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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.

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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

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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(C₃H₇O₃)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 H₂SO₄ 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 CH₃CN was added slowly to the transparent reaction mixture to precipitate the dissolved calcium complex. The white precipitates recovered by filtration were washed with CH₃CN, dried under vacuum, and stored inside the glove box. The weight of isolated powder was 3.15 g (yield: 86%). Elemental analysis calcd for CaC₅H₁₀O₆ (%): 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 (\sim 14 nA) was pulsed at 10 kHz and the area analyzed was approximately 100 μ m × 100 μ m. 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 μ m × 100 μ m 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, Na₂O 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

Entry	Catalyst	Convertion of glycerol (%)	Yield of glycerol carbonate (%)	Selectivity to glycerol carbonate (%)
1	Na ₂ O	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), $T = 75 \circ C$, 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_{3}H_{7}O_{3})(OCO_{2}CH_{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.



Fig. 1. Effect of the amount of CaO on the transesterification of dimethyl carbonate with glycerol. Reaction condition: Glycerol (20 mmol), DMC (40 mmol), 75 $^\circ$ C, 30 min.

considerably high activity almost comparable to Na₂O although the basicity of CaO is much weaker than that of Na₂O. When reagent grade CaO was used as a catalyst, glycerol carbonate was produced in 90.2% yield and 98.9% selectivity. The yield of glycerol carbonate increased further to 94.0% when CaO was used after calcination at 900 °C for 3 h. One interesting point observed with the use of calcined CaO is that the dissolution of CaO is completed in 5 min (see Supporting information, Fig. S1). In contrast, the reaction mixture with uncalcined CaO showed a little turbidity even after the completion of the reaction. The reason for this turbidity is not clear at the moment, but it seems that H₂O and or CO₂ adsorbed on the surface of the uncalcined CaO retards the dissolution. The possible effect of water on the dissolution of CaO is somewhat supported by the turbidity of the solution after the exposure of the calcined CaO in air for 3 h. As a whole, the activity of a metal oxide catalyst is greatly affected by the dissolution time and the degree of dissolution: the more soluble the catalyst, the higher the catalytic activity, suggesting that the transesterification proceeds mostly in a homogeneous way. Therefore, the significantly lower activity of MgO and ZnO can be ascribed in part to their extremely poor solubilities in the reaction mixtures. In the metal oxide-catalyzed transesterification between glycerol and DMC, it is easily conceivable that the first step for the generation of an active species is the acid-base interaction between a hydroxyl group of glycerol and metal oxide. In this context, the generation of the active species from the less basic MgO would be much more difficult than that from the more basic CaO. In other word, the basicity of MgO is not sufficiently high enough to generate the similar homogeneous active species to that observed in the CaO-catalyzed transesterification [20,21]. Considering the extremely low activity and solubility of MgO, the transesterification in the presence of MgO seems to proceed in a heterogeneous way.

The effect of catalyst loading on the yield of glycerol carbonate also supports the idea that CaO-catalyzed transesterification take places in a homogeneous way. As illustrated in Fig. 1, the yield and the selectivity of the glycerol carbonate did not vary much when the catalyst loading was decreased from 3 to 0.5 mol% with respect to glycerol. Likewise, the yield of glycerol carbonate remained almost constant with the decrease of catalyst loading from 1 to 0.5 mol%. However, the yield of glycerol carbonate was reduced to 62.9% when the catalyst loading was further decreased to 0.25 mol%. The turbidity of the reaction mixture was affected by the catalyst concentration. When 1 mol% CaO (uncalcined) was used, the solution



Fig. 2. Effect of the reaction time (CaO uncalcined) on the yield of glycerol carbonate. Reaction condition: catalyst/glycerol = $1 \mod \%$, $T = 75 \degree C$.

became slightly turbid, but, at the catalyst concentrations lower than 1 mol%, the solution was completely transparent.

