



Efficient synthesis of dimethyl carbonate via transesterification of ethylene carbonate over a new mesoporous ceria catalyst

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ABSTRACT

Mesoporous ceria materials (CeO₂-meso) have been prepared through a soft-templating method using cetyltrimethylammonium bromide as a template and cerium nitrate as a precursor. The synthesized CeO₂-meso materials possess narrow pore size distributions of 5.1–5.4 nm and tunable surface areas (109–182 m² g⁻¹). As heterogeneous catalysts in the transesterification of ethylene carbonate (EC) with methanol to dimethyl carbonate (DMC), CeO₂-meso materials demonstrate superior catalytic performance to the commercial ceria. N₂ adsorption–desorption and CO₂-TPD characterization results indicate that the catalytic activity obtained over various CeO₂-meso samples depends on their surface areas and basicity. The highest activity is achieved over CeO₂-meso-400, affording a DMC yield as much as 73.3%, together with excellent recycling ability. Besides the transesterification of EC with methanol, CeO₂-meso is found to be able to catalyze the reactions of other cyclic carbonates and alcohols. In view of the high catalytic performance along with the convenience in catalyst preparation, CeO₂-meso-400 compares favorably with the ionic liquids as well as other ceria-based catalytic systems.

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1. Introduction

Dimethyl carbonate (DMC) has been used for a variety of applications in the chemical industries owing to its versatile chemical reactivity and unique physical properties [1,2]. It is a potential additive to fuel oil because of its high octane number and rapid biodegradability [3,4]. More importantly, DMC is an environmentally friendly and promising alternative to highly toxic phosgene and conventional dimethyl sulfate in carbonylation and methylation reactions, respectively [5,6]. Traditionally, DMC is synthesized via the phosgenation or oxidative carbonylation of CH₃OH, which involves high-risk compounds including COCl₂ and CO [7,8]. To circumvent this issue, much effort has been devoted to the direct manufacture of DMC from CO₂ and CH₃OH in the presence of organometallic complexes, inorganic bases, etc. Unfortunately, due to the high inertness of CO₂ as well as the thermodynamic limitations, the DMC yield of the process is relatively low [9–11].

The transesterification of cyclic carbonate (e.g. ethylene carbonate (EC) or propylene carbonate (PC)) with CH₃OH has been regarded as a clean and sustainable synthetic route for the

production of DMC (Scheme S1) [10,12], since cyclic carbonates can be synthesized in a quantitative yield via cycloaddition of CO₂ to epoxides [10]. Furthermore, the co-products obtained in the transesterification, i.e. ethylene glycol (EG) and propylene glycol (PG), are also important industrial reagents [13]. A wide range of heterogeneous catalysts, including basic metal oxides [14], alkali-metal hydroxide [15], anion-exchange resin [16], hydrotalcite [17], dawsonite [18], smectite [19], mesoporous carbon nitride [20], etc. have been developed for the transesterification reactions. Up to now, the most efficient catalysts proposed for the process have been confined to ionic liquids (ILs) [4,21]. However, the thorny issue associated with such ILs is the catalyst–product separation [22]. Although immobilization the ILs onto solid support (e.g. porous silica materials) can solve this problem, the high cost of siliceous coupling agents and tedious preparation for the immobilized ILs still restrict their practical applications [20]. In this context, it is highly desired to develop a new catalyst that can allow a robust activity along with easy separation for the transesterification reactions.

Ceria is one of the most important rare earth oxides. As a key redox component, ceria has been extensively used in for many catalytic processes [23], such as three-way-catalyst for exhaust treatment, low-temperature CO oxidation [24], and water-gas shift [25]. Moreover, ceria is also a typical Lewis-base catalyst, which is

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responsible for its application in several base-catalyzing processes. Tomishige et al. [26] have reported the utilization of high-surface-area ceria ($40\text{--}131\text{ m}^2\text{ g}^{-1}$) for the direct synthesis of organic carbonate from the reaction of CO_2 with CH_3OH . Wherein, the catalytically active sites were attributed to the (1 1 1) faces of ceria. Adopting SBA-15 as a hard template through a nanocasting pathway, Liu et al. [27] have prepared a series of mesoporous ceria ($S_{\text{BET}} = 135\text{ m}^2\text{ g}^{-1}$) catalysts loaded with NaOH/KOH . As a superbase, the synthesized mesoporous ceria material showed excellent catalytic performance (DMC yield = 65%) in transesterification of EC with CH_3OH at 65°C . Corma et al. [28] also revealed that cerias loaded with nanosized gold could promote the transesterification of PC with CH_3OH to DMC at 140°C , affording a maximum DMC yield of 35%. Also, ceria-based mixed oxides (e.g. MgO-CeO_2 [29]) have been reported to be able to catalyze the transesterification of cyclic carbonates.

The effort above has verified the catalytic capability of ceria for the transesterification reactions of cyclic carbonates to DMC. In the continued search for a more effective ceria for the transesterification of cyclic carbonates to DMC, there is a definite demand for an economic and facile method for the preparation of ceria that can allow efficient activity for the production of DMC. In our previous work [30], we reported the synthesis of mesoporous ceria materials using a soft-templating approach, which showed potential catalytic application for the oxidative dehydrogenation of ethylene benzene to styrene. Herein, we employ the mesoporous ceria catalyst ($\text{CeO}_2\text{-meso}$) as a new catalyst for the transesterification reaction of cyclic carbonates and alcohol. The $\text{CeO}_2\text{-meso}$ materials exhibit high and steady activity in the transesterification of EC with CH_3OH . Based on the characterization results of N_2 adsorption–desorption and $\text{CO}_2\text{-TPD}$, the high surface area and the abundant basicity are responsible for its high catalytic activity. Besides EC, $\text{CeO}_2\text{-meso}$ could also promote a series of transesterification of other cyclic carbonates.

