Mechanism of CaO catalyst deactivation with unconventional monitoring method for glycerol carbonate production via transesterification of glycerol with dimethyl carbonate

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Abstract

Glycerol carbonate (GC) was synthesized by transesterification of glycerol with dimethyl carbonate (DMC) using calcium oxide (CaO) derived from eggshell as a catalyst. The best results of 96% glycerol conversion and 94% GC yield were achieved under the following reaction conditions: 0.08 mole ratio of CaO to glycerol, 1:2.5 molar ratio of glycerol to DMC, 60 °C reaction temperature and 3 h reaction time. As expected, CaO showed deteriorated catalytic performance when recycling as observed by a rapid decrease in GC yield. This research showed that the active CaO phase firstly was converted to calcium methoxide $(Ca(OCH_3)_2)$ and calcium diglyceroxide $(Ca(C_3H_7O_3)_2)$ and finally to carbonate phase $(CaCO_3)$ which can be confirmed by XRD patterns. According to the phase transformation, the basicity decreased from 0.482 mmol/g to 0.023 mmol/g, and basic strength altered from strong basic strength $(15.0 < H\_< 18.4)$ to weak basic strength $(7.2 < H\_< 9.8)$, resulting in the lower catalytic activity of the consecutive runs. Despite the fact that the GC selectivity was almost 100%, the reaction products (methanol and GC) were not obtained in their stoichiometric ratio and their extents corresponded with that of the catalyst phase transformation to $CaCO_3$. The mechanism of CaO catalyzed transesterification based on the condensation reaction of glycerol and catalyst was proposed, and in situ formation of water-derivative species was hypothesized as a cause of CaO transformation. CaO could react with DMC and water, generating methanol and $CaCO_3$. This enabled unconventional monitoring of catalyst deactivation by checking if the mole ratio of methanol to GC was higher than 2:1 of its reaction stoichiometric ratio. It was also demonstrated that calcination of post-run catalyst at 900 °C to CaO exhibited almost constant catalytic activity, and the mole ratio of methanol to GC was constant at its reaction stoichiometry (2:1) for at least 4 times use.

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1. Introduction

There has been an increasing demand for biodiesel as a renewable fuel to substitute fossil fuels, leading to worldwide high biodiesel production capacity. The growth of biodiesel production capacity rapidly increased by 5 times from 2006 to 2020.[1] Conventional biodiesel production is generally based on vegetable oils as a substrate with alcohols using a base catalyst that obtains glycerol as a by-product. About 10% (w/w) of glycerol is generated from biodiesel production. In Europe alone, a surplus of 2.4 million tonnes of glycerol is produced p.a. which cannot be used by other industries.[2] This is expected to triple by 2030 to achieve the Sustainable Development Scenario.[3] This large amount of glycerol production affects its market price, making it a very cheap raw material (price of crude glycerol was approximately 240 USD/ton before 2012 and quite stable around 150 USD/ton in during 2018-2020).[1] Therefore, the transformation of glycerol to a value-added compound is significant to enhance the sustainability of biodiesel industry in term of cost competitiveness.

Glycerol can be converted to fuel extender [4, 5] and various chemicals such as hydrogen/syngas, propanediol, acrolein, propylene glycol, and glycerol carbonate through different pathways, steam[6-8]/dry reforming[9], hydrogenolysis[10], dehydration, oxidation and transesterification, respectively.[11] One of the most promising products is glycerol carbonate (4-hydroxymethyl-1,3-dioxolan-2-one, CAS #931-40-8) due to its excellent biodegradability, high boiling point, high flash point, low toxicity and water solubility. Furthermore, it is known as a potential biobased chemical building block to synthesize polymers, such as polycarbonates, hyperbranched polyols, polyglycerol esters, and non-isocyanate polyurethanes which can be used in many applications.[12, 13]

Glycerol carbonate (GC) can be synthesized from glycerol via several routes such as carboxylation of glycerol with CO_2 and carbon monoxide which may not industrially possible due to very low conversion resulting in low GC yield. GC synthesis via glycerolysis of urea

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85 under vacuum (ca. 0.02 MPa-0.1 MPa) operating condition can obtain moderate to high of GC

86 yield[14, 15] but energy intensive due to the vacuum processing.[16] The transesterification of

