

Article

Mesostructured CeO₂ as Catalyst in the Direct Synthesis of Dimethyl Carbonate

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Abstract

The direct synthesis of dimethyl carbonate (DMC) from methanol and CO₂ requires the use of a dehydrating agent such as 2-cyanopyridine (2-CP) to overcome thermodynamic limitations, alongside controlled catalyst surfaces to limit competing side reactions. In this study, mesostructured CeO₂ catalysts were synthesized via a nanocasting approach using SBA-15 as a hard template. The specific impact of the precursor infiltration method and the final thermal treatment on catalytic performance were evaluated. While a one-step precursor infiltration route yielded the most ordered mesostructure after template removal, the final calcination step emerged as the dominant variable governing catalyst activity and selectivity. Textural analysis confirmed that calcination preserved the interconnected nanorod morphology with only a minor decrease in specific surface area. Temperature-programmed desorption (TPD) revealed that the thermal treatment induced a redistribution of surface acid-base sites, specifically increasing the ratio of medium-strength basic to acidic sites. In situ DRIFTS demonstrated that this tailored surface chemistry facilitated CO₂ activation, promoted the formation of bidentate carbonates, and favored the monomethyl carbonate (MMC) intermediate formation. Consequently, the calcined CeO₂-OS catalyst achieved 74% methanol conversion and 91% DMC yield at 120 °C and 5 MPa, outperforming its uncalcined counterpart by suppressing 2-CP-related secondary reactions.

Keywords: dimethyl carbonate; cerium oxide; nanocasting; surface basicity; in situ DRIFTS; 2-cyanopyridine

Academic Editor: Javier Ereña

Received: 31 May 2026

Revised: 17 June 2026

Accepted: 26 June 2026

Published: 30 June 2026

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1. Introduction

The direct catalytic synthesis of dimethyl carbonate (DMC) from carbon dioxide and methanol offers a straightforward route for CO₂ utilization and green solvent production [1]. Despite its environmental appeal, the reaction is heavily restricted by its thermodynamics [2–4]. Water is formed as a primary stoichiometric byproduct, rapidly shifting the chemical equilibrium back toward the reactants and limiting methanol conversion to values typically below 1% under standard conditions. To drive the reaction forward, physical and chemical water-removal strategies must be integrated into the process. The use of organic dehydrating agents, particularly nitriles such as 2-cyanopyridine (2-CP), effectively circumvents this thermodynamic barrier [5]. In the presence of a suitable catalyst,

2-CP reacts with water to form 2-picolinamide (2-PA), keeping the water activity in the reaction medium extremely low and driving DMC formation.

In this integrated system, cerium oxide (CeO_2) acts as a dual-purpose catalyst. It must activate both CO_2 and methanol for DMC synthesis while simultaneously catalyzing the hydration of the nitrile [6,7]. The catalytic performance of CeO_2 depends directly on its dynamic surface chemistry, characterized by oxygen vacancies (O_v), $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox pairs, and the density of Lewis acid-base sites. Medium-strength acid-base pairs are generally required for the co-activation of the reactants [8]. One approach to controlling the abundance of these sites relies on the morphology of the catalyst. For instance, CeO_2 nanorods exhibit a higher concentration of active acid-base pairs compared to nanocubes or octahedra, leading to superior catalytic performance [9]. This enhanced activity is attributed to the preferential exposure of the (111) and (110) surface planes; density functional theory (DFT) calculations demonstrate that the (110) facet is particularly active, presenting the lowest formation energy of O_v [10].

Balancing the surface acid-base sites remains a complex challenge. Stoian et al. [11] demonstrated that a basic-to-acidic site ratio greater than one shifts the reaction favorably, leading to a higher DMC yield by prioritizing the role of basic sites in reactant activation. Building on this, Zhang et al. [12] investigated the reaction mechanism over Zn-modified CeO_2 and showed that a surface presenting fewer acidic sites and an enriched moderate basicity significantly raises the energy barriers of side reactions. Specifically, the enhanced Lewis basicity restricts the excessive interaction of methanol with the 2-CP dehydrating agent and its derivative 2-PA, effectively increasing the activation energies required to form undesired byproducts such as methyl picolinate (MP) and methyl-2-pyridinecarboximate (MPCI). Consequently, moderate strength basicity actively suppresses these parasitic pathways, improving overall DMC selectivity.

Mesoporous CeO_2 materials synthesized via nanocasting offer high surface areas and highly accessible active sites, making them ideal candidates for this reaction network. While the morphological advantages of these templated structures are well documented, the specific impact of post-synthesis thermal treatments on their surface reaction mechanisms under CO_2 /methanol/2-CP conditions remains unclear. This study evaluates mesoporous CeO_2 catalysts prepared via three different SBA-15 nanocasting routes. It demonstrates that the final calcination step overrides the structural differences induced by the synthesis routes themselves. By coupling quantitative TPD analysis with in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), it shows how calcination redistributes the acid-base sites, stabilizes the key monomethyl carbonate (MMC) intermediate, and actively suppresses secondary reactions.

2. Results and Discussion

2.1. Textural and Structural Properties

Negative replication of the SBA-15 template succeeded across all synthesis routes. As shown in Figure 1a, the uncalcined catalysts exhibited type IV isotherms featuring H1 hysteresis loops with a sharp capillary condensation step at relative pressures (P/P_0) above 0.8, characteristic of well-defined mesoporous architectures. However, the precursor infiltration method influenced the pore size distribution. The CeO₂-W-U catalyst displayed a broader distribution centered at ~5 nm (Figure 1b), indicating partial mesopore obstruction, likely resulting from the multiple cycles of wet impregnation and intermediate thermal decompositions required by this synthesis route. Conversely, the CeO₂-OS-U and CeO₂-I-U catalysts exhibited narrower pore size distributions centered at ~4 nm, reflecting a higher fidelity to the original template structure.

