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Synthesis of glycerol carbonate from glycerol and diethyl carbonate over CeO_2-CdO catalyst: The role of Ce^{4+} doped into CdO lattice

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ABSTRACT

A series of $Ce_{1-x}Cd_xO$ mixed oxide catalysts prepared by co-precipitation method were tested for synthesis of glycerol carbonate (GC) from glycerol and diethyl carbonate (DEC). The microstructural and physicochemical properties of the bimetal catalysts were characterized by XRD, SEM, TEM, XPS, CO_2-TPD, N_2-adsorption, TG-DSC and ^1H NMR. The results show that the spherical particles of CdO were uniformly dispersed on the surface of lamellar CeO_2. Besides, a noticeable increase was observed in the moderate basic sites concentration, because more oxygen atoms were adsorbed on the bimetal sample surface which was attributed to Ce^{4+} doped into CdO lattice. The $Ce_{0.7}Cd_{0.3}O$ sample annealed at 500 °C was observed with the highest catalytic activity. 96.84% of glycerol conversion and 100% selectivity to GC were obtained over this catalyst under the optimized conditions (5 wt.% catalyst of glycerol, 90 °C, 180 min, glycerol/DEC molar ratio of 1:3). Besides, it was found that the conversion of glycerol carbonate was synergistically accelerated by the moderate and strong basic sites.

1. Introduction

Biodiesel, as a green alternative to fossil sources, plays an important role in the sustainable energy. Latterly, the increase in biodiesel production results in a large surplus amounts of glycerol, as a co-product, which blocks the price of glycerol in the market [1–3]. Hence, the transformation of glycerol into highly value-added chemicals is greatly significant to suppress its surplus and lessen the expense of biodiesel industry. Several pathways for glycerol conversion have been reported for synthesis of useful glycerol derivatives [4–7], of which glycerol carbonate (GC) is one of the significant chemicals. GC possesses excellent physicochemical property such as high boiling point, low toxicity and biodegradability, which can be used as novel solvent, surfactant, carries in batteries and monomer for polymers [8–11].

Furthermore, synthesis of highly valued-added GC is also interesting both for academic and industrial viewpoint [12]. The traditional routes described for conversion of glycerol to produce GC require utilization of different carbonyl agents [13]. The use of phosgenation and carbon monoxide as carbonyl source is limited because of the toxicity and processing difficulty in industries [14,15]. Glycerolysis of urea needs the intermittent removal of ammonia from the reactor and its purification process is also complicated [16]. The use of CO_2 as carbonyl source is attractive with high atom utilization efficiency. The main drawback of this reaction is thermodynamically limited in glycerol conversion [17,18]. Glycerol transesterification with alkyl carbonates like ethylene carbonate is also an important approach. Nevertheless, GC was difficultly separated from the reaction system [19]. Therefore, carbonylation of glycerol with dialkyl carbonates can be considered as the desired method for GC synthesis because the reaction starts with non-toxic materials under the mild conditions [20]. Thus, synthesis of GC from glycerol and diethyl carbonate (DEC) was more interesting for industry, of which only ethanol was regarded as the byproduct. Besides, the newly-synthesized GC can be further transformed to glycidol [21,22].

Most literature available on glycerol transesterification has been reported on homogeneous reaction [23,24], nonetheless, the separation of homogeneous catalysts is not easily to perform, which is not beneficial for subsequent purification of the generated products. On the other hand, some heterogeneous catalysts such as Li/ZnO [25], KNO_3/CaO [26], KF modified hydroxyapatite [27], $LiNO_3/Mg_4AlO_{5.5}$ [28], CaFeAl mixed oxide [29], Mg/Al/Zr mixed oxides [30] have also been adopted for transesterification process. However, most of these catalysts have their drawbacks such as rapid deactivation, requirement of long reaction time, additional solvent and a high reactant molar ratio. Hence, development of a highly efficient and stable catalyst is important and desired for

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glycerol transesterification. It has been reported that ceria as a basic catalyst is not very active in transesterification reactions, but it can be as the efficient component to improve the basicity of solid basic catalyst [31,32], therefore enhancing the catalytic activity in base-catalyzed reaction. For example, the utilization of Ce-MgO in the synthesis of dimethyl carbonate (DMC) from ethylene carbonate and methanol resulted in 95% DMC selectivity and 64% DMC yield, which were far superior to that of MgO (DMC yield was only 49%) [33]. Because the basic site concentration was enhanced with the incorporation of Magnesium into cerium lattice.

To the best of our knowledge, the performance of CeO_2-CdO sample, as solid base catalysts, was not investigated in the synthesis of GC from glycerol and DEC. Thus, in this paper, CeO_2-CdO catalyst was simply prepared by a co-precipitation method and employed in glycerol transesterification. The effects of reaction parameters including calcination temperature, Ce/Cd ratio, reaction temperature, catalyst amount, DEC/glycerol molar ratio, reaction time on the catalytic performance as well as the catalyst recyclability were studied in detail.

2. Experimental

2.1. Chemicals

The chemicals: $Ce(NO_3)_3$•$6H_2O$ (>99.0%), $Cd(NO_3)_2$•$4H_2O$ (>99.0%), $NaCO_3$ (>99.8%) and ethylene glycol monobutyl ether (>98.0%) were purchased from sigma-Aladdin Corporation (shanghai, China). Glycerol (>99.0%), DEC (>99.0%) and ethanol (>99.7%) were purchased from Sinopharm Chemical Reagent Co. Shanghai, China. All the reagents were of analytical grade without further purification.