87 glycerol with dimethyl carbonate (DMC) is another potential pathway as it requires mild

88 operating conditions. Not only this route obtains high glycerol conversion and GC yield, but

89 also offers easy separation of product due to the difference of boiling points between reactants

90 and products.[17, 18] CaO is a promising catalyst as it is inexpensive and widely available, and

91 demonstrates high activity[19, 20]. Generally, CaO can be derived from natural calcium sources,

92 such as dolomite, crab shell, and eggshell, having calcium carbonate ($CaCO_3$) as a major

93 component that can be transformed to CaO by calcination. Among those, eggshells are the most

94 superior resource as it mainly contains calcium carbonate (96% by weight).[21] Hence, the waste

95 eggshells have been effectively utilized as CaO source in several catalytic processes such as

96 biodiesel production[22, 23], DMC synthesis [24], H_2/syngas synthesis [25-27] and in non-catalytic

97 processes such as CO_2 capture[28] and wastewater treatment.[29] There are several researches

98 presenting the preparation and performance of CaO based catalyst in GC production.[30] CaO

99 could achieve the complete glycerol conversion and 95.3% of GC yield under the molar ratio

100 of DMC to glycerol 3.5:1 at 95 °C of reaction temperature and 90 min of reaction time, as

101 reported by Ochoa-Gomez et al. (2009) [31]. It has been well known that the recycling of CaO

102 shows dramatic decrease in catalytic activity; however, explanation of catalyst deactivation

103 remained controversial due to contrasting hypothesis and observable evidence. From the

104 literature, the surface of CaO catalyst may expose to air during catalytic runs which considerd

105 as a cause of deactivation [31]. Algoufi (2016) [32] described that the calcined dolomite as CaO-

106 MgO mixed oxide catalyst presented decreasing catalytic activity for a consecutive cycle due

107 to CaO transformation to unstable phase which reacted with CO_2 in air to carbonate phase

108 whereas MgO phase enhanced the stability of CaO phase which concluded that calcined

109 dolomite can be reused in several times compared with unstable bulk CaO. On the other hand,

Li et al. (2011) [33] investigated that exposure in the air of alkali solid catalysts was not the cause of catalyst deactivation. They proposed that the interaction of catalyst with glycerol and glycerol carbonate would be responsible for conversion to the basic calcium carbonate $Ca_x(OH)_y(CO3)_z$, leading to a decrease in catalytic activity. Simanjuntak et al. (2011) [34], particularly, found a highly active species, $[Ca(C_3H_7O_3)(OCO_2CH_3)]$ occurred from the interaction of CaO with glycerol and DMC. An exposure to air could undergo transformation to $CaCO_3$ by interaction with atmospheric CO_2, lowering its catalytic activity. Moreover, a similar phenomenon was observed in calcium methoxide $(Ca(OCH_3)_2)$ and calcium diglyceroxide $(Ca(C_3H_7O_3)_2)$ when using CaO in transesterification of triglyceride with methanol to produce biodiesel (FAME).[35] However, the previous researches have never reported the mole to mole relationship among the reactants and products. An important consideration in mole balance of reaction stoichiometry could make a notification on difference between glycerol and DMC consumption which could lead to a new finding on the cause and reactions of catalyst deactivation as present in this study.

This research utilized eggshell-derived CaO as a catalyst in the transesterification reaction of glycerol and DMC. Particular focus was on its catalytic activity and reusability. Understanding the reaction mechanism and cause of catalyst deactivation is a crucial factor for catalyst reusability. The proposed mechanism of CaO catalyzed in transesterification was based on the condensation pathway of glycerol and catalyst. Unconventional monitoring of catalyst deactivation was proposed by tracking a methanol to GC ratio of the reaction product deviated from its stoichiometric ratio.

2. Experimental

2.1 Chemicals

Glycerol (99.5%) from Ajax Finechem Ltd. (Australia) and DMC (99%) from Merck (Germany) were used as feedstocks. An internal standard of butanol (99.8%) and calibration standard of GC (99%) from Sigma Aldrich (Singapore) were used in the analysis.

