



Short communication

# Synthesis and characterization of Ce–La oxides for the formation of dimethyl carbonate by transesterification of propylene carbonate



Praveen Kumar, Vimal Chandra Srivastava\*, Indra Mani Mishra

Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee 247667, Uttarakhand, India

## ARTICLE INFO

## Article history:

Received 6 October 2014

Received in revised form 5 November 2014

Accepted 7 November 2014

Available online 14 November 2014

## Keywords:

Dimethyl carbonate

Propylene carbonate

Transesterification

Ce/La catalysts

## ABSTRACT

A series of cerium–lanthanum catalysts prepared using the co-precipitation method were investigated for transesterification of propylene carbonate (PC) with methanol to produce dimethyl carbonate (DMC). Synthesized catalysts were characterized by XRD, CO<sub>2</sub>- and NH<sub>3</sub>-TPD, N<sub>2</sub> adsorption/desorption and SEM–EDX techniques. Studies were carried out to study the effect of reaction conditions such as methanol/PC molar ratio (4–12), catalyst dose (2–10 wt.% of PC), reaction time (2–10 h) and temperature (140–180 °C) on the DMC yield. Highest PC conversion and DMC yield of 72% and 74%, respectively, were observed with catalysts having a 1:4 Ce/La molar ratio.

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## 1. Introduction

Dimethyl carbonate (DMC) is considered as an environmental friendly green chemical and is widely used in the synthesis of polymers, pesticides, flavoring agents, foodstuff, solvents, dyestuff and composite materials [1]. DMC contains higher oxygen content (53.3%) as compared to methanol (50%), ethanol (34.89%) and methyl tert-butyl ether (MTBE) (17.6%), and is consequently used as an oxygenate in gasoline based fuels [1]. Various methods such as are phosgenation, oxidative carbonylation of methanol, direct syntheses from CO<sub>2</sub> and transesterification of cyclic carbonate and from reaction of urea with methanol can be used for the synthesis of DMC [1–6]. DMC synthesis by transesterification of propylene carbonate (PC) with methanol in the presence of catalyst is an environmentally benign synthesis route as compared to other routes and has gained a lot of research attention [7,8].

Some catalysts such as tungstate-based catalysts [9], double metal cyanide [10], hydrotalcite [11], oxides and mixed oxides [12,13] have been investigated previously for the synthesis of DMC by transesterification reaction (Table 1). It may be seen that mixed oxides of metals Ce and La have been used previously individually or in combination with other metals, however, mixed oxides of Ce and La together have not been used for DMC synthesis. Few authors have previously synthesized ceria–lanthanum based catalysts for various other applications (Table S1).

In the present study, Ce–La mixed oxide catalysts (with different ratios of cerium and lanthanum) have been synthesized by the co-precipitation method and characterized by various techniques. Catalytic

performance of these synthesized catalysts was further tested for the transesterification of PC with methanol to produce DMC and propylene glycol (PG) as a co-product. The effects of molar ratio of methanol/PC, catalyst dose, reaction time and temperature have been studied for all the synthesized catalysts.

## 2. Experimental

## 2.1. Catalyst preparation and characterization

Ceria and lanthanum oxide solid solution were synthesized with different Ce/La molar ratios (0.2; 0.4; 0.6; and 0.8) by the co-precipitation method using liquid ammonia solution as a precipitated agent. First, cerium and lanthanum precursors namely Ce(NO<sub>3</sub>)<sub>3</sub>·6 H<sub>2</sub>O and La(NO<sub>3</sub>)<sub>3</sub>·6 H<sub>2</sub>O, respectively, were dissolved separately in 100 mL double distilled water with a given molar ratio and mixed together under continuous stirring at room temperature. Liquid ammonium solution was added drop-wise in mixed metal solution over a period until the pH reached at ~8.5. The obtained light yellow/orange color slurry was washed several times with double distilled water until it was free from anion impurities. The obtained precipitate was dried at 120 °C in air atmosphere for 24 h and calcined at 500 °C for 4 h in air atmosphere to obtain the ceria/lanthanum mixed oxides.