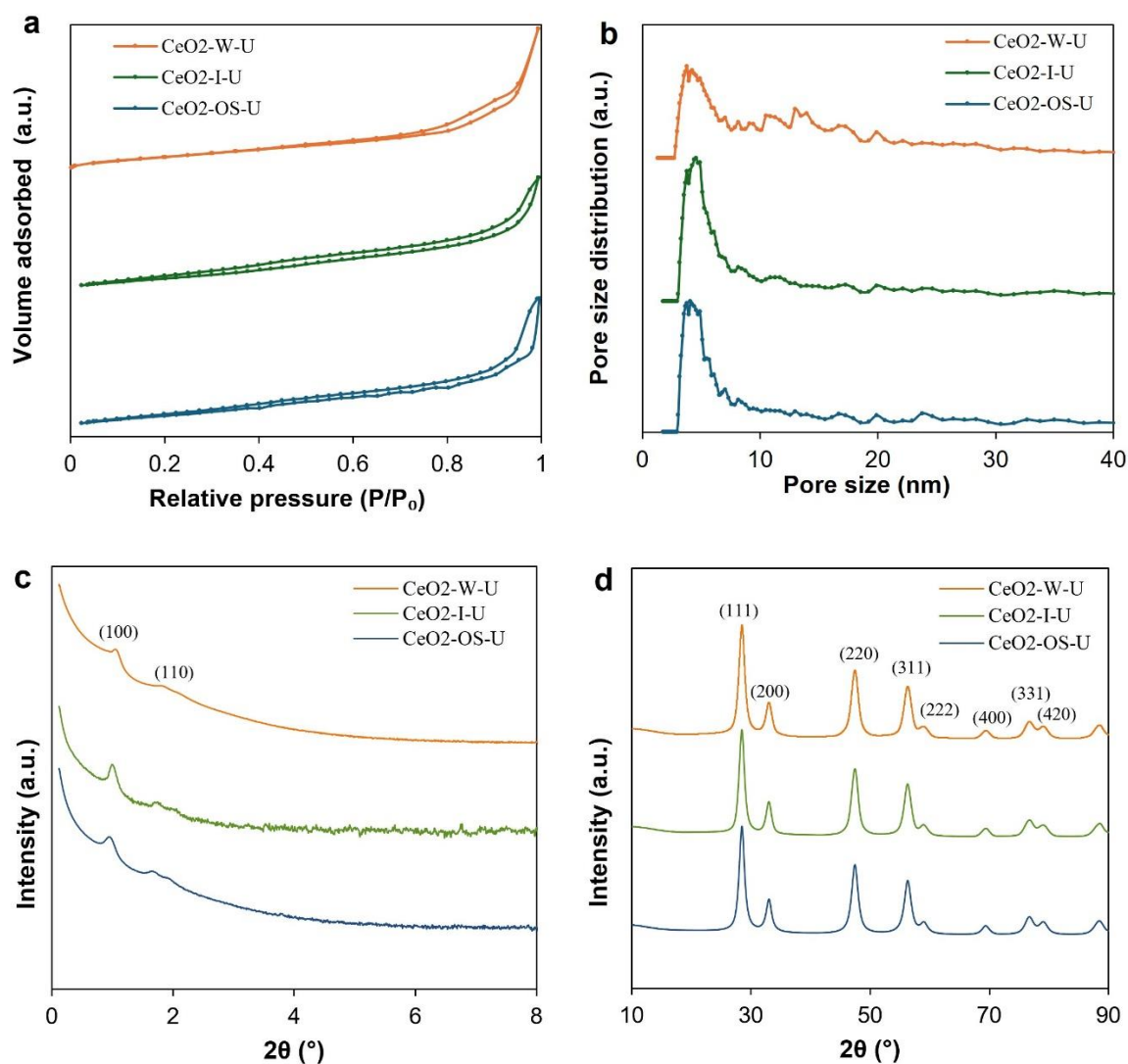


Figure 1. (a) Nitrogen adsorption–desorption, (b) Pore sizes distribution calculated by NLDFT, (c) low angle and (d) wide angle X-ray scattering.

SAXS profiles (Figure 1c) indicate that CeO₂-OS-U and CeO₂-I-U retained the highest degree of mesostructural ordering after template removal, as evidenced by the more clearly defined low-angle reflection compared with CeO₂-W-U. This trend is consistent with the corresponding TEM images, which show a more regular mesostructural

arrangement for CeO₂-OS-U (Figure 2c). The improved structural order is attributed to the continuous refluxing conditions combined with the use of a non-polar solvent (*n*-hexane). This medium forces the polar cerium precursor into the hydrophilic silica channels, reducing capillary stress and facilitating a homogeneous precursor distribution within the mesopores [17]. Wide-angle XRD patterns confirmed that all synthesized materials crystallized in a phase-pure face-centered cubic fluorite structure. Application of the Scherrer equation revealed average crystallite sizes ranging between 7.5 and 10.5 nm for the templated catalysts, which closely matches the channel diameter of the original SBA-15 (8.1 nm). This agreement indicates that crystallite growth was effectively confined within the silica pores. This confinement was visually corroborated by TEM imaging (Figure 2), which revealed the interconnected CeO₂ nanorod arrays characteristic of the hard-templating method using SBA-15 as the hard template. The nanorods exhibited well-defined lattice fringes corresponding primarily to the (111) and (220) planes [10,18], consistent with an anisotropic growth pattern that favors the exposure of the active (110) surface facets.

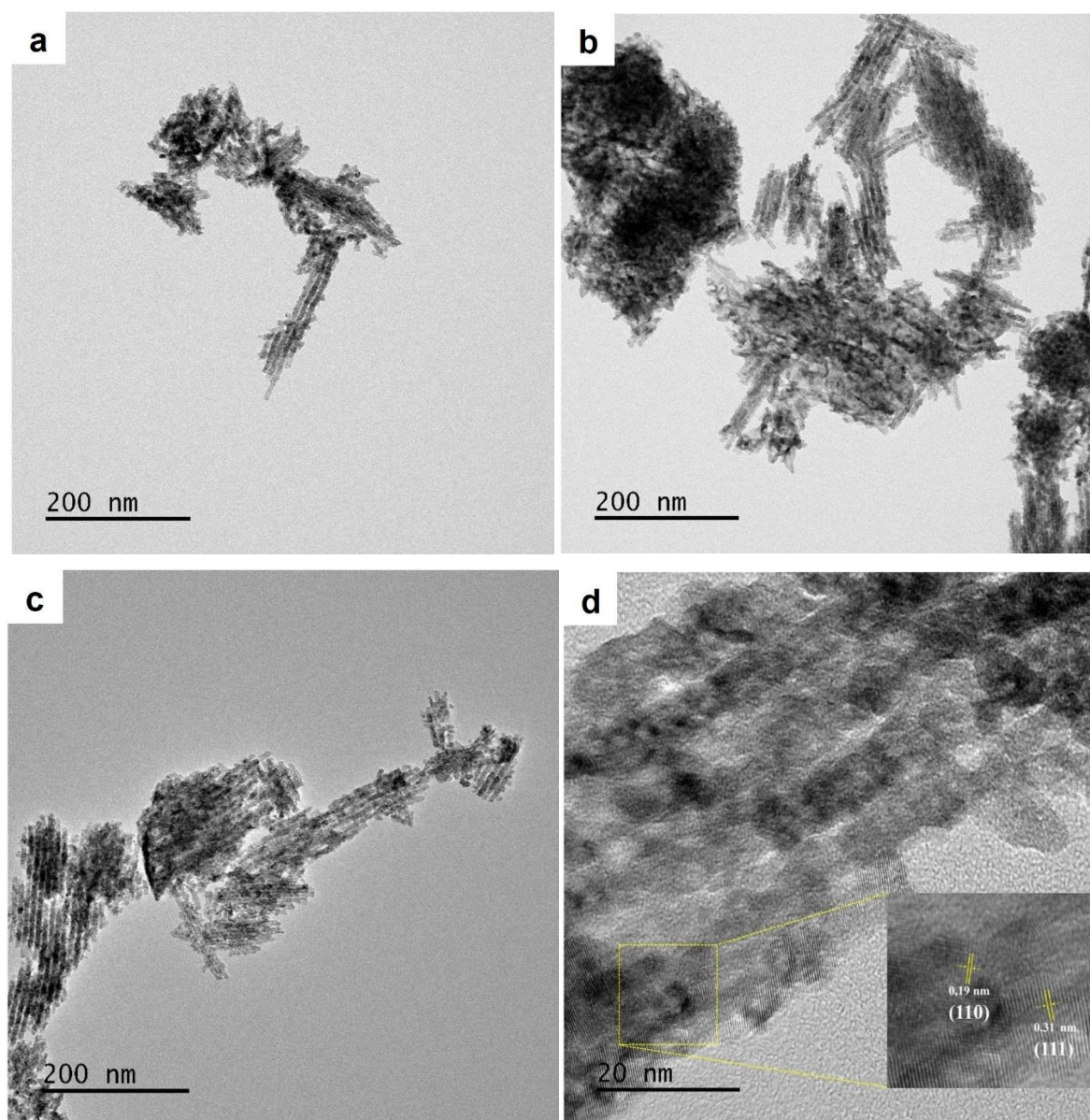


Figure 2. TEM images of (a) CeO₂-W-U, (b) CeO₂-I-U, and (c,d) CeO₂-OS-U.

Subjecting the recovered CeO₂ to a final calcination step at 450 °C caused a minor structural contraction without inducing pore collapse. The BET specific surface area of sample CeO₂-OS was the highest and presented a moderate decrease from 142.5 m²/g (uncalcined) to 133.8 m²/g (calcined). The total pore volume remained virtually unchanged, indicating that the thermal treatment preserved the internal mesoporous network required for reactant diffusion while increasing the local crystallinity of the nanorods. Table 1 provides complete information on textural and structural parameters of the synthesized catalysts and the SBA-15 template used.

