Structure–Activity Relationships In Hydrothermally Synthesized CeO_2 Nanocatalysts For CO_2 Conversion To Dimethyl Carbonate

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The catalytic conversion of CO_2 into value-added chemicals is a major challenge in sustainable chemistry and Carbon Capture and Utilization (CCU) technologies. Among the possible approaches, the direct synthesis of dimethyl carbonate (DMC) from CO_2 and methanol is particularly attractive because DMC is a versatile compound employed in Li-ion batteries, fuel additives, pharmaceuticals, and polycarbonate production. However, the high thermodynamic stability of CO_2 and the equilibrium limitations associated with water formation still restrict DMC productivity, requiring the development of efficient catalytic systems and optimized reaction environments. Among them, ceria-based systems are particularly promising due to their chemical stability, redox properties, and easy regenerability under ambient conditions [1]. In recent years, various synthetic strategies have been developed to tune ceria morphology and increase defect density and oxygen vacancy concentration, key parameters for enhancing catalytic performance [2].

In this work, nanostructured CeO_2 catalysts were synthesized via hydrothermal methods using different cerium precursors and thermal treatments in order to investigate the correlation between morphology, defect structure, surface properties, and catalytic performance in DMC synthesis. CeO_2 prepared from cerium nitrate mainly formed nanorods (CeO_2-HT), while ammonium cerium nitrate produced aggregates of mesoporous nanoparticles (CeO_2-HT AN) characterized by higher surface area and increased structural disorder, as evidenced by TEM analysis (Figure 1). A non-calcined counterpart of the nanorod sample (CeO_2-HT NC) was also investigated to evaluate the influence of calcination on structural ordering and catalytic behavior.

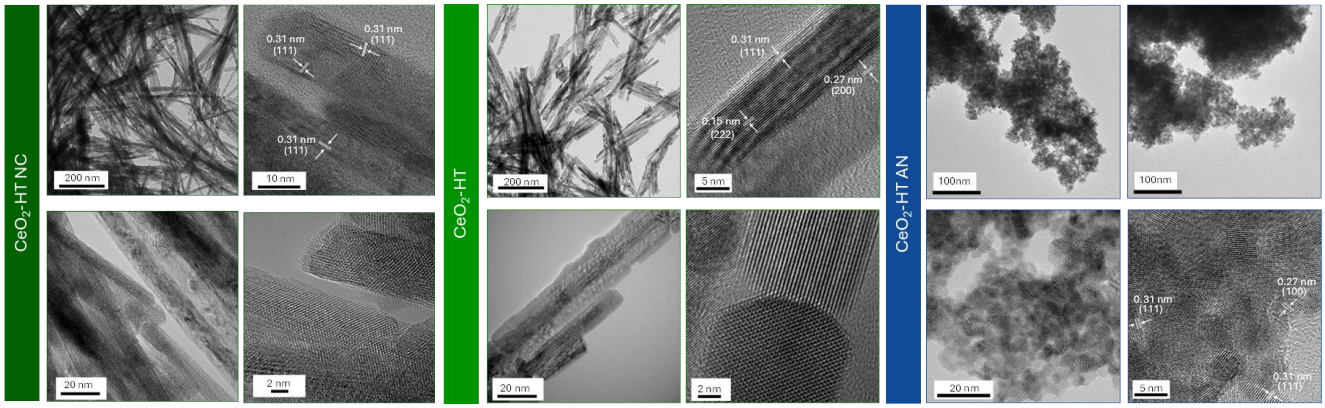

Figure 1- HRTEM micrographs of the CeO_2 samples

A comprehensive characterization approach combining powder X-ray diffraction (XRD), high-temperature XRD (HT-XRD), high-resolution transmission electron microscopy (HRTEM) coupled with electron energy loss spectroscopy (EELS), energy-dispersive X-ray spectroscopy (EDX), Raman spectroscopy, N_2 physisorption, X-ray photoelectron spectroscopy (XPS), and CO_2/NH_3 temperature-programmed desorption (TPD) was employed to investigate crystallinity, defect density, morphology, and acid–base surface properties. The non-calcined sample exhibited lattice expansion, broader Raman bands, and a higher density of structural

defects, while calcination promoted recrystallization and partial defect annealing, leading to improved crystallinity and enhanced catalytic activity. Conversely, CeO_2-HT AN displayed smaller crystallite sizes, higher surface area, and a mesoporous texture, highlighting the strong influence of precursor chemistry on the structural and textural properties of ceria nanomaterials.

Catalytic tests for DMC synthesis were carried out in a pressurized batch reactor both in the absence and in the presence of dehydrating agents. Catalytic tests show low activity without dehydrating agents (4–9 $mmol_{DMC}$ g_{cat}^{-1}), mainly due to thermodynamic limitations associated with CO_2 activation and water formation. The introduction of dehydrating agents markedly enhances DMC production (Figure 2), reaching 110–140 $mmol_{DMC}$ g_{cat}^{-1} with 2-cyanopyridine (2-CP) and 308–349 $mmol_{DMC}$ g_{cat}^{-1} with methyl trichloroacetate (MTCA).
The catalytic trend strongly depends on both the reaction environment and the surface properties of the catalysts. In particular, calcined CeO_2 nanorods (CeO_2-HT) exhibit the highest activity in the absence of dehydrating agents, whereas mesoporous nanoparticle-based catalysts (CeO_2-HT AN) become more efficient in the presence of 2-cyanopyridine (2-CP). The observed differences suggest the involvement of distinct reaction pathways and catalyst–dehydrating agent interactions, which significantly affect the overall DMC productivity.

In contrast, methyl trichloroacetate (MTCA) promotes a more favorable equilibrium shift toward DMC formation, resulting in markedly higher yields.

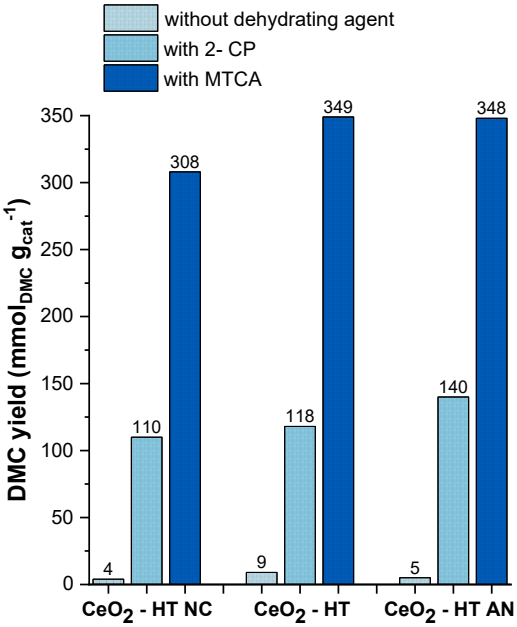

Figure 2- Catalytic results without and with dehydrating agents

The results demonstrate how precursor chemistry, microstructural features, and reaction environment synergistically affect catalytic performance, providing valuable insights into structure–activity relationships in ceria-based catalysts for sustainable CO_2 valorization.

REFERENCES

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