2.2 Catalysts preparation and characterization

Calcium oxide (CaO) was derived from waste eggshell ($CaCO_3$) by calcination at 900 ºC for 2.5 h under N_2 atmosphere.[36] The catalyst was kept in a desiccator to avoid humidity from the ambient. Calcium diglyceroxide was prepared by CaO immersion into the mixture of glycerol with equivalent volume of methanol at 60 ºC for 6 h. [37] After these procedures, the catalyst was then filtered and dried at 110 ºC overnight. Calcium methoxide was prepared at the same condition with calcium diglyceroxide but reflux with methanol only [38]. Calcium diglyceroxide and calcium methoxide were synthesized as references for identifying the active phase of the collected catalyst.

The catalyst was characterized by X-ray diffraction (XRD) to analyze the structure and crystalline phases of the catalyst. XRD measurements were performed using a SIEMENS D-5000 X-ray diffractometer with Cu Kα connected with Diffract ZT version 3.3 for full control of the XRD analyzer with a scanning rate of 2 °/min and recording within a range of 2θ from 10° to 80°.

The decomposition of the catalyst was investigated by thermogravimetric analysis (TGA) under air atmosphere with a heating rate of 10 ºC/min from 25 ºC to 1000 ºC.

N_2 physisorption was used to examine the surface area and pore volume of the catalyst using a BEL-sorp mini, Japan. The catalyst pre-treatment was carried out with 50 mL/min helium at 180 °C for 3 h before the N_2 physisorption analysis.[39]

The total basic site was characterized by the Hammett indicator method by the following indicators: bromothymol blue (H_= 7.2), phenol-phthalein (H_= 9.8), 2,4-dinitroaniline (H_=

15.0) and 4-nitroaniline (H_ = 18.4). The catalyst 0.5 g was dissolved in 1 mL of a solution of Hammett indicator diluted in 20 mL methanol and stirred to equilibrate for 60 min. The basicity (mmol/g) was determined by titration with benzoic acid (0.02 mol/L anhydrous ethanol solution) until the colour change back to the beginning colour.[40, 41]

The morphology of the catalyst was examined by scanning electron microscope (SEM) measurements performed with MX2000s microscopy, which could produce a three-dimensional image representation.

2.3 Catalytic activity and reusability test

The transesterification reaction of glycerol with DMC was carried out in a 250 mL three-necked batch reactor equipped with magnetic stir, condenser, and water bath. Effects of operating parameters were investigated, and the suitable conditions were as follows: 2.5:1 molar ratio of DMC to glycerol, 0.08 molar ratio of catalyst to glycerol, and 60 °C reaction temperature with 3 h reaction time. For the reusability test, the catalyst was separated by filtration after the reaction. The collected catalyst was handled via different routes before reuse including without pretreatment, pretreatment by washing with methanol, and pretreatment by calcination at 900 °C for 2.5 h.

All the samples were examined using a gas chromatograph (Shimadzu GC-14B) equipped with a flame ionization detector and a capillary column BP-20WAX (30 m long, 0.32 mm, 0.5 µm). In addition, the side product such as glycidol and glycerol dicarbonate (GDC) were examined by gas chromatography, model Agilent 7890A with DB-wax capillary column (60m x 0.25mm, 0.25 um) coupled with a mass spectrometer, model Agilent 7000B.

The glycerol conversion, the selectivity and yield of GC were calculated from equations (1-3),

$$\text{Conversion of glycerol (\%)} = \frac{\text{mole of glycerol,feed} - \text{mole of glycerol,final}}{\text{mole of glycerol,feed}} \times 100 \quad (1)$$

184 Selectivity of glycerol carbonate (%) = $\dfrac{\text{mole of glycerol carbonate ,produced}}{\text{mole of glycerol,feed} - \text{mole of glycerol,final}}$ x 100   (2)

185 Yield of glycerol carbonate (%) = $\dfrac{\text{mole of glycerol carbonate ,produced}}{\text{mole of glycerol,feed}}$ x 100   (3)

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3. Results and discussion

3.1 Characterization of CaO-based catalyst

189 It was observed that the surface area of eggshell-derived CaO was equal to 4.92 m^2/g

190 (Table 1). CaO derived from eggshell was a mesoporous material (pore diameter range 2-50

191 nm) (Fig.S1). This mesoporous structure could promote diffusion and adsorption of reactants