Table 1. Textural and structural properties of SBA-15 and CeO₂ samples.

Sample	S _{BET} (m ² /g)	V _{pore} (mL/g)	d _{pore} ^a (nm)	Crystallite Medium Size ^b (nm)
SBA-15	835.6	0.98	8.2	-
CeO ₂ -W-U	135.0	0.33	3.8	10.4
CeO ₂ -I-U	138.6	0.21	4.1	8.3
CeO ₂ -OS-U	142.5	0.32	4.1	7.5
CeO ₂ -W-C	120.9	0.21	3.8	10.5
CeO ₂ -I-C	118.5	0.21	4.4	8.5
CeO ₂ -OS-C	133.8	0.28	4.9	7.6

^a Calculated from NLDFT distribution of pore size. ^b Calculated from Scherrer equation using XRD (111) plane.

2.2. TPD Analysis

The acid-base properties of the synthesized materials were characterized by CO₂-TPD and NH₃-TPD (Figures 3 and 4), and the quantitative results are summarized in Table . Weak, medium-strength, and strong sites were assigned to desorption events occurring below 200 °C, between 200 and 450 °C, and above 450 °C, respectively [19].

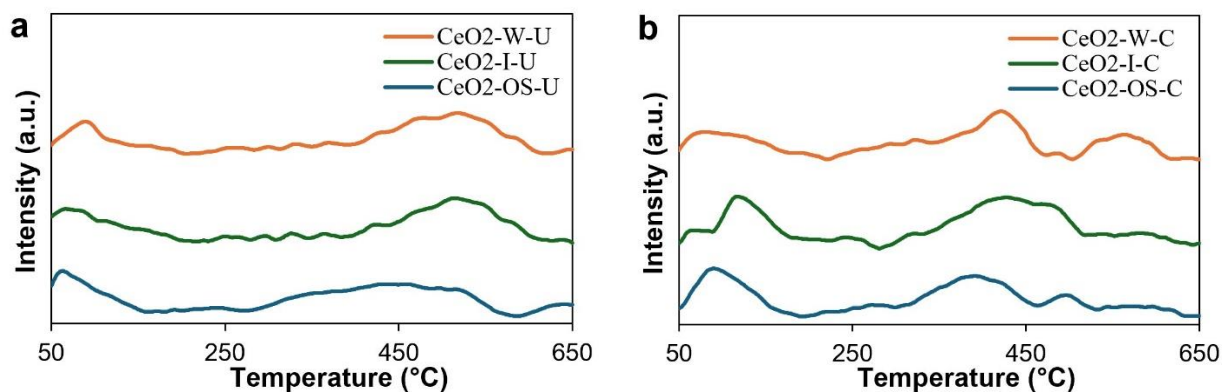


Figure 3. CO₂-TPD of samples (a) uncalcined and (b) calcined.

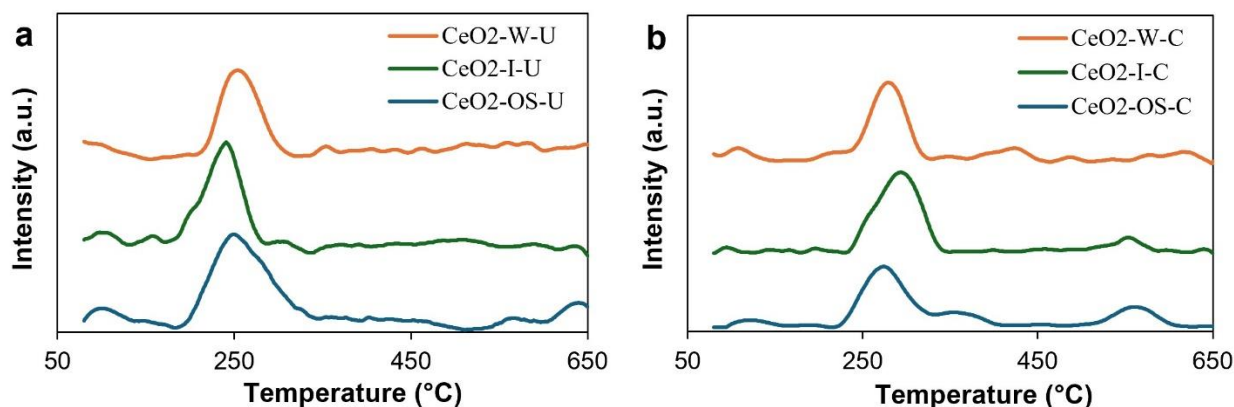


Figure 4. NH_3 -TPD of samples (a) uncalcined and (b) calcined.

The CO_2 -TPD profiles (Figure 3) reveal that calcination induces a distinct shift in the basic site speciation. For all three catalysts, weak basic sites—typically attributed to surface hydroxyl groups that interact with CO_2 to form bicarbonate species [20]—shifts to slightly higher temperatures (approximately 80–110 °C) after the thermal treatment. In contrast, the peak corresponding to strong basic sites displaces toward lower desorption temperatures. This reorganization is consistent with changes reported for other mesoporous CeO_2 systems after calcination under comparable conditions [21] and can be interpreted in terms of the underlying surface restructuring induced by the thermal step. Specifically, calcination at 450 °C promotes the consolidation of $\text{Ce}^{4+}\text{--O}^{2-}$ ionic pairs, which are primarily associated with medium-strength basic sites forming bidentate carbonates [20], while concurrently depleting the population of highly coordinatively unsaturated oxygen anions, reported to be responsible for strong basicity [11,20,22]. This redistribution is accompanied by a net increase in the total density of basic sites, as reported in Table .

Table 2. Acid-base properties of CeO_2 samples.

Sample	Acidity ^a ($\mu\text{mol/g}$, NH_3 -TPD)			Basicity ^a ($\mu\text{mol/g}$, CO_2 -TPD)		
	Weak	Medium	Strong	Weak	Medium	Strong
CeO ₂ -W-U	24	183	80	53	51	117
CeO ₂ -I-U	58	199	53	69	36	119
CeO ₂ -OS-U	31	237	41	63	98	66
CeO ₂ -W-C	16	144	19	72	132	55
CeO ₂ -I-C	15	212	46	76	105	68
CeO ₂ -OS-C	10	131	37	88	128	49

^a Weak (<200 °C), Medium (200–450 °C) and strong (>450 °C).

The NH_3 -TPD profiles (Figure 4) exhibit a complementary trend. After calcination, a decrease in the total acid site density is observed, accompanied by a shift of the main acid desorption peak (located around 250 °C for uncalcined materials) toward higher temperatures (~280 °C). This displacement suggests the selective stabilization of specific Lewis acid sites. This behavior is likely linked to the elimination of surface hydroxyl groups during calcination [23], which reduces the number of weakly acidic --OH species while preserving the medium-strength Lewis acid sites associated with under-coordinated Ce^{4+} cations [22]. Contributions from strong acid sites (>450 °C) remain negligible across all samples.

Notably, all samples displayed very similar TPD profiles regardless of the synthesis route. This suggests that the different infiltration routes had only a minor influence on the acid-base properties, which is consistent with the small differences observed in their

textural and structural characteristics. In contrast, calcination clearly induced the main changes in the distribution and strength of the surface acid-base sites.

