



Full Length Article

The preparation and efficacy of SrO/CeO₂ catalysts for the production of dimethyl carbonate by transesterification of ethylene carbonate

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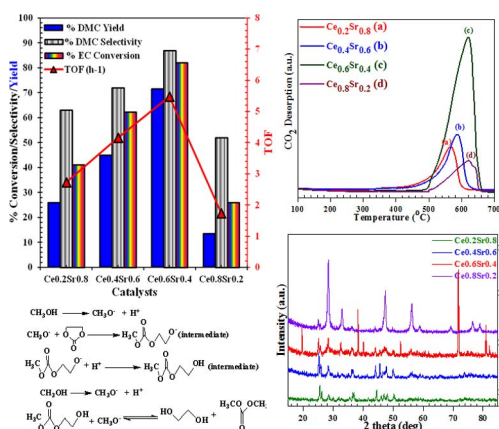
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GRAPHICAL ABSTRACT



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ABSTRACT

The need for eco-friendly fuels has given a fillip to search for new molecules and their cost-effective synthesis. A series of ceria-strontium ($\text{Ce}_x\text{Sr}_{1-x}\text{O}_2$; $x = 0$ to 1) catalysts were prepared by a citric acid assisted sol-gel method. These catalysts were characterized by BET, XRD, SEM-EDAX, ICP-MS, FTIR, NH_3 -TPD and CO_2 -TPD techniques and tested for the synthesis of dimethyl carbonate (DMC) in a batch reactor for the transesterification of ethylene carbonate (EC). The activity of the synthesized catalysts was found to be closely related to basic and acidic sites, and the surface area of the catalysts. The catalyst, $\text{Ce}_{0.6}\text{Sr}_{0.4}$, showed highest basicity and acidity, and was found to be most effective in the formation of DMC from transesterification of EC. Reactions were carried out by varying the particle size (50–800 μm) and agitation speed (200–600 rpm) for minimizing the internal mass transfer resistance and the external mass transfer resistance, respectively. Further, $\text{Ce}_{0.6}\text{Sr}_{0.4}$ catalyst was used to optimize the reaction conditions such as methanol/EC molar ratio (in the range of 4–12), catalyst dose (in the range of 2–5 wt% of EC), reaction time (in the range of 2–6 h) and temperature (in the range of 100–180 $^\circ\text{C}$) for DMC yield and EC conversion. At the optimum conditions of methanol/EC molar ratio of 8,

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3 wt% of catalyst, 5 h reaction time and 150 °C temperature, the DMC selectivity was 87% and EC conversion of 82%, with a reaction rate of ~ 0.547 mol/L.h (with respect to EC). The reusability of the $\text{Ce}_{0.6}\text{Sr}_{0.4}$ catalyst for EC conversion with turn-over frequency and DMC selectivity were also studied.

1. Introduction

Dimethyl carbonate (DMC) is widely used in the green chemical industry due to its versatility and unique physico-chemical properties. It is used as an additive in gasoline and for the replacement of methyl tert-butyl ether (MTBE) due to its high octane number, good blending properties, low toxicity and rapid biodegradability [1–6]. More importantly, DMC is a promising and environmentally friendly alternative for dimethyl sulphate and phosgene in methylation and carbonylation reactions, respectively. It is also used as a solvent for the synthesis of various organic compounds such as polyurethane, glycerol carbonate, diphenyl carbonate, polycarbonate and lithium batteries [7–13]. Traditionally, DMC was synthesized by phosgenation, oxidative carbonylation, and methyl nitrite process [2,14–17]. The phosgenation of methanol is now abandoned due to the toxicity and the formation of hazardous by-products. Currently, DMC is predominantly produced using methanol oxidative carbonylation and methyl nitrite processes. These methods also suffer from low productivity and the formation of carbon monoxide, nitric oxide and hydrogen chloride [2]. Some other pathways such as urea methanolysis, transesterification of ethylene carbonate (EC) or propylene carbonate with methanol and direct syntheses from CO_2 are also used for DMC production [18–21]. These processes are, however, in the developmental stage. Transesterification of EC with methanol is a promising method for DMC synthesis due to high EC conversion and DMC yield, no waste formation and non-corrosive nature. In this transesterification reaction, only ethylene glycol (EG) is formed as a by-product. Moreover, EC is available cheaply and abundantly enough to be a realistic feed for the production of DMC as a fuel additive.