192 and products since the molecular diameters of glycerol and glycerol carbonate are 0.52 and

193 0.65 nm, respectively[42, 43], leading to an increase in glycerol conversion and GC yield when

194 compared with previously demonstrated microporous material.[44] A SEM image shown in

195 supporting information Fig.S2, confirms mesoporous geometry with generally irregular crystal

196 structure as an aggregate of CaO eggshell, particle size between 5-10 μm, corresponding to

197 other works.[45, 46] CaO eggshell exhibits high strength of basic site 15.0 < H_< 18.4 and the

198 total basicity of CaO eggshell is 0.481 mmol/g, leading to high basic-site density within the

199 allocated pore volume and surface area of the dense egg-shell derived CaO.

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3.2 Factors influencing transesterification reaction using CaO as a catalyst

3.2.1 Effect of reaction temperature

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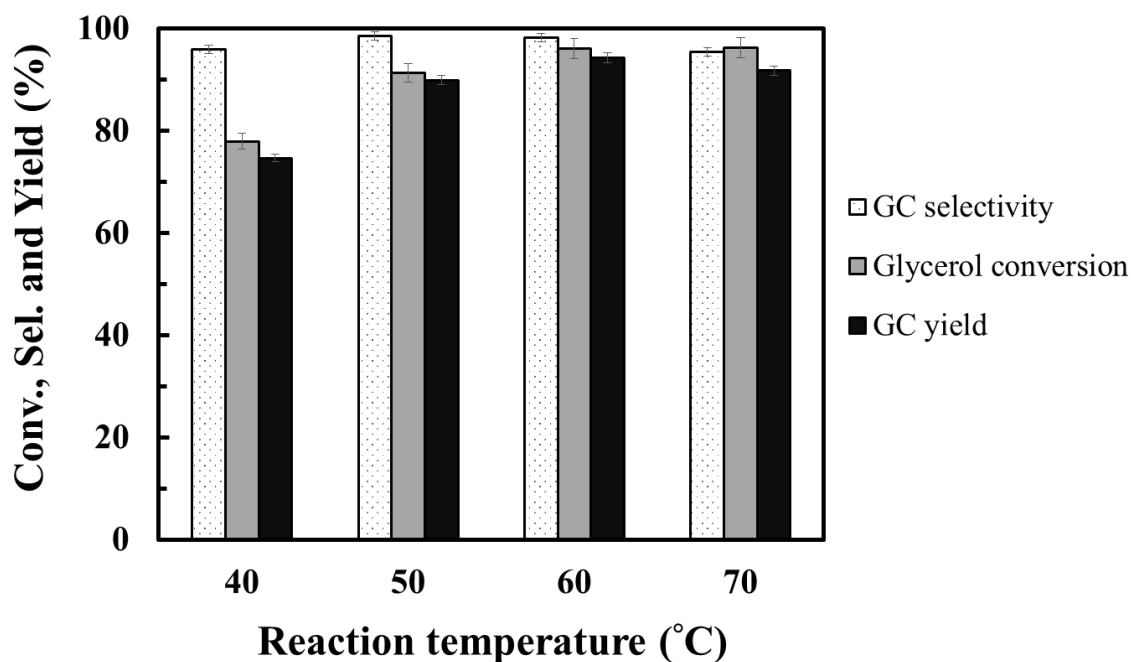
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Fig.1. Effect of reaction temperature on catalytic activity (molar ratio of CaO : DMC : glycerol = 0.08 : 2.5 : 1, and reaction time = 180 min).
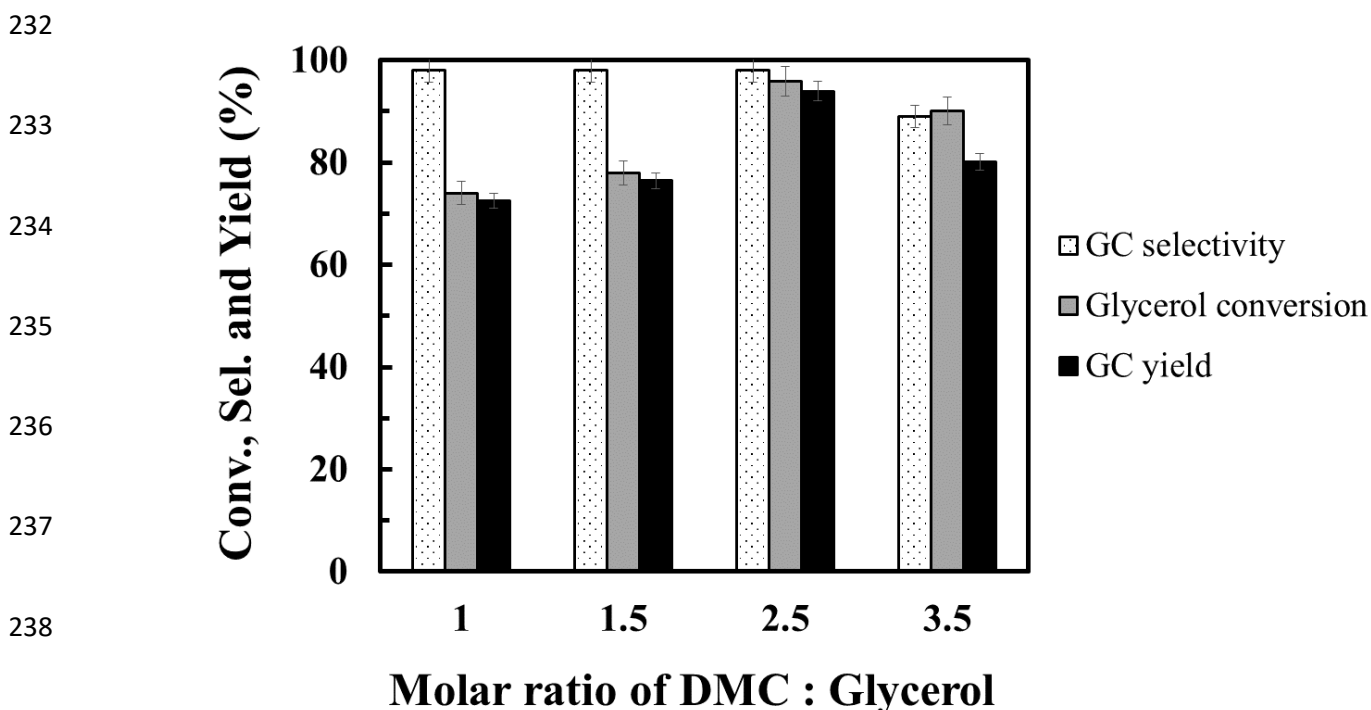
The effect of reaction temperature on glycerol conversion, GC yield and GC selectivity was investigated at temperatures between 40 °C and 70 °C with 0.08 molar ratio of catalyst to glycerol at 1:2.5 molar ratio of glycerol to DMC, shown in Fig.1. According to the results, when increasing reaction temperature from 40 °C