2.3. Activity Test

Catalytic tests showed that calcination systematically improved methanol conversion and DMC yield for all three nanocast catalysts, regardless of the infiltration route (Figure 5). Among the samples studied, CeO₂-OS-C was the slightly more active catalyst, with methanol conversion increasing from about 58% for the uncalcined material to 74% after calcination. For comparison, a calcined commercial CeO₂ reference (6.4 m²/g) evaluated under identical conditions yielded 68% DMC with only 15% methanol conversion at an equivalent catalyst mass (0.21 g) (Figure S1). Even after scaling the commercial catalyst loading to 3.18 g to provide an equivalent total surface area, the conversion reached 70%, remaining slightly below that of the mesoporous CeO₂-OS-C. The overall results indicate that, among the synthesized materials, the final calcination step, rather than the specific nanocasting route, was the dominant factor governing catalytic performance, consistent with the calcination-induced redistribution of surface acid-base sites discussed above.

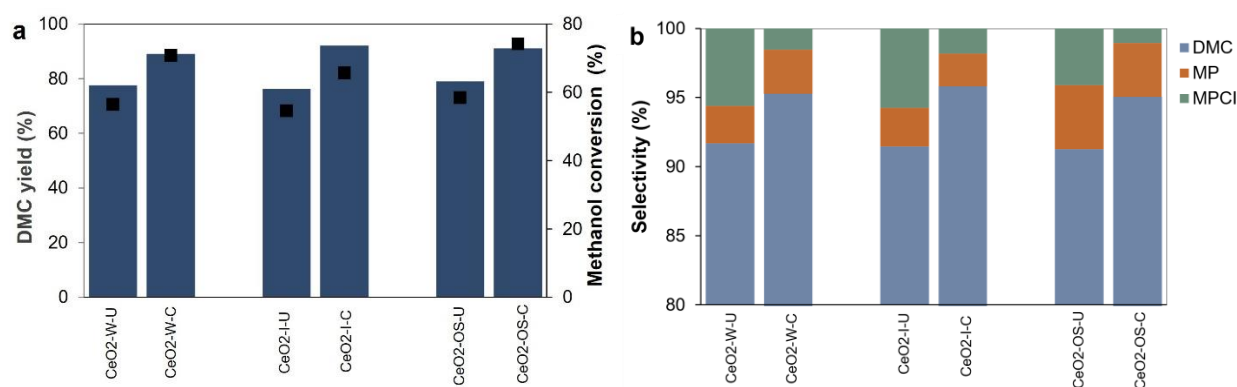
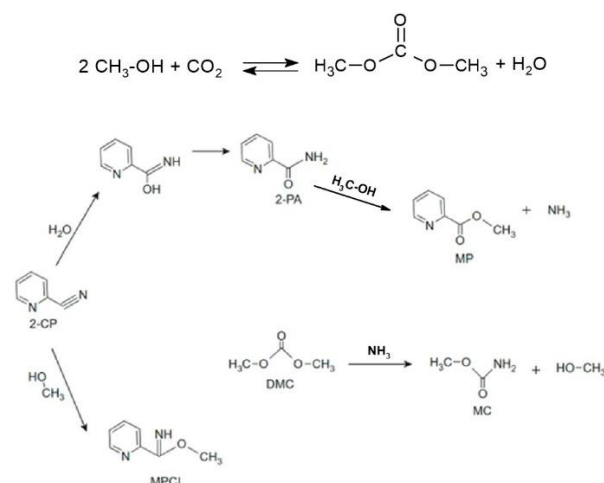


Figure 5. (a) DMC yield (bars), methanol conversion (symbols), and (b) selectivity of uncalcined and calcined catalysts. Reaction conditions: Catalyst 0.21 g, methanol 100 mmol, 2-CP 50 mmol, CO₂ 5 MPa, T = 120 °C, 16 h.

Table 3 further shows that 2-CP conversion evolved in parallel with methanol conversion and remained within the same order of magnitude for all catalysts. This behavior is consistent with the coupled reaction network, in which water formed during DMC synthesis is consumed by 2-CP to produce 2-PA. At the same time, the DMC and 2-PA yields did not coincide exactly, and the product identification by MS revealed the formation of MP and MPCl, confirming that methanol and 2-CP also participate in competitive secondary reactions, as reported for CeO₂/2-CP systems in previous mechanistic studies [24,25]. Scheme 1 represents the possible reaction pathways taking place in the system when 2-CP is used as a dehydrating agent. Alongside the main formation of DMC and the expected hydration of 2-CP to 2-PA, the scheme highlights the parallel secondary reactions of the system.



Scheme 1. Possible reaction pathways of 2-CP.

Table 3. Catalytic activity of CeO₂ calcined and uncalcined samples.

Sample	X _{MeOH} (%)	X _{2-CP} (%)	Y _{DMC} (%)	Y _{2-PA} (%)
CeO ₂ -W-U	56	53	78	82
CeO ₂ -I-U	55	50	76	81
CeO ₂ -OS-U	58	50	79	81
CeO ₂ -W-C	71	66	89	87
CeO ₂ -I-C	66	56	92	88
CeO ₂ -OS-C	74	66	91	86

Reaction conditions: Catalyst 0.21 g, methanol 100 mmol, 2-CP 50 mmol, CO₂ 5 MPa, T = 120 °C, 16 h.

As shown in Figure 5b, calcination systematically increased DMC selectivity from approximately 91% to near 95% across all synthesis routes. Product distribution analysis indicates that this difference is primarily driven by the formation of MPCl. Correlating these catalytic results with the TPD profiles, the uncalcined samples (which exhibit a higher density of surface acid sites and lower overall basicity) show a higher propensity for MPCl production. This suggests that a more acidic surface profile promotes the side reaction between methanol and 2-CP. Following calcination, the reduction in surface acidity and the relative increase in basic sites effectively suppress this parasitic reaction, leading to the observed improvement in DMC selectivity [11,12]. Table 4 compares the optimized CeO₂-OS-C with other CeO₂ catalysts from the literature. Driven by its tuned acid-base profile, our material achieves a 91% DMC yield and 74% methanol conversion at 120 °C, demonstrating a catalytic efficiency that is comparable to recent ceria-based systems for 2-CP assisted DMC synthesis.

Table 4. Comparison of catalytic performance and reaction conditions for direct DMC synthesis assisted by 2-CP over different CeO₂-based catalysts.

Sample	T (°C)	P (MPa)	Cat. Mass (g)	Reaction Time (h)	Y _{DMC} (%)	X _{MeOH} (%)	Reference
CeO ₂ Nanorod	150	5	0.1	2	71	50	[8]
CeO ₂	140	3.5	0.1	4	83	45	[26]
CeO ₂ -FD	140	0.5	0.1	4	84	23	[12]
CeO ₂	120	5	0.34	12	94	96	[5]
CeO ₂ -OS-C	120	5	0.21	16	91	74	This work

