Design of Ceria-based Catalysts via Self-Combustion Approaches for CO_2 Conversion to Dimethyl Carbonate

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Significance and Relevance

The sol-gel self-combustion synthesis (SC) or its combination with an impregnation strategy has allowed the obtaining of cerium oxide based catalysts used for the chemical conversion of CO_2 into dimethyl carbonate (DMC). The different structural and textural properties obtained allowed us to study the effect on the catalytic performance of nanoparticle shape anisometry in a case, and the homogeneous dispersion of the active phase on a mesostructured support with high surface area (SBA-15) in the other. These synthetic strategies are new to obtain catalysts for direct synthesis of DMC from CO_2 and methanol.

Preferred presentation: Oral only

Introduction and Motivations

At present, a key challenge in addressing greenhouse gas emissions is the development of technologies for capturing CO_2 and converting it into value-added products, a process known as Carbon Capture and Utilization (CCU). Among the various approaches, the direct synthesis of DMC offers a promising and sustainable method to convert CO_2 into a valuable eco-friendly solvent with applications in energy storage, such as lithium-ion batteries, and industrial chemistry: in dyes, pharmaceuticals and polycarbonates production. While various synthetic pathways exist for DMC production, many still rely on toxic and hazardous substances, such as phosgene, which poses significant health and environmental risks. This has driven research towards greener, more sustainable alternatives, with the direct synthesis from CO_2 and methanol emerging as the most attractive option. However, due to CO_2's kinetic inertness and thermodynamic stability, the process requires efficient catalysis. Ceria-based systems have emerged as particularly promising catalysts for this application, thanks to their chemical stability, redox properties, easy regenerability and storage under air conditions. In recent years, numerous synthetic methodologies have been used to obtain ceria systems having different morphologies, with the aim of increasing the defects and oxygen vacancies which are key parameters for improving their catalytic performance. For this reason, the self-combustion method (SC) was selected as it is fast (2-3 hours), green, scalable and allows to obtain platelet anisometric ceria nanoparticles. While, the combination of SC method with an impregnation strategy had the goal of reducing the amount of cerium used in the catalyst considering that it is a critical raw material and expensive.

Materials and Methods

Low porosity CeO_2 was prepared through SC synthesis and highly porous ordered CeO_2@SBA-15 nanocomposite was obtained by impregnation combined with SC method, with a final loading of 20 wt% CeO_2. In addition, as a reference, CeO_2 nanorods were prepared by hydrothermal synthesis (HT), the most promising systems proposed in the literature for the presence of oxygen vacancies due from their anisometric shape. The as-obtained catalysts were characterized using powder X-ray diffraction (XRD), Transmission electron microscopy (Conventional TEM, HRTEM, STEM-EDX), N_2-physisorption. In some cases, Raman spectroscopy, Electron paramagnetic resonance spectroscopy (EPR) and CO_2/NH_3 temperature-programmed desorption (CO_2/NH_3-TPD) measurements were performed. The direct synthesis of DMC was carried out in a batch reactor with a volume of 100 mL and GC-MS was used to evaluate the DMC formation.

Results and Discussion

The various synthetic strategies led to the obtainment of ceria-based systems with different microstructures and textures. More specifically, the following values of crystallite size and specific surface area were observed: ≈6 nm and 80 m^2/g for the CeO_2_SC sample, ≈8 nm and 622 m^2/g for the CeO_2@SBA-15 nanocomposite, ≈21 nm and 80 m^2/g for the CeO_2_HT sample. All catalysts showed catalytic activity for the direct synthesis of DMC. The CeO_2_SC sample showed a slightly higher DMC yield (1.6 $mmol_{DMC}\ g_{cat}^{-1}$) than the CeO_2@SBA-15 nanocomposite (1.4 $mmol_{DMC}\ g_{cat}^{-1}$), and the reference (CeO_2_HT), showed the best catalytic performances (3.8 $mmol_{DMC}\ g_{cat}^{-1}$). The better catalytic performances obtained of the CeO_2_HT sample compared to the CeO_2_SC catalyst are due to the fact that the CeO_2_HT sample has a higher concentration of oxygen vacancies and a lower concentration of strong basic sites. This result highlights how these key parameters have an important role in the direct synthesis of DMC. On the other hand, the CeO_2@SBA-15 nanocomposite showed the worse catalytic performance, due to its lower amount of active phase (20%). By normalizing the catalytic activity as a function of the active phase of the catalyst, however, it can be noticed how the CeO_2@SBA-15 composite shows the best performance (7.0 $mmol_{DMC}\ g_{act.ph.}^{-1}$) compared to the pure ceria samples, presumably due to the fine dispersion of the active phase throughout the mesostructured matrix, leading to a high exposed area of the active phase. This result highlights that the homogeneous dispersion of ceria on SBA-15 through proper impregnation strategy (CeO_2@SBA-15) could be a promising approach to design efficient catalysts. In addition, the effect of dehydrating agents is under study. In fact, the in *situ*-water removal due to the addition of dehydrating agents to the reaction involves the shift of the chemical equilibrium towards a greater conversion of methanol with a consequent increase in the yield of DMC.

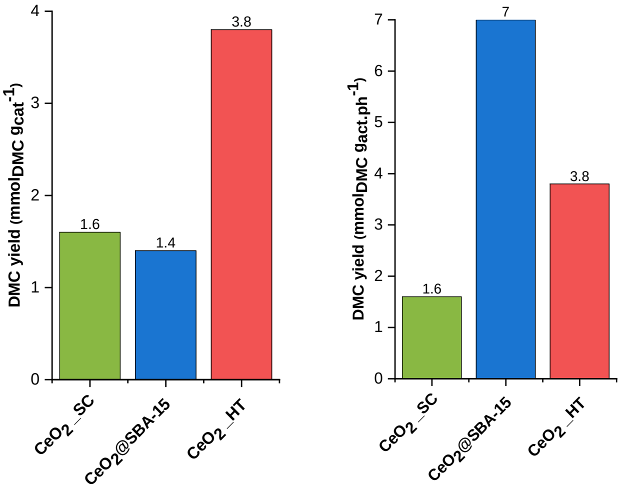

Figure 1. DMC yield (sx), DMC yield normalized as a function of active phase (dx)