Catalysts were characterized by X-ray diffraction (XRD), energy dispersive X-ray (EDX), field emission scanning electron microscope (FE-SEM), Barrett–Joyner–Halenda (BJH), Brunauer–Emmett–Teller (BET) and CO<sub>2</sub>/NH<sub>3</sub>-temperature programmed desorption (TPD). Details of characterization methods and instruments are given in the Supporting information.

\* Corresponding author. Tel.: +91 1332 285889; fax: +91 1332 276535.  
E-mail addresses: [vimalcsr@yahoo.co.in](mailto:vimalcsr@yahoo.co.in), [vimalfch@iitr.ac.in](mailto:vimalfch@iitr.ac.in) (V.C. Srivastava).

**Table 1**  
Comparative study of transesterification of PC with methanol using different solid catalysts.

Catalyst	Reaction time (h)	Reaction temp. (°C)	% PC conversion	% DMC yield/selectivity*	% PG yield	Reference
Mg–Al–La	2.0	150	65.4	88*	–	[11]
Mg–Al–Ce	1.0	150	20.4	79.8*	–	[11]
TiO <sub>2</sub>	6.0	140	22	15	–	[12]
Fe-promoted TiO <sub>2</sub>	6.0	140	0	–	–	[12]
MgO	6.0	140	55	15	–	[12]
ZrO <sub>2</sub>	6.0	140	14	50	–	[12]
CeO <sub>2</sub>	6.0	140	33	30	–	[12]
Au/CeO <sub>2</sub>	6.0	140	63	55	–	[12]
Ce <sub>0.2</sub> La <sub>0.8</sub>	6.0	170	74	74	45	This work
Ce <sub>0.4</sub> La <sub>0.6</sub>	6.0	170	67	59	49	This work
Ce <sub>0.6</sub> La <sub>0.4</sub>	6.0	170	59	49	51	This work
Ce <sub>0.8</sub> La <sub>0.2</sub>	6.0	170	43	36	56	This work

PC = propylene carbonate; methanol/PC molar ratio = 10; \*Selectivity.

## 2.2. Catalytic activity

Synthesis of DMC using the transesterification of the PC and methanol was carried out in a stainless-steel autoclave reactor with different moles of PC and methanol and with different wt.% of the catalysts for the reaction. Product mixture was cooled down at room temperature and the catalyst was separated by centrifugation. Thereafter, the liquid reaction products were analyzed by gas chromatograph (Perkin Elmer) equipped with a flame ionization detector (FID) with elite wax capillary column.

## 3. Results and discussion

### 3.1. Characterization of the catalyst

#### 3.1.1. Structural analysis

Scanning electron microscopy studies were carried out so as to study the morphology of the synthesized catalysts (Fig. S1). Synthesized Ce<sub>0.8</sub>La<sub>0.2</sub> catalysts show spherical morphology with size of the crystal being 20–30 nm. All other catalysts have a nanorod shape with length varying in the range of 50–300 nm. EDX elemental mapping (Fig. S2) shows even distribution and homogeneous dispersion of Ce and La in all synthesized catalysts. EDX of catalysts (Table 2) showed the presence of the cerium, lanthanum and oxygen in all the catalysts.

Synthesized Ce<sub>x</sub>La<sub>1-x</sub>O<sub>2-δ</sub> (x = 0.2; 0.4; 0.6 and 0.8) are presented in Fig. S3. The XRD patterns of Ce<sub>x</sub>La<sub>1-x</sub> (x = 0.4, 0.6, and 0.8) exhibit peaks at 2θ = 28°, 33°, 46°, 55°, 58°, 68° and 75°, corresponding to the (111), (200), (220), (311), (222), (400) and (331) planes of face-centered cubic (fcc) structure, respectively. These reflections indicate the presence of cubic fluorite structure of CeO<sub>2</sub> (JCPDS No. 810792) phase only. No reflections corresponding to La<sub>2</sub>O<sub>3</sub> were observed in these three catalysts Ce<sub>x</sub>La<sub>1-x</sub> (x = 0.4, 0.6, and 0.8). Wang et al. [14] also reported the absence of La oxides in Ce–La mixed samples for La content as high as 75%. Ce<sub>0.2</sub>La<sub>0.8</sub> showed a minor reflection of hexagonal close-packed (hcp) structure of La<sub>2</sub>O<sub>3</sub> (JCPDS No. 401284) phase along with CeO<sub>2</sub> (JCPDS No. 810792). In all the XRD patterns, (111) is