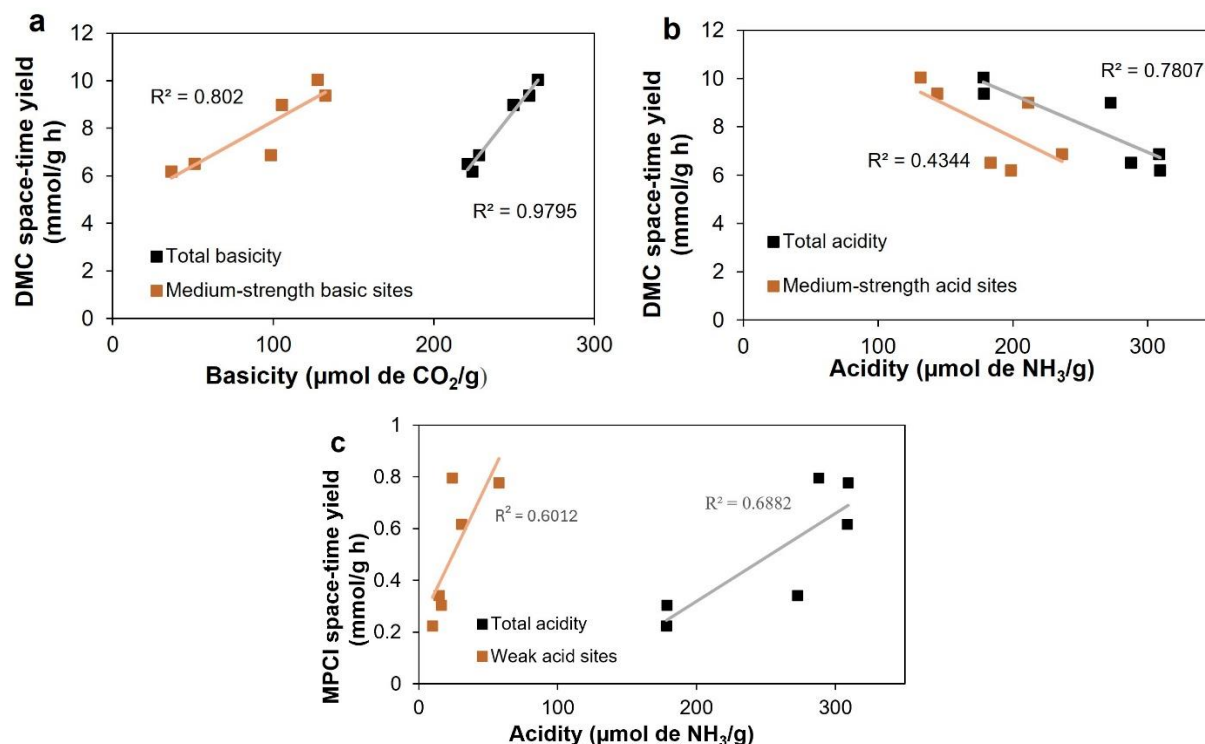


Figure 6. Correlation between the DMC space-time yield and (a) total and medium-strength basicity, and (b) total and medium-strength acidity. (c) Correlation of the MPCl space-time yield with total acidity and weak acid sites. Reaction conditions: Same as in Table 3.

A similar conclusion emerges from the correlations presented in Figure 6a,b. The DMC space-time yield increased with both total and medium-strength basicity, (Figure 6a). This interpretation is highly consistent with literature reports demonstrating that catalytic activity is fundamentally linked to the presence of accessible basic sites, which are essential for CO₂ adsorption and the subsequent formation of reactive carbonate species. Specifically, bidentate carbonates have been identified as the key reactive intermediates in the primary DMC formation pathway [20,22,27]. Conversely, the DMC space-time yield decreased with total acidity (Figure 6b). The correlation with medium-strength acid sites was notably weaker, suggesting that medium-strength acidity is not the primary factor hindering DMC production. Rather, the competitive reactions between methanol and 2-CP appear to be driven primarily by the weaker acid sites. This interpretation is corroborated by Figure 6c, which demonstrates a positive correlation between the space-time yield of the byproduct MPCl and both total acidity and weak acid sites. Therefore, while basicity selectively drives the formation of reactive bidentate carbonates for DMC synthesis, it is the abundance of weak acid sites that actively promotes the undesired secondary pathway, ultimately lowering the overall DMC performance.

2.4. In Situ DRIFTS

In situ DRIFTS experiments were performed on CeO₂-OS-U and CeO₂-OS-C to clarify how calcination modifies the evolution of adsorbed surface species under conditions relevant to DMC synthesis. All measurements were carried out at 120 °C.

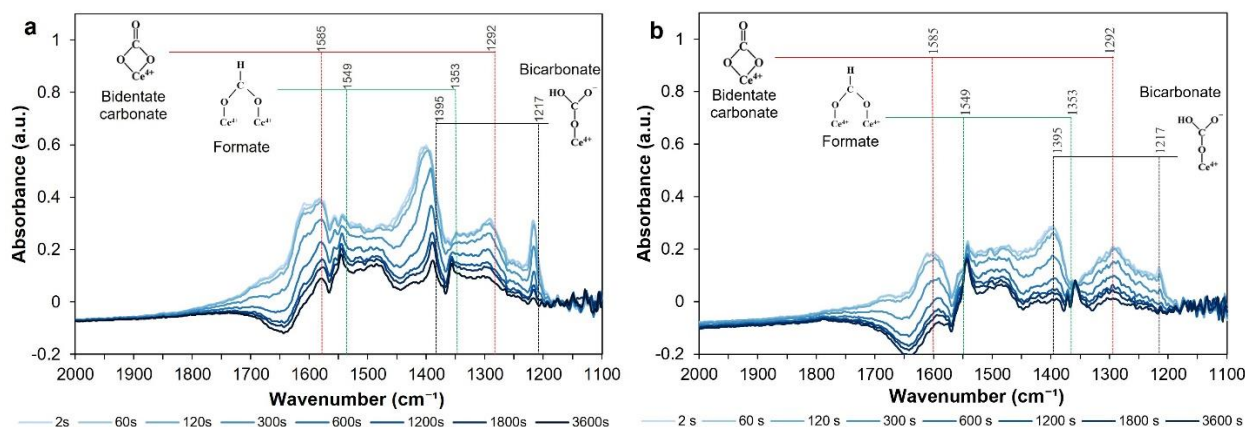
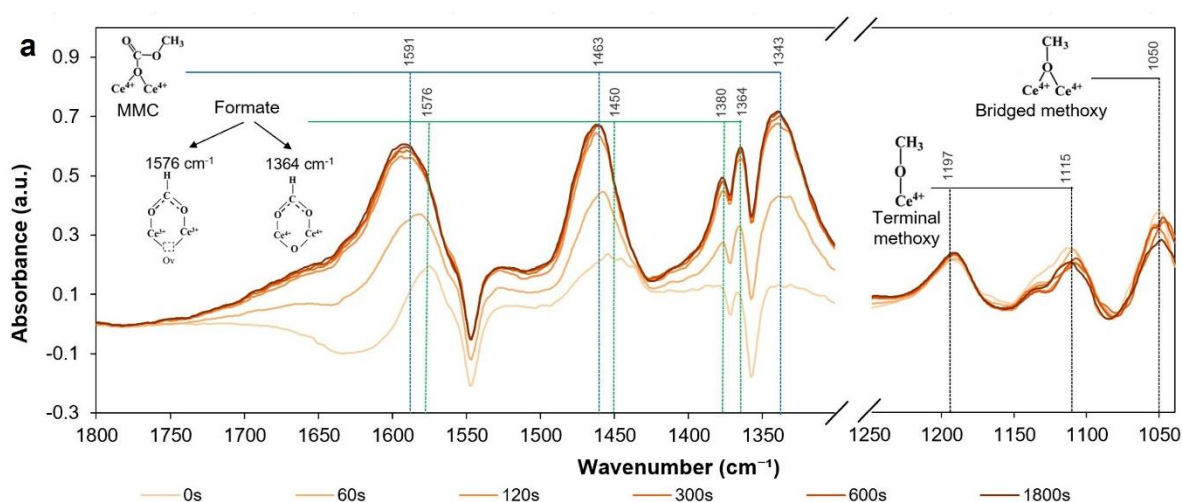


Figure 7. In situ DRIFTS spectra recorded during Ar purge following CO₂ adsorption on (a) CeO₂-OS-C and (b) CeO₂-OS-U samples.

Figure 7a,b show the spectra recorded during Ar purge after CO₂ adsorption. For the calcined sample, the spectra are dominated by bands assigned to bidentate carbonates (1585 and 1292 cm^{−1}) and bicarbonates (1395 and 1217 cm^{−1}), together with more persistent contributions attributed formate species at 1549 and 1353 cm^{−1} [20,22,27]. In contrast, the uncalcined sample displays a markedly lower relative contribution of bidentate carbonates, while formate species (at 1549 and 1353 cm^{−1}) become comparatively more prominent at longer purge times [26,28,29].