The effect of reaction time was also investigated at 75 °C at varying molar ratio of DMC/glycerol. The catalyst loading was maintained at 1 mol% with respect to glycerol. Fig. 2 reveals that, at the early stages of the reaction up to 2–3 min, the formation of glycerol carbonate was negligible. However, the yield of glycerol carbonate started to increase rapidly thereafter, implying that there exists an induction period for the formation of an active calcium species from CaO. It is interesting to notice that the reaction time to reach equilibrium increases with the increasing molar ratio of DMC/glycerol from 2 to 6. This result may imply that, above the molar ratio of 2, heterogeneous catalysis is also functioning in the CaO-catalyzed transesterification (*vide infra*).

The effect of molar ratio of DMC to glycerol was also investigated at 75 °C for 15 min. As shown in Fig. 3, the yield of glycerol carbonate reaches a maximum of 85.4 at the molar ratio of 2 and then decreases steadily with the increase of the molar ratio up to 10, again suggesting that, above the molar ratio of 2, heterogeneous catalysis is also functioning in the CaO-catalyzed transesterification. In fact, the turbidity of the reaction mixture increased with the increase of DMC concentration. It is likely that the increased concentration of DMC in the reaction solution limits the interaction of CaO with glycerol, thereby preventing the formation of soluble Ca species.

To see the correlation between the amount of dissolved Ca species and the catalytic activity, the amount of dissolved Ca species was analyzed (Fig. 3). When the molar ratio of DMC/glycerol increased from 1 to 2, the dissolved Ca content decreased from 15.6 to 11.5 mg. Considering that the initial Ca content in CaO was 17 mg, approximately 91.8% and 67.6% of CaO transformed into soluble species at the DMC/glycerol molar ratios of 1 and 2, respectively. It is worth to note that, in spite of decrease in the amount of dissolved Ca species as going from 15.6 to 11.5 mg, the yield of glycerol carbonate increased from 68.0 to 85.3%. On further increase of the molar ratio to 4, the dissolved Ca content drastically dropped down to 0.3 mg, which is only 2.6% of that measured at the molar ratio of 2. On the contrary, the reduction of glycerol carbonate yield was much smaller from 85.3 to 63.9% as the molar ratio was decreased from 2 to 4. It is surprising to observe that the transesterification proceeds smoothly even in the presence of such a low dissolved Ca content in the solution. These results may suggest that DMC plays a pivotal role to shift the transesterification toward the formation of glycerol carbonate is strongly affected by the concentration of DMC.



Fig. 3. Effect of DMC/glycerol molar ratio. Reaction condition: Glycerol (20 mmol), CaO (0.2 mmol), 75 °C, 15 min.

Or, there is a considerable contribution of heterogeneous catalyst to the transesterification, especially at the molar ratio of DMC/glycerol higher than 2.

The effect of temperature on the transesterification was investigated in the temperature range of 35-125 °C at the catalyst concentration of 0.5 mol% with respect to glycerol. As shown in Fig. 4, the yield of glycerol carbonate increased with the temperature rise up to 100 °C, and then remained constant on further increase of the temperature to 125 °C. The formation of side products was not observed in the temperature range tested.

3.2. Characterization of active Ca species

To identify the active species generated in situ from the CaOcatalyzed transesterfication of DMC with glycerol, the dissolved Ca species was isolated and characterized by means of TOF-SIMS analysis. As summarized in Table 2 and Fig. S2 in Supporting information many kinds of calcium-containing cations were detected at the positive ion target. Below the mass range of 100, Ca species like Ca, CaH, CaO, and CaOH were also detected with high intensities, most of which seemed to be instantly formed from the



Fig. 4. Effect of reaction temperature. Reaction condition: Glycerol (50 mmol), DMC (100 mmol), CaO (0.25 mmol), 75 $^\circ$ C, 15 min.

