**CeO2 and CexZr1-xO2 for the direct synthesis of diethyl carbonate from CO2 and ethanol in presence of 2-cyanopyridine as dehydrating agent**

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**1.Introduction**

The exponential increase of carbon dioxide levels in the atmosphere has attracted a great attention because of its significant impact on global warming. The reduction of atmospheric CO2 concentration by carbon capture and utilization technologies is recognized as one of the possible solutions to mitigate the climate change. Among the various CO2 utilization paths, organic carbonates attract a great deal of interest because of their promising properties[1,2]. Short chain dialkylcarbonates, such as DMC or DEC, are gaining popularity as replacements for hazardous chemical reagents or reactive solvents. DEC is most extensively researched as an electrolyte for lithium-ion batteries. Being an excellent solvent, it is widely used in pharmaceutical products, fertilizer, pesticide and manufacture of dyes. The presence of ethoxy and carbonyl groups in DEC help in its conversion to important chemicals which include polycarbonates and carbamates. Furthermore, due to its high oxygen content (40.6 wt%), it has been proposed to replace the gasoline fuel additive MTBE (methyl tertiary-butyl ether)[3,4]. With the global phase-out of the harmful phosgenation processes, the ENIChem process (liquid-phase oxycarbonylation of EtOH), the UBE process (ethylnitrite carbonylation) and the Texaco process (transesterification of EtOH and ethylene carbonate) have been successively transferred to the industrial scale for the production of DEC[4,5]. However, the corrosion, separation and catalyst deactivation remain bottlenecks of these processes despite recent significant improvements[6]. On the other hand, new synthetic routes are put forward under the framework of sustainable developments for the DEC synthesis, such as the alcoholysis of urea [7] and the direct conversion of ethanol and CO2 [8–11]. However, the direct synthesis is extremely constrained by kinetics and thermodynamic limitations, hence, great efforts have been made to overcome these issues. A wide range of homogeneous and heterogeneous catalysts have been tested for this purpose. Heterogeneous catalysts are more suitable from the viewpoint of the easier separation of the catalyst from the products. Ceria (CeO2), zirconia (ZrO2) and ceria-zirconia (CexZr1-xO2) mixed oxides have extensively studied as catalysts for direct DEC synthesis because of the bifunctionality of their active sites[9,10,12,13]. To shift the equilibrium and improve product yields, dehydrating agents such as orthoesters, and molecular sieves have been explored for the direct synthesis route. Nevertheless, nitriles were more effective as they are efficiently hydrated by CeO2. Furthermore, water capture with nitriles leads to amides, which can later be converted back to the corresponding nitrile and enable the regeneration of the dehydrating species[14,15].

In this work CeO2 and CexZr1-xO2 catalysts with different morphologies and various Ce/Zr ratio were synthesized and tested, coupled with 2-cyanopyridine (2-CP) as dehydrating agent, for the direct synthesis of DEC from ethanol and CO2 with the aim of developing a process which can operate at mild conditions of moderate temperature and pressure.

**2. Methods**

CeO2 and CexZr1-xO2 catalysts were prepared by the precipitation, hydrothermal and sol-gel methods and characterized by various techniques, such as N2-adsorption (BET-SA), XRD, FE-SEM, CO2-TPD and NH3-TPD analyses.

Tests were carried out in a laboratory scale autoclave reactor with an inner volume of 310 mL. A known amount of catalyst, dehydrating agent and ethanol were charged, the reactor was then purged three times with CO2 at room temperature. The reaction system was then pressurized up to 2 MPa with CO2. After a stabilization time, required for the CO2 dissolution in ethanol, the reactor was then heated to the desired temperature and mechanically stirred constantly for a given time. Finally, the reactor was cooled to about room temperature and depressurized. The catalyst was then separated by filtration and the reaction mixture was analysed by GC-MS.

**3. Results and discussion**

The scanning electron micrograph was used to determine the morphology of the synthesized CeO2 and   
CexZr1-xO2 catalyst. Three types of morphologies were obtained: cubes, octahedra and rods. The morphology highly influenced the properties of the catalysts such as the amount of acidic and basic sites. Ceria cubes exhibited the lowest catalytic activity while octahedra and rods showed better performances.

The addition of a dehydrating agent was crucial to enhance the process yield. Furthermore, an increase in the quantity of 2-CP increased the selectivity.

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