This difference indicates that calcination favors the activation of CO₂ and the formation of absorbed reactive specie bidentate carbonate [20,22,27]. This is fully consistent with the CO₂-TPD results (Figure 4), which showed that calcination increases the relative contribution of medium-strength basic sites. The uncalcined catalyst, possessing fewer basic sites, provides an environment that is less favorable for the stabilization of these bidentate carbonates.



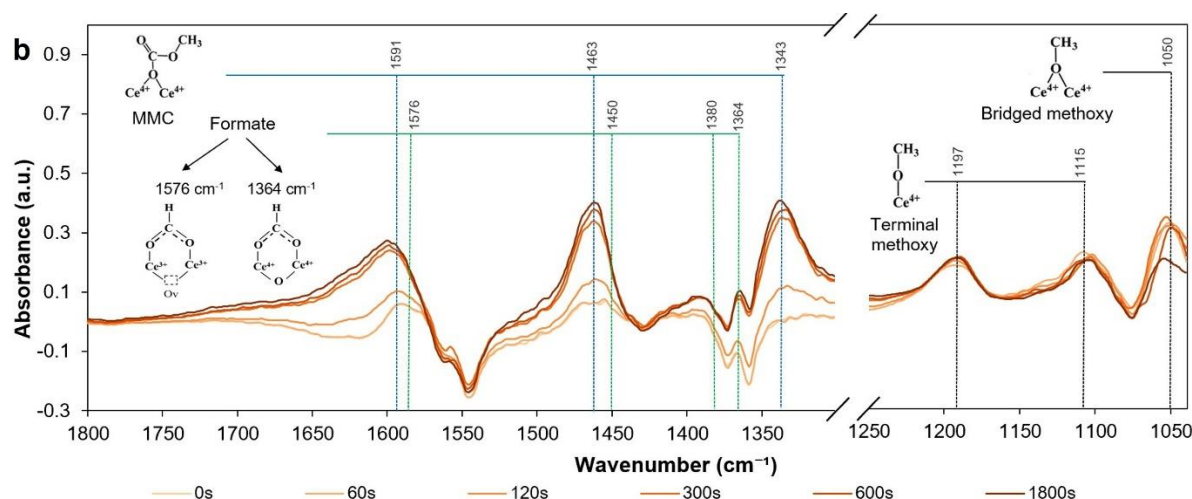


Figure 8. In situ DRIFTS spectra during CO₂ adsorption after prior methanol adsorption on (a) CeO₂-OS-C and (b) CeO₂-OS-C samples.

Figure 8a,b present the evolution of surface species during CO₂ adsorption after prior methanol adsorption (methanol saturation representing $t = 0$). In the 1250–1020 cm^{−1} region, bands at 1197 and 1115 cm^{−1} are assigned to terminal methoxy species, whereas the band at 1050 cm^{−1} corresponds to bridging methoxy species [26,27,30]. The overall intensity of these methoxy-related bands is similar for the calcined and uncalcined samples, indicating that both surfaces are able to activate methanol to a comparable extent. This observation is further nuanced by the OH region (Figure S2), in which the uncalcined catalyst exhibits a more pronounced depletion of the band at 3645 cm^{−1}, assigned to bibridged surface -OH groups [27], suggesting a greater involvement of these sites in methanol activation relative to the calcined material.

The main difference, however, appears after CO₂ introduction. In the 1300–1600 cm^{−1} region, bands at 1591, 1463, and 1343 cm^{−1} assigned to MMC species increase more clearly on the calcined catalyst, while the methoxy bands decrease simultaneously with time [27,30]. This behavior reflects a more efficient transformation of adsorbed methoxy species into MMC when the catalyst has been calcined. Conversely, MMC formation remains less pronounced on the uncalcined material, even though the initial methoxy population is of similar magnitude.

In addition, two bands are observed around 1380 and 1364 cm^{−1}, which may be assigned to the C–H deformation of formates and to the stretching vibration of formates coordinated to Ce⁴⁺ sites, respectively [31]. The lower intensity of the 1364 cm^{−1} band on the uncalcined catalyst suggests a lower availability of Ce⁴⁺ sites, potentially contributing to the weaker stabilization of bidentate carbonates. These observations point to a more defective surface state for the uncalcined material. This confirms that the primary limitation of the uncalcined catalyst is not methanol activation itself, but rather its less effective CO₂ activation and a less favorable coupling between adsorbed methoxy species and bidentate carbonate surface intermediate.

Those results highlight the critical role of basicity in DMC formation and selectivity. In our system, calcination appears to modify the surface defect density, which likely implies a reorganization of the Ce⁴⁺/Ce³⁺ redox couples along with the distribution and strength of the acid-base sites. This interpretation aligns well with the results reported by Zhang et al. [12], who demonstrated that a surface presenting fewer acid sites and more moderate basic sites strongly increases the energy barriers for secondary reactions, thereby reducing MPCl formation.

Based on this, two complementary hypotheses can be proposed to explain the behavior of the studied catalysts. (1) On the uncalcined catalyst, the reduced basic site density disfavors CO₂ activation. This slows down the DMC synthesis pathway relative to the secondary routes involving 2-CP, leading to a relatively higher formation of MPCl. (2) The preferential consumption of bibridged –OH groups (3645 cm^{−1}) on the uncalcined surface promotes methoxy species in surface environments that are more accessible to 2-CP, which could facilitate the formation of MPCl. In contrast, calcination reduces the density of these specific sites while promoting a surface chemistry more conducive to CO₂ activation and DMC formation. In this sense, our results may complement the mechanism proposed by Zhang, where a high density of Lewis basic sites disfavors the initial step of the proton-assisted formation of the Py-CNH* intermediate, the key step in the secondary pathway leading to MPCl. Although their study does not identify the exact surface environments where this secondary route takes place, our results suggest that the local environments associated with bibridged –OH groups may be involved in promoting the interaction between methanol-derived species and adsorbed 2-CP on the uncalcined catalyst.

3. Experimental Section

3.1. Catalyst Preparation

Mesoporous silica SBA-15 was synthesized using Pluronic P123 (BASF) as the structure-directing agent and tetraethyl orthosilicate (TEOS, Sigma Aldrich) as the silica source under acidic conditions. The resulting gel was aged and calcined at 550 °C to generate the rigid template [13]. Mesoporous CeO₂ was then prepared by nanocasting using Ce(NO₃)₃·6H₂O (Sigma-Aldrich) as the cerium precursor through three different infiltration routes as follows.

3.1a. CeO₂-W was synthesized by a wet impregnation method involving multiple impregnation–decomposition cycles [14]. For each cycle, 0.64 g of precursor was dissolved in 9 mL of ethanol (Greenfield), followed by the addition of 1 g of SBA-15 under stirring for 30 min. Solvent evaporation was carried out at 60 °C for 2 h, and the subsequent decomposition of the nitrate salt was achieved by calcination in static air at 500 °C for 5 h.

3.1b. CeO₂-I was prepared by an incipient wetness impregnation route, following the wet impregnation protocol but relying on the adjustment of the precursor solution volume. This volume was calculated to match the available pore volume of the intermediate CeO₂/SBA-15 composite (previously determined by N₂ physisorption), aiming to achieve a CeO₂ mass loading of approximately 50% per cycle [15].

3.1c. CeO₂-OS was obtained by a one-step synthesis under reflux using a concentrated precursor slurry in a non-polar solvent (*n*-hexane, Ficher Chemicals) to promote direct capillary infiltration during an 18 h reflux period at 70 °C [16].

After precursor infiltration, the silica template was removed by stirring the composite in a 2 M NaOH solution three times over 24 h at room temperature. The recovered CeO₂ powders were split into two batches: one left uncalcined and another calcined at 450 °C for 4 h to evaluate the isolated effect of the thermal treatment. Hereafter, samples are denoted with the suffix -U for uncalcined and -C for calcined; thus, the corresponding materials are labeled CeO₂-W-U/C, CeO₂-I-U/C, and CeO₂-OS-U/C.