2.2. Catalyst preparation

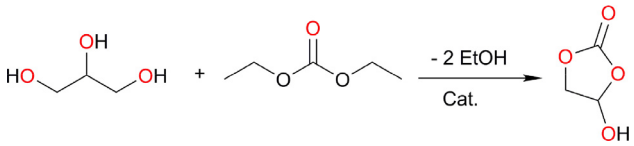
The CeO_2-CdO with different components (Ce/Cd ratio) was prepared by co-precipitation method. Typically, a mixed aqueous solution ($Ce(NO_3)_3$•$6H_2O$, $Cd(NO_3)_2$•$4H_2O$) and 3 mol/L Na_2CO_3 were simultaneously added dropwise to 10 mL deionized water under vigorous stirring to achieve pH value of 10 (room temperature). After 24 h reaction, the precipitate was separated via filtration, and washed with deionized water to remove sodium ion until the precipitate was nearly neutral. Thereafter, the precipitate was dried at 80 °C for 10 h, and then treated in static ambient air at 500 °C for 5 h. Finally, the as-prepared catalyst was ground into the designated size and used for catalytic conversion of glycerol with DEC to produce GC. The Ce and Cd mixed oxide catalysts with different composition were denoted as $Ce_{1-x}Cd_xO$-500, where, x represents mole of Cd taken, such that the sum of Cd and Ce is one (x=0, 0.1, 0.2, 0.3, 0.5, 0.7 and 1.0, respectively). To study the effects of the calcination temperature, the $Ce_{0.7}Cd_{0.3}O$ catalysts were annealed at different temperature and this catalysts were named as $Ce_{0.7}Cd_{0.3}O$-T (T=300, 400, 500, 600, 700, respectively), where T represents the calcination temperature.

2.3. Catalyst characterization

X-ray diffraction (XRD) patterns of the CeO_2-CdO were recorded in 2θ range of 5–85° on the Rigaku D/max-A instrument (Cu kα, 40 kV, 20 mA, 10 o/min). The mean crystal size of CdO and CeO_2 inside solids was calculated according to main plans (2 0 0) and (1 1 1) corresponding to CdO and CeO_2 by Scherrer equation [34], respectively.

Microscopic morphology of the catalysts was characterized by field emission scanning election microscopy (FESEM).

X-ray photoelectron spectroscopy (XPS) measurements were conducted on an ESCALAB-250 (Thermo-VG Scientific, USA) spectrometer equipped with Al Kα (1486.6 eV) irradiation. The binding energies value were calibrated internally based on the adventitious carbon deposit C (1 s) peak at 284.6 eV.



Scheme 1. One-pot synthesis of glycerol carbonate from glycerol and diethyl carbonate.

Transmission electron micrograph (TEM) with selected area electron diffraction (SAED) was recorded on a JEM-2100 microscope. The sample was dispersed in ethanol and then treated ultrasonically in order to achieve individual particles over a copper grid.

Specific surface area (S_{BET}) and pore characteristics of the catalyst were detected by N_2 physisorption at −196 °C, using a Beishide 3H-2000 analyzer after the catalyst was degassed at 200 °C for 12 h.

Basic sites of the catalyst were measured by temperature-programmed desorption of CO_2 (CO_2-TPD) performed using the TP-5056 equipment connected to a TCD detector. The catalysts (0.10 g) were firstly pretreated in Helium atmosphere at 200 °C for 1 h, then cooled down to 100 °C maintained in the CO_2 flowing gas (30 ml/min) for 30 min and then purged with He for 50 min in order to eliminate the physically adsorbed CO_2. Subsequently, the sample was heated to 800 °C (10 °C/min) in order to acquire the CO_2 desorption profiles.

Thermo gravimetric (TG) analysis of the catalyst was performed on a synchronous thermal analyzer STA449 F3. The sample (10 mg) was heated with a linear rate (10°/min) from 30 °C to 800 °C under dry air atmosphere.

2.4. Catalytic reaction

Synthesis of GC from glycerol and DEC, depicted in Scheme 1, was performed in a round bottom flask equipped with a magnetic stirrer and a thermocouple.

Typically, glycerol, DEC and catalyst were charged into the glass reactor heated by oil bath with a set point. During the reaction, the system was stirred variously. After 4 h reaction, the system was cooled down to room temperature. The catalyst from mixture was separated via centrifugation, washed with ethanol to remove organic components, and dried at room temperature overnight for further research. The catalyst-free liquid (ethylene glycol monobutyl ether as the internal standard) was collected and detected by flame ionization detector Gas chromatograph (Teng Hai, Shandong, China, GC-6890) equipped with a SE-54 capillary column (30 m × 0.32 mm × 1 μm). Glycerol conversion and GC selectivity were calculated with the use of Eqs. (1) and (2), respectively.

$$\text{Glycerol conversion} = 1 - \frac{\text{mole of the residual glycerol}}{\text{mole of the initially added glycerol}} \quad (1)$$

$$\text{Glycerol carbonate selectivity} = \frac{\text{mole of glycerol carbonate}}{\text{mole of all the products}} \quad (2)$$

3. Results and discussion

3.1. Characterization of catalysts

The wide-angle XRD patterns of CeO_2-CdO catalysts with different composition and calcined at 500 °C for 5 h are shown in Fig. 1a. In the diffraction pattern of CeO_2, peaks ascribable to

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