ionization process. Above the mass range of 100 m/z, the strongest peak was observed at 112.99 m/z, which could be assigned as a dehydrated calcium monoglycerol species. Interestingly, except 112.99 m/z, major peaks detected seem to be related to the calcium species with both the glycerol and methyl carbonate moieties, including Ca(C₃H₇O₃)(OCO₂CH₃), Ca(C₃H₇O₃)(OCO₂CH₃)₂, $[Ca(C_3H_7O_3)(OCO_2CH_3)][Ca(C_3H_7O_3)], and [Ca(C_3H_7O_3)(OCO_2)]$ CH₃)]₂. Among these, Ca(C₃H₇O₃)(OCO₂CH₃) seems to be the most probable structure of the active species on the basis of elemental analysis. Other species are believed to be formed instantly during the ionization condition. In fact, the presence of an intensive peak at 112.99 m/z could imply the existence of other calcium glycerol compounds such as calcium monoglyceroxide (Ca(C₃H₆O₃)), calcium diglyceroxide ($C_{4}(C_{3}H_{7}O_{3})_{2}$), and tricalcium octaglyceroxide $(Ca_3(C_3H_7O_3)_6(C_3H_7O_3)_2)$. Fuji et al. reported that Ca-glycerol complexes such as calcium diglyceroxide $(C_{3}(C_{3}H_{7}O_{3})_{2})$ could be produced by the interaction of CaO with glycerol [22]. The formation of calcium diglyceroxide as an active species was confirmed by Kouzu et al. in the CaO-catalyzed transesterification of triglyceride with methanol [18]. Calcium diglyceroxide was also expected to form in the transesterification of DMC by glycerol through the direct interaction of CaO with glycerol. However, TOF-SIMS, FT-IR and X-ray diffraction results clearly reveal that calcium diglyceroxide is not generated in this transesterification reaction, implying that the presence of DMC prohibits the formation of calcium diglyceroxide (see Figs. S3 and S4 in Supporting information).

The presence of a carboxylate group in the isolated calcium species is evident from a series of FT-IR spectra shown in Fig. 5.

Table 2

Relative intensities of detected positive ion at the TOF-SIMS and their estimated structures.

Detected positive ion mass	Relative intensity	Estimated positive ion structure (mass)
112.99 168.98 208.03 225.03 281.05 319.00 337.01 202.20	50765 13124 1948 7131 2184 526 1912	$\begin{array}{l} Ca(C_{3}H_{7}O_{3}) - H_{2}O\\ Ca(C_{3}H_{7}O_{3}) \left(OCO_{2}CH_{3}\right) - 2H_{2}O - H\\ Ca(C_{3}H_{7}O_{3}) \left(OCO_{2}CH_{3}\right) + 2H\\ Ca(C_{3}H_{7}O_{3}) \left(OCO_{2}CH_{3}\right) + 2O + H\\ Ca(C_{3}H_{7}O_{3}) \left(OCO_{2}CH_{3}\right)_{2}\\ [Ca(C_{3}H_{7}O_{3}) \left(OCO_{2}CH_{3}\right)] [Ca(C_{3}H_{7}O_{3})] - H_{2}O\\ [Ca(C_{3}H_{7}O_{3}) \left(OCO_{2}CH_{3}O_{3}\right)] - H_{2}O\\ [Ca(C_{3}H_{7}O_{3}) \left(OCO_{2}CH_{3}O_{3}O_{3}O_{3}O_{3}O_{3}O_{3}O_{3}O$
555.00	500	$2[ca(c_{3}n_{7}o_{3})(0co_{2}cn_{3})] - n_{2}0 - n_{3}$



Scheme 2. A plausible reaction mechanism for the CaO-catalyzed transesterification of dimethyl carbonate with glycerol.

The strong peak observed at 1058 cm^{-1} corresponds to the C–O stretching frequency of glycerol group in the complex [23]. Upon the interaction of CaO with glycerol and DMC, two strong peaks appeared at 1640 and 1324 cm⁻¹, which can be associated with the carbonyl (C=O) stretching frequency and C–O–C vibrational band of the CH₃–O–CO₂–Ca, respectively [24–26].