3.2. Characterization

All the prepared catalysts were characterized using different techniques. Textural properties were determined from N₂ physisorption at 77 K with a Autosorb iQ TPX (Anton Paar) after degassing the samples under vacuum at 250 °C for 3 h. The BET method was used to calculate the specific surface area, whereas pore size distributions were

obtained from the adsorption–desorption isotherms by NLDFT using the equilibrium model for N₂ at 77 K.

Wide-angle X-ray diffraction (XRD) patterns were recorded on an Aeris diffractometer (PANalytical, 2017) using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) over a 2θ range of $10\text{--}90^\circ$ to identify the fluorite CeO₂ phase and estimate the average crystallite size from line broadening using the Scherrer equation. Small-angle X-ray scattering (SAXS) measurements were carried out on a SAXSpoint 2.0 instrument (Anton Paar) to evaluate mesostructural order and periodicity, and to verify the preservation of the mesostructured framework after synthesis and thermal treatment.

Catalyst morphology and local crystallographic organization were examined by transmission electron microscopy (TEM) using a JEOL JEM-2100 Plus microscope equipped with a LaB₆ source and operated at 200 kV. Interplanar spacings were measured using ImageJ. Surface acidity and basicity were quantified by NH₃-TPD and CO₂-TPD using an RXM-100 apparatus (ASDI). Prior to adsorption, the samples were pretreated under inert gas at 250 °C for 1 h and then cooled to room temperature. The catalysts were saturated with 15 vol% NH₃/Ar for 15 min or 15 vol% CO₂/He for 45 min, followed by purging with the corresponding carrier gas at 30 mL min^{−1} to remove physisorbed probe molecules. The desorption step was then performed from 50 to 650 °C, and the signal was monitored continuously with a thermal conductivity detector (TCD).

Surface intermediates were identified by in situ DRIFTS using a Spectrum 3 spectrometer (PerkinElmer) equipped with an in situ (Harrick) reaction cell. For each experiment, the catalyst powder was pretreated at 250 °C for 1 h under Ar. The temperature was then stabilized at 120 °C, and a background spectrum was recorded before reactant exposure. The reactive sequence consisted of adsorption of CO₂ or methanol for 30 min, followed by Ar purging or sequential co-adsorption with the second reactant for 1 h, depending on the protocol as indicated in the legends of Figures 7 and 8. Spectra were collected at different times with a resolution of 4 cm^{−1}.

3.3. Catalytic Testing

Catalytic tests were carried out in a 50 mL T316 stainless steel high-pressure batch reactor (Parr Series 4590). In a typical experiment, 100 mmol of methanol, 50 mmol of 2-CP, and 0.21 g of catalyst were introduced into the reactor, which was then purged three times with CO₂ to remove residual air at room temperature. The reactor was subsequently charged with CO₂ to an initial pressure of 5 MPa, stirred at 400 rpm for 15 min to promote gas dissolution in the liquid phase, and heated to 120 °C. The reaction time was fixed at 16 h from the moment the target temperature was reached. At the end of the run, the reactor was cooled in a cold-water bath, depressurized slowly after reaching about 35 °C, and the reaction mixture was recovered for analysis.

The catalyst was separated from the liquid phase by filtration, and the products were quantified by gas chromatography using a Varian CP-3800 instrument equipped with a flame ionization detector (GC-FID). Prior to quantitative analysis, product identities were verified by GC-MS. For a typical GC analysis, the reaction mixture was diluted in acetone, and methyl benzoate was added as an internal standard to correct for injection variability. External calibration curves were established for methanol, DMC, and 2-CP using standard solutions of concentration. The amounts of 2-PA, MP, MPCI, and MC were determined using the effective carbon number (ECN) method. Methanol conversion, 2-CP conversion, DMC/2-PA yield were calculated according to Equations (1)–(4).

$$X_{MeOH} = \frac{2 \times n_{DMC} + n_{MP} + n_{MC}}{2 \times n_{DMC} + n_{MP} + n_{MC} + n_{unreacted\ MeOH}} \times 100\% \quad (1)$$

$$X_{MeOH} = \frac{2 \times n_{DMC} + n_{MP} + n_{MC}}{2 \times n_{DMC} + n_{MP} + n_{MC} + n_{unreacted\ MeOH}} \times 100\% \quad (2)$$

$$Y_{DMC} = \frac{2 \times n_{DMC}}{n_{reacted\ MeOH}} \times 100\% \quad (3)$$

$$Y_{2-PA} = \frac{n_{2-PA}}{n_{reacted\ 2-CP}} \times 100\% \quad (4)$$

The selectivity towards the product i was defined as in Equation (5)

$$S_i = \frac{N_i \times n_i}{\sum N \times n\ (products\ derived\ from\ methanol)} \times 100\% \quad (5)$$

4. Conclusions

This work allowed establishing that using the mesostructured silica SBA-15 as a hard template in the synthesis of CeO₂ catalysts, generated this oxide under the form of nanorods. This morphology is known to be beneficial for the direct catalytic production of dimethyl carbonate in the presence of 2-cyanopyridine as dehydrant. The reported results confirmed that the hard templated nanorods of CeO₂ displayed a high density of exposed (110) crystal faces associated with the satisfactory catalytic behavior in this reaction.

This study moreover examined the differences in catalytic behavior associated with both the hard templating procedure and the calcination process. It was found that the effect of calcination is more significant. The latter was shown to result from evolution of the basic and acidic surface sites which affect differently the activation of CO₂ and methanol.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal16070606/s1>.

Author Contributions: Conceptualization, D.A.S.A. and M.R.; methodology, S.K.; software, D.A.S.A.; validation, M.R., S.K. and L.F.; formal analysis, D.A.S.A.; investigation, D.A.S.A.; resources, S.K.; data curation, D.A.S.A.; writing—original draft preparation, D.A.S.A.; writing—review and editing, S.K.; visualization, M.R.; supervision, S.K. and M.R.; project administration, S.K.; funding acquisition, S.K. and L.F. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: The data presented in this study are available in this article.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Santos Araque, D.A.; Mozaffari, N.; Fradette, L.; Kaliaguine, S. Revisiting the Synthesis of Dimethyl Carbonate from Methanol and Carbon Dioxide. *Can. J. Chem. Eng.* **2026**.
2. Zhang, Y.; Khalid, M.S.; Wang, M.; Li, G. New Strategies on Green Synthesis of Dimethyl Carbonate from Carbon Dioxide and Methanol over Oxide Composites. *Molecules* **2022**, *27*, 5417.
3. Wang, D.; Shi, F.; Wang, L. A Review of Catalysts for Synthesis of Dimethyl Carbonate. *Catalysts* **2024**, *14*, 259.
4. Kohli, K.; Sharma, B.K.; Panchal, C.B. Dimethyl Carbonate: Review of Synthesis Routes and Catalysts Used. *Energies* **2022**, *15*, 5133.
5. Honda, M.; Tamura, M.; Nakagawa, Y.; Sonehara, S.; Suzuki, K.; Fujimoto, K.I.; Tomishige, K. Ceria-Catalyzed Conversion of Carbon Dioxide into Dimethyl Carbonate with 2-Cyanopyridine. *ChemSusChem* **2013**, *6*, 1341–1344.
6. Tamura, M.; Wakasugi, H.; Shimizu, K.I.; Satsuma, A. Efficient and Substrate-specific Hydration of Nitriles to Amides in Water by Using a CeO₂ Catalyst. *Chem.-Eur. J.* **2011**, *17*, 11428–11431.