Various types of catalysts have been investigated for the transesterification of EC in the presence of methanol in heterogeneous or homogeneous reaction phases for DMC production such as double metal cyanide [22], hydrotalcite [23,24], ionic liquid [25,26], pure metal oxides and mixed metal oxides [13,27], polymers [28], tungstate-based catalyst [29], etc. The comparative performances of various catalysts for DMC production is shown in Table 1 [23,30–33]. Yang et al. [31] reported 97% selectivity and 77% DMC yield with methanol/EC molar ratio of 8 at 70 °C after 3 h reaction time. Xu et al. [33] reported the use of mesoporous ceria for the EC conversion of 76% and DMC selectivity of 96% with methanol/EC molar ratio of 10 at 140 °C after 2 h. Wang

et al. [34] reported 55% EC conversion and 54% DMC yield with methanol/EC molar ratio at 65 °C 8 after 1 h using zinc-yttrium oxides catalyst. Abimanyu et al. [35] reported 56% DMC yield and 67% EC conversion. These studies showed that the basic functionalities and surface acidic properties play major roles in the EC transesterification reaction. The disadvantages of many of these catalysts for DMC formation are the formation of large amount of by-products, longer reaction time, low reusability, usage of large amount of solvent and high reaction temperatures.

Ceria is the most important rare earth oxide due to its pair of acidic/basic sites and redox properties. Ceria has most extensively been used in various applications such as water-gas shift, oxidative coupling of methane, low-temperature CO oxidation, three-way-catalyst for exhaust treatment, methane steam reforming, partial oxidation of palm fatty acids, steam reforming of palm fatty acid, etc. [36–41]. Cerium-strontium mixed oxide based catalysts have good chemical stability and the basicity-acidity which are responsible for the EC transesterification for DMC synthesis.

To the best of the author's knowledge, cerium-strontium oxide catalysts have not yet been reported for the EC transesterification for the synthesis of DMC and propylene glycol. In the present study, a series of cerium-strontium composite oxide catalysts were prepared by citric acid assisted sol-gel method. The prepared cerium-strontium oxide catalysts have been characterized by their composition using inductively coupled plasma optical emission spectroscopy (ICP-OES). Further characterization was carried out using N_2 -sorption, X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and the scanning electron microscopy (SEM). The acidity/basicity was investigated by temperature-programmed desorption of NH_3/CO_2 . The best catalyst was further used for optimizing reaction parameters such as methanol/EC molar ratio, catalysts dose (wt% of EC), reaction temperature/time and the reusability of the catalyst.

2. Materials and methods

2.1. Materials

Cerium nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6 \text{H}_2\text{O}$), strontium nitrate Sr ($\text{NO}_3)_2$ and citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$) (Hi-media Chemicals, India), ammonia solution (25 wt% in H_2O), methanol and ethanol (Renkem,

Table 1
Catalysts used in the literature for the synthesis of DMC by transesterification of EC with methanol at various reaction conditions.

Catalyst	Condition	Dose of catalyst (wt% of EC)	Reaction Time (h)	Reaction Temp. (°C)	% EC Conversion	% Selectivity/Yield*	References
K_2CO_3	Methanol/EC = 4 @ CO_2 atmosphere	2.5	1.5	140	73	25*	[30]
Al_2O_3	Methanol/EC = 8	5	3	70	–	29/5*	[31]
$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$	Methanol/EC = 10 @ CO_2 atmosphere	2.5	5	150	82	71*	[29]
Mg–Al (HTLc)	Methanol/EC = 4 @ N_2 atmosphere	3.0	3	70	58	83	23
Mg–Al (HTLc)/ NH_4^+ , Na^- and K^-	Methanol/EC = 4	10	6	70	–	60	[32]
CeO_2 -Com	Methanol/EC = 10	4.0	2	140	23.6	11.9*	[33]
CeO_2 -meso-400	Methanol/EC = 10	4.0	2	140	76.3	73.3*	[33]
$\text{Ce}_{0.2}\text{Sr}_{0.8}$	Methanol/EC = 8	3.0	5.0	150	41.1	63/26*	This work
$\text{Ce}_{0.2}\text{Sr}_{0.8}$	Methanol/EC = 8	3.0	5.0	150	62.4	72/45*	This work
$\text{Ce}_{0.2}\text{Sr}_{0.8}$	Methanol/PC = 8	3.0	5.0	150	71.5	87/71.5*	This work
$\text{Ce}_{0.2}\text{Sr}_{0.8}$	Methanol/PC = 8	3.0	5.0	150	13.6	52/15.6*	This work

EC: Ethylene carbonate.

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