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Doctoral Dissertation  
Doctoral Program in Chemical Engineering (36<sup>th</sup> Cycle)

# **Direct conversion of carbon dioxide into diethyl carbonate on nanosized cerium-based catalysts**

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# Summary

The exponential rise in atmospheric CO<sub>2</sub> levels has drawn significant attention due to its role in global warming. Carbon capture and utilization technologies are recognized solutions to mitigate climate change, with organic carbonates, like diethyl carbonate (DEC), being of particular interest for their biodegradability and low toxicity. DEC is widely studied as a lithium-ion battery electrolyte and is used in pharmaceuticals, fertilizers, pesticides, and dyes. Its industrial production has shifted from harmful phosgenation to methods like liquid-phase oxycarbonylation of ethanol, ethylnitrite carbonylation, and ethanol transesterification with ethylene carbonate, but challenges such as corrosion, separation, and catalyst deactivation persist. Sustainable alternatives like the direct conversion of ethanol and CO<sub>2</sub> are emerging but face significant kinetic and thermodynamic barriers. Various catalysts have hence been investigated for this purpose and cerium-based catalysts have shown promise due to their bifunctional active sites, which activate both ethanol and CO<sub>2</sub>, and their morphology may further enhance reactant activation. However, understanding these catalyst properties remains complex but could lead to novel synthesis strategies to enhance their catalytic activity. Thus, this work aimed to first optimise the process conditions for DEC direct synthesis and then, through the combination of in situ FTIR and high-resolution TEM techniques, to gain a comprehensive understanding of the nature of the active species and investigate the role of the catalysts' textural properties and morphological features. To this end, nanosized cerium-based catalysts were synthesized, characterized and tested for the direct synthesis of DEC. Tests were carried out in an autoclave reactor to investigate the influence of various parameters, including catalyst loading, temperature, pressure, the amount of dehydrating agent, and the effectiveness of using 2-cyanopyridine as a dehydrating agent. DEC production reached a maximum at 130°C while at higher temperatures, the exothermic behaviour prevailed and an increase in the byproducts production was observed. Afterwards, catalysts were synthesized by precipitation (P) and hydrothermal (HT) synthesis techniques. Three distinct morphologies were achieved through the synthesis process. Nanoparticles (NP), nanocubes (C) and nanorods (R). The morphology highly influenced the properties of the catalysts such as the surface area and the amount of acidic and basic sites. Hydrothermally synthesized ceria cubes (HT2-CeO<sub>2</sub>-C), displaying the

lower surface area and lower amount of active sites, exhibited the lowest catalytic activity while rods (HT1-CeO<sub>2</sub>-R) showed improved performances. Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> with rod morphology and various Ce/Zr ratios were then tested to investigate the effect of the Zr doping on the catalyst activity since zirconium is an active component that can enhance the acidic properties of catalysts and it is well known for its thermal stability, maintaining its acidic properties at high temperatures. However, despite the Zr doping being effective in tailoring the number of acidic sites, the catalytic activity of Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> was lower than pure CeO<sub>2</sub>. This seems to imply that the catalyst basicity is more relevant than acidity. The stability of the rod CeO<sub>2</sub> catalyst was also investigated demonstrating almost constant performances after four cycles of reaction. The in situ FTIR study revealed that: (i) CO<sub>2</sub> primarily converts into bicarbonates and bidentate carbonates on both catalysts; (ii) a key difference in the ethanol activation mechanism was observed, with type I standing-up ethoxy species identified as the most reactive intermediate; (iii) during DEC adsorption and the exposure of ethanol pre-adsorbed ceria to CO<sub>2</sub>, signals indicating the formation of monoethyl carbonate intermediates were detected on the rod-shaped catalyst, while numerous unreacted species were observed on the cube-shaped CeO<sub>2</sub>. High-resolution TEM analysis was conducted to assess the impact of catalyst morphology on activity. The results showed that (i) the rod-shaped CeO<sub>2</sub> has a higher density of surface defects compared to the cube-shaped catalyst; (ii) these defects, generated during synthesis, were identified as surface voids and surface steps. Based on all these findings a reaction mechanism was hence proposed, where the high amount of surface defects is the main factor responsible for the highest activity of the rod-shaped cerium oxide catalysts through the fastest activation of intermediate species to form DEC. Finally, an initial approach to developing a continuous flow system was explored using the HT1-CeO<sub>2</sub>-R catalyst.