7. Tamura, M.; Satsuma, A.; Shimizu, K.I. CeO₂-Catalyzed Nitrile Hydration to Amide: Reaction Mechanism and Active Sites. *Catal. Sci. Technol.* **2013**, *3*, 1386–1393.
8. Darbha, S. Direct Synthesis of Dimethyl Carbonate from CO₂ and Methanol over CeO₂ Catalysts of Different Morphologies. *J. Chem. Sci.* **2016**, *128*, 957–965.
9. Wang, S.; Zhao, L.; Wang, W.; Zhao, Y.; Zhang, G.; Ma, X.; Gong, J. Morphology Control of Ceria Nanocrystals for Catalytic Conversion of CO₂ with Methanol. *Nanoscale* **2013**, *5*, 5582–5588.
10. Zhu, D.; Liu, H.; Huang, Y.; Luo, X.; Mao, Y.; Liang, Z. Study of Direct Synthesis of DMC from CO₂ and Methanol on CeO₂: Theoretical Calculation and Experiment. *Ind. Eng. Chem. Res.* **2022**, *61*, 10804–10817.
11. Stoian, D.; Medina, F.; Urakawa, A. Improving the Stability of CeO₂ Catalyst by Rare Earth Metal Promotion and Molecular Insights in the Dimethyl Carbonate Synthesis from CO₂ and Methanol with 2-Cyanopyridine. *ACS Catal.* **2018**, *8*, 3181–3193.
12. Zhang, Q.; Zhang, D.; Mao, W.; Zhu, D.; Liu, L.; Liu, H.; Liang, Z. Synthesis of Dimethyl Carbonate from CO₂ and Methanol over Zn Modified CeO₂ with 2-Cyanopyridine: Theoretical Calculation and Experiment. *Sep. Purif. Technol.* **2024**, *339*, 126217.
13. Choi, M.; Heo, W.; Kleitz, F.; Ryoo, R. Facile Synthesis of High Quality Mesoporous SBA-15 with Enhanced Control of the Porous Network Connectivity and Wall Thickness. *Chem. Commun.* **2003**, 1340–1341.
14. Moreno de la Calle, Á.; Vizcaíno, A.J.; Carrero, A.; Calles, J.A.; Megía, P.J. Study of Mesostructured CeO₂ Synthesis via Nanocasting Using SBA-15 as a Template: Influence of the Cerium Precursor. *Int. J. Mol. Sci.* **2024**, *25*, 13016.
15. Gong, H.; Zhu, J.; Lv, K.; Xiao, P.; Zhao, Y. Templating Synthesis of Metal Oxides by an Incipient Wetness Impregnation Route and Their Activities for CO Oxidation. *New J. Chem.* **2015**, *39*, 9380–9388.
16. Yen, H.; Seo, Y.; Guillet-Nicolas, R.; Kaliaguine, S.; Kleitz, F. One-Step-Impregnation Hard Templating Synthesis of High-Surface-Area Nanostructured Mixed Metal Oxides (NiFe₂O₄, CuFe₂O₄ and Cu/CeO₂). *Chem. Commun.* **2011**, *47*, 10473–10475.
17. Nair, M.M.; Yen, H.; Kleitz, F. Nanocast Mesoporous Mixed Metal Oxides for Catalytic Applications. *Comptes Rendus Chim.* **2014**, *17*, 641–655.
18. Jiang, F.; Wang, S.; Liu, B.; Liu, J.; Wang, L.; Xiao, Y.; Xu, Y.; Liu, X. Insights into the Influence of CeO₂ Crystal Facet on CO₂ Hydrogenation to Methanol over Pd/CeO₂ Catalysts. *Acs Catal.* **2020**, *10*, 11493–11509.
19. Zhang, B.; Ma, L.; Shen, J.; Tian, X.; Zhang, R.; Ding, M. Engineering of Metal–Support Interfaces and Cun-Ov Synergistic Sites in Cu/CeO₂ Catalyst for Enhanced Low-Temperature CO₂ Hydrogenation. *ACS Catalysis.* **2025**, *16*, 491–503.
20. Zhang, J.; Zhao, S.; Zhao, Y.; Ma, X.; Wang, S. Influence of Valence State of Cerium Ion on Dimethyl Carbonate Synthesis from Methanol and Carbon Dioxide over CeO₂. *Asia-Pac. J. Chem. Eng.* **2021**, *16*, e2517.
21. Yang, G.; Jia, A.; Li, J.; Li, F.; Wang, Y. Investigation of Synthesis Parameters to Fabricate CeO₂ with a Large Surface and High Oxygen Vacancies for Dramatically Enhanced Performance of Direct DMC Synthesis from CO₂ and Methanol. *Mol. Catal.* **2022**, *528*, 112471.
22. Zhang, G.; Zhou, Y.; Yang, Y.; Kong, T.; Song, Y.; Zhang, S.; Zheng, H. Elucidating the Role of Surface Ce⁴⁺ and Oxygen Vacancies of CeO₂ in the Direct Synthesis of Dimethyl Carbonate from CO₂ and Methanol. *Molecules* **2023**, *28*, 3785.
23. Laha, S.; Ryoo, R. Synthesis of Thermally Stable Mesoporous Cerium Oxide with Nanocrystalline Frameworks Using Mesoporous Silica Templates. *Chem. Commun.* **2003**, 2138–2139.
24. Honda, M.; Tamura, M.; Nakagawa, Y.; Nakao, K.; Suzuki, K.; Tomishige, K. Organic Carbonate Synthesis from CO₂ and Alcohol over CeO₂ with 2-Cyanopyridine: Scope and Mechanistic Studies. *J. Catal.* **2014**, *318*, 95–107.
25. Sun, W.; Li, P.; Yabushita, M.; Nakagawa, Y.; Wang, Y.; Nakayama, A.; Tomishige, K. Comparative Study between 2-Furonitrile and 2-Cyanopyridine as Dehydrants in Direct Synthesis of Dialkyl Carbonates from CO₂ and Alcohols over Cerium Oxide Catalyst. *ChemSusChem* **2023**, *16*, e202300768.
26. Xue, C.; Liu, L.; Si, Y.; Huang, Y.; Yang, S.; Xue, K.; Cheng, Y. High-Efficiency Direct Esterification of CO₂ and Methanol over Co-Doped CeO₂ Catalysts. *Ind. Eng. Chem. Res.* **2025**, *64*, 1152–1163.
27. Zhao, S.-Y.; Wang, S.-P.; Zhao, Y.-J.; Ma, X.-B. An in Situ Infrared Study of Dimethyl Carbonate Synthesis from Carbon Dioxide and Methanol over Well-Shaped CeO₂. *Chin. Chem. Lett.* **2017**, *28*, 65–69.
28. Yoshida, Y.; Arai, Y.; Kado, S.; Kunimori, K.; Tomishige, K. Direct Synthesis of Organic Carbonates from the Reaction of CO₂ with Methanol and Ethanol over CeO₂ Catalysts. *Catal. Today* **2006**, *115*, 95–101.
29. Wang, Y.; Moncada, J.; Sahoo, S.; Deng, K.; Chen, X.; Liu, P.; Zhu, H.; Bravo-Suárez, J.J.; Martínez-Arias, A.; Rodríguez, J.A. Transient Studies of CO₂ Adsorption over CeO₂ Nanostructures with In Situ DRIFTS and Modulation Excitation. *J. Phys. Chem. C* **2025**, *129*, 22363–22376.
30. Li, X.; Cao, L.; Jia, D.; Sun, Y. Direct Synthesis of Dimethyl Carbonate from Methanol and Carbon Dioxide over Co-Ce-Zr Ternary Metal Solid Solution. *Fuel Process. Technol.* **2024**, *266*, 108157.

31. Yue, Y.; Li, Y.; Wang, T.; Wang, S.; Han, L.; Du, C. Enhancement of Methanol Oxidation Performance over Pd/CeO₂ Derived from MOF and Mechanism Investigation via in Situ Studies. *Catal. Lett.* **2022**, *152*, 3437–3446.

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