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Synthesis and characterization of ceria-supported catalysts for carbon dioxide transformation to diethyl carbonate

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ABSTRACT

The support materials Al₂O₃, SiO₂ and TiO₂ were modified with 16 wt% CeO₂, using two different preparation methods evaporation-impregnation and precipitation-deposition. The synthesized 16 wt% CeO₂-Al₂O₃, 16 wt% CeO₂-SiO₂ and 16 wt% CeO₂-TiO₂ materials were characterized by means of X-ray powder diffraction for the phase purity, scanning electron microscopy for the morphology, nitrogen physisorption to determine the specific surface area and X-ray photo electron spectroscopy for the oxidation state of the Ce in the TiO₂, Al₂O₃ and SiO₂ matrices. Transmission electron microscopy was used to study the particle size of CeO₂ whereas CO₂-temperature programmed desorption (TPD) was used to determine the basicity of ceria-modified TiO₂, Al₂O₃ and SiO₂ catalysts. Furthermore, the catalytic performance of the as prepared CeO₂-modified catalysts were compared in the synthesis of diethyl carbonate starting from ethanol and CO₂ using butylene oxide as the dehydrating agent. The physico-chemical characterization results were correlated with the catalytic activity results and discussed in detail.

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1. Introduction

Over the past few decades, rare-earth oxides have gained substantial attention and have been widely investigated as structural and electronic promoters to improve the activity, selectivity and thermal stability of catalysts. Undoubtedly, cerium oxide (CeO₂) is the most significant one of rare-earth element oxides in the industrial catalysis owing to its unique structural, redox and acid-base properties [1]. Due to the high oxygen storage capacity arising from the ability to be easily and reversibly reduced, ceria has become a key component in the three way catalysts (TWC) [1,2]. Simultaneously, ceria provides key features that are utilized in the most efficient route to reduce pollutants released from automotive exhaust gases. Moreover, cerium oxide finds use in a wide range of other applications and is applied as UV absorbents and filters [3], glass polishing material [4], oxygen ion conductor in solid oxide fuel cells (SOFCs) [5], catalytic wet oxidation catalyst [6], NO

removal catalyst [7] as well as being an important catalyst support and promoter [8–10].

Frequently, supported-catalysts are given preference over the individual components due to their combined and comprehensive properties which enable to overcome the shortcomings of the single phase materials. Since cerium oxide exhibits rather low specific surface area, its dispersion on the high specific surface area supports such as SiO₂, Al₂O₃ and/or TiO₂ could represent a suitable way of enhancing the amount of the active sites available for the reaction and, at the same time, stabilize the structural/textural and acid-base properties of CeO₂. Numerous studies on ceria dispersed on SiO₂ and Al₂O₃ have been conducted whereby the thermal durability of alumina and silica played an important role in case of processes performed at high temperatures. Examples thereof include gas purification, high temperature hydrogen separation as well as catalytic membrane reactors [11–15]. In turn, titanium oxide finds broad application in heterogeneous catalysis as a catalyst and catalyst support [16]. Besides anatase phase, TiO₂ can also be present as rutile and brookite phases, depending on the synthesis method and calcination temperature. It was demonstrated that introduction of refractory modifiers such as cerium oxide improves resistance to thermal loss and stabilize the active phase of TiO₂ in

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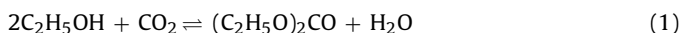
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CuO/Ce-TiO₂ catalysts for the oxidation of CO, ethanol, ethyl acetate [17] and in NO + CO reduction [18].

This study, however, was focused on in-house synthesis and characterization of ceria-based catalysts supported on silica, alumina and titanium oxide applying different synthesis methods and varying ceria loading and calcination temperature. The catalytic activities of prepared materials were compared in the reaction of carbon dioxide transformation to diethyl carbonate (DEC).

DEC is an important homologue in the family of dialkylcarbonates possessing eco-friendly features such biodegradability to ethanol and carbon dioxide. Moreover, the fact that it can be prepared from bioethanol gives a “bio-derived” label to DEC and all the processes in which it is applied. DEC is used in a variety of applications such as a raw material upon manufacturing of polycarbonates, an intermediate for various pharmaceuticals, an electrolyte in lithium ion batteries and as an alternative to ethyl halides and phosgene in ethylation and carbonylation processes [19,20]. Furthermore, DEC is also considered as a promising replacement for methyl-*tert*-butyl ester (MTBE) as an attractive oxygen-containing fuel additive due to its high oxygen content (40.6%). Conventional synthesis method of DEC involves the use of extremely poisonous phosgene [21] and, therefore, considerable effort has been devoted to the development of alternative technologies such as transesterification of methanol [22], oxidative carbonylation of ethanol [23], carbonylation of ethyl nitrite [24], reaction of ethanol with urea [25] and decarbonylation of diethyl oxalate [26]. Nevertheless, the practical application of these non-phosgene routes is still restricted due to several disadvantages such as the toxicity of carbon monoxide and ethyl nitrite, deactivation of the catalysts and low product yields.