2. Experimental

2.1. Catalyst preparation

Mesoporous ceria materials were synthesized via a template-assisted precipitation method [30,31]. Typically, $4.34\text{ g Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was added into 200 mL of 0.03 mol L^{-1} solution of cetyltrimethylammonium bromide ($\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3\text{Br}$, CTAB), and stirred vigorously for 3 h. Next, a NaOH solution (2 g in 300 mL of water) was added into the above solution and then stirred overnight. After that, the mixture was transferred into an autoclave and aged at 90°C for 12 h. The as-received yellow precipitate was filtered and washed with hot water (ca. 80°C) for several times to remove the residual CTAB. The resultant yellow powder was dried at 110°C for 6 h and then calcined for 4 h. The resultant ceria samples are denoted as $\text{CeO}_2\text{-meso-}T$, where T stands for the calcination temperature.

2.2. Sample characterization

X-ray diffraction patterns were recorded with a Rigaku D/max 2500 PC X-ray diffractometer equipped with a graphite monochromator (40 kV , 40 mA) using Ni-filtered $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5418\text{ \AA}$).

Nitrogen adsorption–desorption isotherms were measured at -196°C using a Micromeritics ASAP 2020 analyzer. Prior to the analysis, the samples were degassed ($1.33 \times 10^{-2}\text{ Pa}$) at 150°C for at least 4 h. The specific surface area was calculated according to the Brunauer–Emmet–Teller (BET) method, and pore size distribution was determined by the Barret–Joyner–Halenda method.

Transmission electron microscopy (TEM) experiments were conducted on a JEOL 2010 electron microscope operating at 200 kV . Before being transferred into the TEM chamber, the samples dispersed in ethanol were deposited onto holey carbon films supported on Cu grids.

Diffused reflection infrared Fourier transform (DRIFT) spectra were collected using a Bruker Tensor 27 spectrometer. The samples were placed in in-situ cell and pretreated with heating at 200°C for 1 h under N_2 flow.

The basicity of the samples was measured by CO_2 temperature-programmed desorption ($\text{CO}_2\text{-TPD}$) on a Quantachrome ChemBET-3000 analyzer. A 200 mg of the sample was pretreated at 300°C for 1 h in dry He flow (30 mL min^{-1}), cooled to 50°C , and then exposed to CO_2 for 0.5 h. After purging the sample with He for 0.5 h, the TPD data was recorded from 50 to 550°C with a ramping rate of $10^\circ\text{C min}^{-1}$.

2.3. Catalytic test

The transesterification reactions of EC with CH_3OH were carried out in 80 mL stainless steel autoclave equipped with a magnetic stirrer. 25 mmol of EC and 250 mmol of CH_3OH were mixed well, followed by the introduction of 0.1 g of the catalyst. The reactor was pressurized with CO_2 to 0.6 MPa and heated to 140°C under stirring for 2 h. After the reaction, the autoclave was cooled down in ice water and the mixture was centrifuged and analyzed by a GC equipped with a PEG-2000 capillary column coupled with a FID detector. The quantity of reagents and products are calculated by an area-normalization method. The carbon balance was $100 \pm 5\%$. In the transesterification of EC with CH_3OH , DMC and 2-hydroxyethyl methyl carbonate (HEMC) is the target molecule and by-product, respectively. The glycol is co-product. The conversion (Conv.) of EC and selectivity (Sel.) to DMC are calculated as follows:

$$\text{Conv.}\% = \frac{n_{\text{EC, fed}} - n_{\text{EC, unconverted}}}{n_{\text{EC, fed}}}, \text{ and Sel.}\% = \frac{n_{\text{DMC}}}{n_{\text{EC, fed}} - n_{\text{EC, unconverted}}}$$

The filtered catalyst was washed with methanol (50 mL) for two times, dried overnight, and then investigated for its next running. The catalytic activity for each catalyst is based on its specific reaction rate (r_s , $\text{g}_{\text{EC}}\text{ g}_{\text{catal.}}^{-1}\text{ h}^{-1}$), which is calculated as follows:

$$r_s = \frac{m_{\text{EC, converted}}}{W_{\text{catal.}} \times t} = \frac{n_{\text{EC}} \times \text{Conv.}\%(\text{EC}) \times M_{\text{EC}}}{W_{\text{catal.}} \times t}$$

where n_{EC} , M_{EC} , t , and $W_{\text{catal.}}$ are the molar amount (mol), formula weight (88 g mol^{-1}) of EC, reaction time (h), and the mass of the catalyst (g), respectively.

3. Results and discussion

3.1. Catalyst characterization

XRD patterns of the commercial and mesoporous ceria samples are shown in Fig. 1. All samples present intensive diffraction peaks at $2\theta = 28.5^\circ$, 33.1° , 47.46° , and 56.3° , corresponding to the characteristic diffractogram of cubic fluorite structure (JCPDS: 34-0394). The commercial ceria shows very strong and sharp diffraction lines. Calculated by Scherrer equation based on the (1 1 1) plane, the crystallite size of $\text{CeO}_2\text{-com}$ is ca. 54.7 nm (Table 1). By contrast, the diffraction peaks acquired over $\text{CeO}_2\text{-meso}$ materials are broader and weaker than $\text{CeO}_2\text{-com}$, suggesting that the average particle sizes of ceria are rather small. As the calcination temperature increases from 400 to 600°C , the diffraction peaks become sharper, indicating that the crystallinity is improved. Meanwhile, the corresponding crystallite sizes of cerias, calculated by Scherrer's equation (based on the (1 1 1) plane), increase from 8.8 to 9.5 nm as the annealing temperature is raised from 400 to 600°C .

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