The catalytic activity of the isolated $Ca(C_3H_7O_3)(OCO_2CH_3)$ was also evaluated for the reaction of glycerol and glycerol carbonate. As expected, $Ca(C_3H_7O_3)(OCO_2CH_3)$ exhibited the similar activity to CaO. However, the catalytic activity of $Ca(C_3H_7O_3)(OCO_2CH_3)$ decreased after exposure to air. As listed in Table 1, the yield



Fig. 5. IR of glycerol carbonate (a), glycerol (b), Ca complex (c), Ca complex exposed to air for 1 h (d) and for 3 h (e), and CaCO₃ (f).

of glycerol carbonate was reduced by more than 50% when $Ca(C_3H_7O_3)(OCO_2CH_3)$ was exposed to air for 1 h (entry 5). The catalytic activity of $Ca(C_3H_7O_3)(OCO_2CH_3)$ was negligible after the exposure to air for 3, strongly indicating that the calcium species is transformed into an inactive form, most possibly due to the interaction with atmospheric CO₂. This is supported by a FT-IR experiment. When $Ca(C_3H_7O_3)(OCO_2CH_3)$ was exposed to air for 1 h, a strong peak centered at 1392 cm⁻¹ appeared, whereas the intensities of the peaks related to glyceroxyl and methoxycarboxylate groups $(1324, 1640, and 1058 \text{ cm}^{-1})$ were reduced significantly (Fig. 5(c)). The peak at 1392 cm⁻¹ became more pronounced after 3 h of exposure to air (Fig. 5(d)). The appearance of the peak at 1392 cm^{-1} and the extinction of the peaks at 1324, 1640, and $1058 \,\mathrm{cm}^{-1}$ clearly suggest that, on exposure to air, $C_{3}(C_{3}H_{7}O_{3})(OCO_{2}CH_{3})$ transformed into CaCO₃ or a species similar to CaCO₃ due to CO₂ present in air, and the glyceroxyl and methoxy carboxylate groups were completely dissociated from the Ca center.

The activation energy for the transesterification between glycerol and DMC was also measured using the $Ca(C_3H_7O_3)(OCO_2CH_3)$ as the catalyst. The molar ratio of glycerol/catalyst was fixed at 0.1 mol%. As depicted in Fig. S5 in Supporting information, the activation energy was calculated as 9.67 kJ/mol, indicating that the transesterification is a feasible reaction in the presence of $Ca(C_3H_7O_3)(OCO_2CH_3)$ (see Supporting information). TOF (h⁻¹, turnover frequency) values of 766, 991, and 1087 at 25, 75 and 85 °C, respectively also demonstrate that $Ca(C_3H_7O_3)(OCO_2CH_3)$ is a highly active catalyst for the transesterification reaction.

3.3. Reaction mechanism

A plausible mechanism for the CaO-catalyzed transesterification between glycerol and DMC is depicted in Scheme 2. The calcium species, I bearing a glyceroxyl and a hydroxyl groups is likely to form first from the interaction of CaO with glycerol, which in turn reacts with DMC to generate species, II with the concomitant loss of CH₃OH. The subsequent attack of a glycerol molecule on the carbonyl carbon of II and the simultaneous loss of CH₃OH would produce an active species III. The intramolecular attack of the hydroxyl oxygen atom on the carbonyl carbon of II would produce glycerol carbonate along with the regeneration of the species **I**.

4. Conclusion

The CaO-catalyzed transesterification of DMC by glycerol was found to proceed in a homogeneous way when the DMC/glycerol molar ration less than 2. Above the molar ration 2, heterogeneous catalyst also seems to play an important role in the reaction. As a homogeneous catalyst, an active species was isolated from the reaction mixture and characterized as $Ca(C_3H_7O_3)(OCO_2CH_3)$ by means of elemental and spectroscopic analysis. The active species, $Ca(C_3H_7O_3)(OCO_2CH_3)$ exhibited surprisingly high activity for the transesterification reaction, producing glycerol carbonate in yield around 90% at the glycerol/catalyst molar ratio of 200.

It is hoped that our findings will provide valuable information to those interested in the development of high performance catalysts for the utilization of glycerol.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcata.2011.05.024.

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