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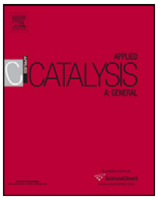

CaO-catalyzed synthesis of glycerol carbonate from glycerol and dimethyl carbonate: Isolation and characterization of an active Ca species

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ABSTRACT

The transesterification of dimethyl carbonate (DMC) with glycerol to produce glycerol carbonate was investigated in the presence of CaO under various reaction conditions. CaO was completely dissolved in the reaction mixture of glycerol and DMC in 5 min at 75 °C and at the molar ratio of glycerol/DMC/CaO of 1/2/0.01.

The isolation and the characterization of the dissolved Ca species by means of TOF-SIMS, elemental analysis, and FT-IR revealed that an active species, $Ca(C_3H_7O_3)(OCO_2CH_3)$ is generated from the interaction of CaO with glycerol and DMC.

The mechanistic pathways to the formations of $Ca(C_3H_7O_3)(OCO_2CH_3)$ and glycerol carbonate are discussed on the basis of experimental and spectroscopic results.

1. Introduction

The interest in renewable feedstocks is increasing rapidly because of their low CO_2 emission potential as fuels and potential uses as substitutes for petroleum-based materials. European Union Directive announced that transportation fuels should contain at least 5.75% of renewable bio-components by the end of 2010. U.S. government also plans to replace 2% of on-road diesel by a biodiesel by 2012 [1].

Of the various types of renewable feedstocks, triglycerides are regarded as good prospective raw materials for biodiesel production, due to their easy availability from vegetable oils and animal fats. In the preparation of biodiesel from triglycerides, however, 10 wt% of glycerol is always co-produced, which inevitably reduces the economics of the process. In this context, transformation of glycerol into high value added chemicals is highly necessary.

Glycerol carbonate is a valuable glycerol derivative, which is being widely used as a solvent in the cosmetics industry, as a membrane component for gas separation, as a component of coatings and detergents, and as a monomer of polycarbonate and polyurethane [2–6].

A number of synthetic processes are known for the preparation of glycerol carbonate from glycerol. Aresta et al. reported that glycerol carbonate could be produced from the reaction of glycerol with CO_2 in the presence of a catalyst at elevated temperature and pressure, but the yield of glycerol carbonate is too low to be used for practical purposes [7].

A direct reaction of glycerol with urea in the presence of a catalyst is another method for preparing glycerol carbonate [8–11]. The process, however, has some disadvantages such as the need for the use of vacuum to remove evolved ammonia to accelerate the reaction and to reduce the formation of undesirable side products such as isocyanic acid and biuret [8].

Dimethyl carbonate (DMC) has also been employed as a carboxylating agent as a green alternative to urea and CO_2 as depicted in Scheme 1 because carboxylation with DMC can be operated at much milder conditions without the production of problematic side products.

Transesterification of an ester with an alcohol is often conducted in the presence of a base catalyst such as an alkali metal hydroxide or alkaline earth metal oxide [12–14]. However, for the facile recovery and reuse of catalysts, heterogeneous catalysts are clearly more desirable [15]. The transesterification between glycerol and DMC using CaO as the catalyst has been extensively investigated by

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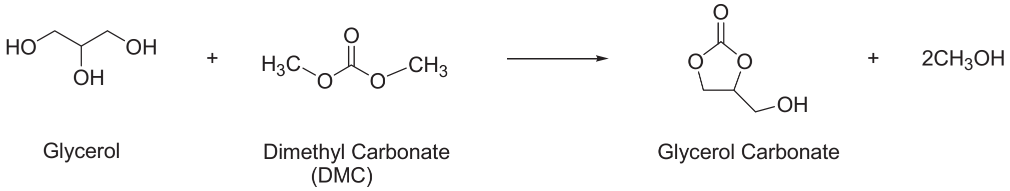

Scheme 1. Synthesis of glycerol carbonate from glycerol and DMC.

many researchers. Recently Ochoa-Gomez et al. reported that CaO is highly active for transesterification and the activity is strongly influenced by the pretreatment temperature [16]. Later, Li et al. explained that the reason for the high activity of CaO could be the formation of active homogeneous species through the interaction with glycerol and DMC, but the characterization of the species was not successful [17]. A similar phenomenon was also observed when CaO was used as a catalyst for the reaction of triglyceride with methanol to produce biodiesel (FAME) and glycerol. In this reaction, calcium diglyceroxide ($Ca(C_3H_7O_3)_2$) was suggested as an active species [18,19].

To have a deeper insight into the nature of the active species for the CaO-catalyzed transesterification of glycerol with DMC, we have conducted the characterization of the isolated Ca species dissolved in the reaction mixture by means of elemental analysis, TOF-SIMS and FT-IR.

Herein, we report that a highly active species, $[Ca(C_3H_7O_3)(OCO_2CH_3)]$ is generated from the interaction of CaO with glycerol and DMC. The mechanistic pathways to the formation of $Ca(C_3H_7O_3)(OCO_2CH_3)$ and glycerol carbonate are also discussed on the basis of experimental and spectroscopic results.