Recently, global warming and successive climate change have gained much attention gathering scientists and engineers from the academia and industry on seeking for new ideas of mitigation of greenhouse gases from the Earth's atmosphere. Carbon dioxide has been considered to be the most prominent greenhouse gas. Therefore, it is not surprising that transformation of CO₂ to other value-added chemicals is today a subject of intensive studies from the standpoint of the environment protection. New technologies such as diethyl carbonate synthesis via a direct route starting from inexpensive and non-toxic ethanol and CO₂ is certainly an attractive approach (Eq. (1)). It should be, however, emphasized that during the last years dimethyl carbonate (DMC) and not diethyl carbonate, has been the main subject of studies in the industry and academia. Therefore, this work has been entirely devoted to the synthesis of diethyl carbonate over in-house made supported ceria catalysts.



Thermodynamic calculations of direct synthesis of DEC revealed that the reaction is exothermic ($\Delta_r H_{298\text{K}} = -16.60 \text{ kJ/mol}$) and does not occur spontaneously under normal conditions ($\Delta_r G_{298\text{K}} = +35.85 \text{ kJ/mol} > 0$) [27]. Moreover, the carbonate synthesis is accompanied with water release (Eq. (1)) which easily shifts the reaction equilibrium towards the reactants. Thus, *in situ* dehydration in direct carbonylation of ethanol could be a powerful methodology to reach an enhanced production of the desired product. The yield of DEC approaching 42% (based on CO₂) was achieved after 24 h reaction time at 423 K and 0.2 MPa of CO₂ pressure applying acetonitrile as the chemical water trap [28]. In addition, a flow reactor was coupled with a pervaporation membrane in order to decrease water content and increase the conversion of ethanol from 0.9 up to 2.3%, resulting in relatively pure DEC (>90%) [29]. Our previous studies, in turn, demonstrated a 9-fold enhancement in the yield of DEC using butylene oxide as the dehydrating agent, in comparison to the synthetic method without any water removal over commercial ceria [27].

Up to date cerium oxide is one of the most studied catalyst in the synthesis of dimethyl and diethyl carbonate [30–32] and it has been identified that basic sites are the active sites in the synthesis of DEC. Also, ceria-zirconia (Ce_xZr_{1-x}O₂) mixed oxides with tunable Ce/Zr ratios were investigated and it was demonstrated that Ce_xZr_{1-x}O₂ (x = 1) exhibited the highest activity towards DEC followed by Ce_xZr_{1-x}O₂ (x = 0.7). This could be attributed to the strong dependence of catalytic properties of Ce_xZr_{1-x}O₂ on the crystal structure and the acid-base sites on the surface with varied Ce/Zr ratios. [33]. Additionally, a highly efficient approach was demonstrated in one-pot synthesis of DEC starting from ethanol, ethylene oxide and CO₂ over KI-based binary catalytic system yielding 63.6% of DEC at 443 K and 3 MPa of CO₂ initial pressure [34]. Moreover, it was shown that 3–10 wt% loading of ceria on alumina with respect to pure ceria prolongs the life-time of the catalyst and improves both the catalytic performance as well as the selectivity towards dimethyl carbonate [8].

Nevertheless, none of the currently available reports in the open literature discuss the one-pot synthesis of DEC starting from CO₂, ethanol and butylene oxide over ceria-supported onto SiO₂, Al₂O₃ and TiO₂ materials. Hence, in this work, the influence of synthesis method of SiO₂, Al₂O₃ and TiO₂ supported ceria catalysts, ceria loading and calcination temperature on the physico-chemical properties of the resulting catalyst was for the first time correlated to the catalytic activity of these materials in DEC synthesis. Since solid base catalysts are preferred over acid catalysts in the synthesis of this linear carbonate particular attention has been paid to the basicity of prepared composites.

2. Experimental

2.1. Catalyst preparation

Catalysts were prepared using SiO₂ (Merck), Al₂O₃ (UOP Versal VGL-25) and TiO₂ (Alfa Aesar) as supports. The support materials were ball-milled and sieved to obtain a particle size smaller than 63 μm. An aqueous solution of cerium (III) nitrate hexahydrate (Sigma Aldrich 99.0%) was used as a ceria precursor. The samples were synthesized applying evaporation-impregnation and deposition-precipitation methods.

In line with the evaporation-impregnation method, 10 g of the metal oxide support materials were added to the solution of the desired amount of cerium (III) nitrate hexahydrate in 250 ml of distilled water. The solution was stirred in a rotary-evaporator for 24 h at 60 °C and, subsequently, water was evaporated under vacuum. The catalyst was dried overnight at 100 °C and calcined at the pre-determined temperature for 3 h.

Upon preparation of the supported CeO₂ catalysts via deposition-precipitation method, 1 M aqueous solution of cerium (III) nitrate hexahydrate was prepared and pH of the solution was adjusted to 11 by the addition of ammonium hydroxide (NH₄OH) (Sigma-Aldrich, ACS reagent 28.0–30.0%). The support material was added and the suspension was kept under continuous stirring for 50 h, at room temperature. Afterwards, the suspension was filtered, washed with water, dried overnight at 100 °C and calcined at the specified temperature for 3 h.

2.2. Catalyst characterization

The structural properties of the support materials and ceria-supported catalysts were investigated by Philips X'Pert Pro MPD X-ray powder diffractometer. The diffractometer was operated in Bragg-Brentano diffraction mode and the monochromatized Cu-Kα radiation was generated with a voltage of 40 kV and a current of 50 mA. The measured 2θ angle range was 3.0°–75.0°, with a step

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