and economical dehydration approach is still needed. Discussion of these practical limitations alongside the performance benefits provides a balanced perspective when evaluating the potential for enhancing DMC production through coupled dehydration strategies.

Table 2. Reaction conditions, methanol conversion, and DMC yield using 2-CP as the dehydrating agent in liquid-phase synthesis.

2-CP (g)	CeO ₂ NPs (g)	Pressure (MPa)	DMC Yield (mmol _{DMC} /g _{cat})	Methanol Conversion (%)
0	0.1	3	6.41	0.33
1.04	0.1	3	27.67	5.54
10.4	0.3	3	239.00	72.52
10.4	0.3	5	289.67	87.00

3.3. Catalytic Performance in Gas Phase

Additionally, we investigate the performance of DMC synthesis in the gas phase (Table 3). In liquid-phase DMC synthesis, the water generated as a byproduct accumulates in the system, inhibiting the progression of the reaction toward the desired DMC product. However, in the gas-phase DMC synthesis, the produced water may desorb from the catalyst surface, which facilitates the continuous formation of the desired DMC product by minimizing the accumulation of water on the active catalytic sites. Consequently, we hypothesize that both methanol conversion and DMC yield will be enhanced in the gas-phase reaction system compared to the case in the liquid phase. To test this, we examined DMC synthesis using CeO₂ NPs mixed with either molecular sieve 3A or fumed silicon dioxide (SiO₂) under gas-phase conditions. Molecular sieve 3A can absorb water, while fumed SiO₂ presents a hydrophobic interface. For comparison, DMC yields were normalized per gram of CeO₂ NP catalyst. Gas-phase DMC yield over CeO₂ NPs alone increased to 8.63 mmol_{DMC}/g_{cat} from 6.41 mmol_{DMC}/g_{cat} in liquid-phase runs, although gas-phase pressure was lower. However, combining CeO₂ NPs with molecular sieve 3A decreased yield to 7.12 mmol_{DMC}/g_{cat}, potentially due to reduced molecular sieve efficacy at higher temperatures [65]. Incorporating fumed SiO₂ boosted yield to 17.8 mmol_{DMC}/g_{cat}, double

that for CeO₂ NPs alone. While fumed SiO₂ does not directly absorb water, it appears to enable rapid diffusion of water from catalyst surfaces. Analogous enhancements have been reported previously [32,66]. Our gas-phase DMC synthesis results align with previous findings showing higher yields without water accumulating on catalyst sites [35]. Specifically, in our tests, switching from liquid to gas phase increased DMC output by over 30% with the same CeO₂ NP catalyst even at lower pressure. This demonstrates better performance by removing water quickly in gas-phase reactions. Additionally, mixing materials that repel water, like fumed silica, into the catalyst further improved DMC yield. As recently reported [32], these hybrid catalyst-adsorbent pairs expedite the removal of water made during the reaction. In our case, fumed SiO₂ physically blended with CeO₂ NPs boosted DMC yield 2-fold up to 17.8 mmol_{DMC}/g_{cat} versus the case with CeO₂ NPs alone as the catalyst. As elucidated by Xiao et al. previously with syngas conversions [32], the hydrophobicity rapidly transferred produced water away from surfaces, thus greatly increasing the conversion. This local interfacial dehydration strategy hence presents a broadly viable approach for improving catalytic transformations impacted by water accumulation. Overall, our results indicated that facilitating prompt water removal was critical to enhancing DMC yields in gas-phase systems versus liquid-phase reactions where water accumulated in the system.

Table 3. Reaction conditions, methanol conversion, and DMC yield in gas-phase synthesis.

Catalysts	Mass (g)	Pressure (MPa)	DMC Yield (mmol _{DMC} /g _{cat})	Methanol Conversion (%)
CeO ₂ NPs	1	1.2	8.63	0.46
20%CeO ₂ /3A	1	1.2	7.12	0.38
20%CeO ₂ /SiO ₂	1	1.2	17.8	0.95
CeO ₂ NPs *	0.1	3	6.41	0.33

* Note: liquid-phase results.

4. Conclusions

This work demonstrated the effects of tuning oxygen vacancies for the CeO₂ catalyst and implementing in situ water removal for enhanced DMC synthesis from CO₂ and methanol. Ce_xZr_yO₂ NRs with abundant oxygen vacancies were successfully synthesized via a hydrothermal method. Compared to CeO₂ NPs, the Ce₁₀Zr₁O₂ NRs exhibited 1.7-times higher DMC yield, attributed to increased oxygen vacancies promoting CO₂ adsorption and activation. The addition of 2-CP as a dehydrating agent dramatically boosted DMC yields by over 45-fold by shifting the reaction equilibrium to the desired product. A maximum of 87% methanol conversion and 99% DMC selectivity were achieved using the water removal approach. Moreover, an enhanced DMC yield in the gas-phase synthesis was observed due to easier water diffusion by mixing CeO₂ NPs with hydrophobic fumed SiO₂. These results provide valuable insights into catalyst design strategies centered on optimizing the nature and concentration of active sites like oxygen vacancies while simultaneously alleviating equilibrium limitations. This study proposes an effective pathway to boost DMC production from CO₂ and methanol. Moreover, the fundamental concept of mitigating water buildup through coupled catalyst and hydrophobic support systems could be broadly applicable to improving the performance of a range of catalytic processes negatively affected by the accumulation of water or hydrated intermediates at the catalytic interfaces.

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