2. Experimental

Glycerol, DMC, and CaO were purchased from Aldrich Chemical Co. Glycerol carbonate and CH_3CN were obtained from the TCI (Japan) and JT Baker, respectively. All reagents were used as received without further purifications. CaO was calcined at 900 °C for 3 h and stored in a glove box filled with Ar.

2.1. Transesterification reaction

Glycerol (1.84 g, 20 mmol), DMC (3.6 g, 40 mmol) and CaO (0.011 g, 0.2 mmol) were loaded into a 100 mL round-bottom flask having condenser and reacted at 75 °C for 15 min with a vigorous stirring. The reactions conducted at temperatures higher than 75 °C were carried using a 170 mL high pressure glass vessel (Andrewss Glass Co., USA). After the completion of the reaction, *t*-butanol was added to the reaction mixture as an external standard. The amount of glycerol carbonate produced and unreacted glycerol were analyzed using a HPLC (Waters) equipped with an Aminex HPX-87H column (Biorad) and a RI detector (Waters 410). The mobile phase used was a 5 mM H_2SO_4 aqueous solution and the flow rate was set at 0.6 mL/min.

2.2. Isolation of an active species; $Ca(C_3H_7O_3)(OCO_2CH_3)$

All the reactions related to the isolation of the calcium complex were conducted using a Shlenk line technique. Glycerol (310.0 mmol, 28.56 g), DMC (618.5 mmol, 55.72 g), and CaO calcined at 900 °C for 3 h (17.8 mmol, 1.00 g) was loaded into a 250 mL round-bottom flask and stirred at 75 °C for 30 min. After the reaction was completed, anhydrous CH_3CN was added slowly to the transparent reaction mixture to precipitate the dissolved calcium complex. The white precipitates recovered by filtration were washed with CH_3CN, dried under vacuum, and stored inside the glove box. The weight of isolated powder was 3.15 g (yield: 86%). Elemental analysis calcd for $CaC_5H_{10}O_6$ (%): Ca, 19.4; C, 29.1: H, 4,9. Found: Ca (ICP-Mass), 18.8; C, 28.4; H, 4.6.

2.3. Instrumentation

Sample preparations for TOF-SIMS and IR experiments were conducted in a glove box filled with Ar. TOF-SIMS analysis was performed with an IONTOF, TOF-SIMS5 equipped with a pulsed Bi^+ ion gun operated at 25 kV. Sample surfaces were biased at +3 or −3 kV with respect to the grounded extraction electrode for positive and negative mode SIMS, respectively. The dc ion beam current (~14 nA) was pulsed at 10 kHz and the area analyzed was approximately 100 μm × 100 μm. The vacuum of the system was held below 1×10^{-6} Torr throughout the TOF-SIMS measurements. To clean the surface, the analysis regions were sputtered for 1 scan using a 100 μm × 100 μm dc rastering bismuth ion gun prior to the SIMS measurements. The pre-analysis cleaning was carried out largely to remove surface contaminants from the polishing process.

FT-IR spectra of catalyst samples were recorded on a Nicolet FT-IR spectrometer (iS10, USA) equipped with a SMART MIRACLE accessory.

3. Results and discussion

3.1. Transesterification of DMC with glycerol

Transesterification of DMC with glycerol was investigated at 75 °C using various basic metal oxides. The molar ratio of glycerol/DMC/catalyst was maintained at 1/2/0.03 for all the transesterification reactions. Among the catalysts tested, as listed in Table 1, Na_2O showed the highest activity, producing glycerol carbonate at a yield of 92.6%. By contrast, the activities of MgO and ZnO were extremely low, producing glycerol carbonate in yields of 10.2% and 0.5%, respectively. However, interestingly, CaO exhibited

Table 1
Effect of metal oxide for the transesterification of dimethyl carbonate with glycerol.[a]

Entry	Catalyst	Convertion of glycerol (%)	Yield of glycerol carbonate (%)	Selectivity to glycerol carbonate (%)
1	Na_2O	95.5	92.6	96.9
2	CaO	91.2	90.2	98.9
3	CaO[b]	94.3	94.0	99.7
4	Calcium complex[c]	91.7	91.4	99.7
5	Calcium complex[d]	46.2 (2.3)	41.8(2.5)	90.4 (92.0)
6	MgO[e]	20.5	10.2	49.9
7	ZnO	0.5	0.5	100.0

[a] Glycerol (20 mmol), DMC (40 mmol), catalyst (0.6 mmol), T = 75 °C, t = 30 min.
[b] Calcined at 900 °C for 3 h.
[c] Calcium complex isolated from the reaction of glycerol, DMC and CaO; $Ca(C_3H_7O_3)(OCO_2CH_3)$.
[d] After 1 h exposure of $Ca(C_3H_7O_3)(OCO_2CH_3)$ to air. The numbers in parentheses are conversion, yield, and selectivity obtained with the air-exposed $Ca(C_3H_7O_3)(OCO_2CH_3)$ for 3 h.
[e] Calcined at 900 °C for 3 h t = 180 min.