the most intensive peak, therefore, it was used for the calculation of unit cell parameters and crystalline size of all the prepared catalysts. Results are summarized in Table 2. XRD spectra shows that an increase in Ce content in Ce<sub>x</sub>La<sub>1-x</sub>O<sub>2</sub> (x = 0.2, 0.4, 0.6 and 0.8) shifts the peaks to a higher diffraction angle [15,16]. Ionic radius of La<sup>3+</sup> (0.106 nm) is larger than that of Ce<sup>4+</sup> (0.094 nm), therefore, an increase in lanthanum in the Ce<sub>x</sub>La<sub>1-x</sub> catalysts results in an increase in the values of unit cell parameters (Table 2) whereas an increase in cerium causes a decrease in unit cell parameters [17,18].

#### 3.1.2. Textural analysis

Textural properties and pore size distribution of the synthesized catalysts (Table 2) were obtained from the nitrogen adsorption–desorption isotherms at 77 K (Fig. 1). Isotherms belong to the “type IV” class in all cases and exhibit a type “H4” hysteresis loop indicating that all Ce–La catalysts are mesoporous in nature. Synthesized catalysts were found to have the surface area in the range from 41–62 m<sup>2</sup>/g and it was found to be in the order: Ce<sub>0.2</sub>La<sub>0.8</sub> < Ce<sub>0.4</sub>La<sub>0.6</sub> < Ce<sub>0.6</sub>La<sub>0.4</sub> < Ce<sub>0.8</sub>La<sub>0.2</sub>. The pore volume of the catalysts also increased in the same order. It is found that an increase the lanthanum content decreases the pore surface area and pore volume.

#### 3.1.3. Basic and acidic nature analysis

CO<sub>2</sub>-TPD profile of synthesized Ce<sub>x</sub>La<sub>(1-x)</sub> catalysts is shown in Fig. 2a. Distinct profiles are seen for different catalysts. Peaks in the NH<sub>3</sub>/CO<sub>2</sub>-TPD profiles are classified as corresponding to: weak (<200 °C), moderate (200–450 °C) and strong (>450 °C) basic sites depending in the temperature they exist. The presence of weak basic sites in the catalysts allows low temperature desorption of the CO<sub>2</sub> gas whereas strong basic sites show the higher temperature desorption of CO<sub>2</sub> [19]. Ce<sub>0.8</sub>La<sub>0.2</sub> catalyst shows peaks corresponding to weak and moderate basic sites whereas all other catalysts show peaks corresponding to weak, moderate and strong basic sites. The intensity of the low and moderate basic sites depends on the Lewis acid–basic pairing and OH<sup>-</sup> bond present on the surface, and higher basic nature is due to the low coordination of surface O<sup>2-</sup> [20]. The amount of total basic sites (per unit mass) for any catalyst was calculated by adding the amount of

**Table 2**  
Crystallite size, textural properties and composition of cerium–lanthanum catalysts.

Catalyst	XRD		Textural properties			Composition of catalysts (from EDX)		
	Unit cell parameter (Å)	Crystallite size (nm) <sup>a</sup>	Surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g) <sup>b</sup>	Average pore diameter (nm) <sup>c</sup>	Ce actual atomic%	La actual atomic%	O actual atomic%
Ce <sub>0.2</sub> La <sub>0.8</sub>	5.753	7.6	41	0.061	5.82	8	29	63
Ce <sub>0.4</sub> La <sub>0.6</sub>	5.598	9.5	42	0.080	6.67	18	26	56
Ce <sub>0.6</sub> La <sub>0.4</sub>	5.539	10.2	60	0.103	5.97	20	14	66
Ce <sub>0.8</sub> La <sub>0.2</sub>	5.452	11.7	62	0.128	6.57	25	9	66

<sup>a</sup> Scherrer equation used for the estimation of crystalline size peak (111).

<sup>b</sup> BJH desorption cumulative pore volume of pores in the range of 17.00 to 3000 Å.

<sup>c</sup> BJH desorption average pore diameter (nm).

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