to 50 °C and 60 °C, GC yield rose from 73% to 90% and 94%, respectively. GC yield relatively increased with an increase of operating temperature because the transesterification of glycerol and DMC is an endothermic reaction. An increase in operating temperature improves the equilibrium constant and the reaction rates to enhance high GC yield, shown in supporting information Fig.S3. Moreover, an increase of reaction temperature led to a decrease of reactant viscosity, improving the miscibility of the reactant mixture. At low temperature (40 °C) the selectivity of GC slightly decreased which was attributed to the formation of methyl glyceryl carbonate as an intermediate (see in Scheme

225 1). The lower reaction temperature lowering the cyclization rate of the methyl glyceryl

226 carbonate intermediate to GC led to decreasing GC selectivity, similarly as observed by Wang

227 et al. [47] On the other hand, the selectivity of GC decreases when increasing reaction temperature

228 to 70 °C due to the formation of a side product as a glycidol which agrees with the previous

229 report. [48, 49]

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231 **3.2.2 Effect of the molar ratio of DMC: glycerol**

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240 **Fig.2.** Effect of molar ratio of DMC: glycerol on catalytic activity (CaO : glycerol = 0.08 : 1,

241 reaction temperature = 60 °C, reaction time = 180 min).

242 One of the most important factors which affect the glycerol carbonate yield is the molar

243 ratio of DMC:glycerol. Other previous works on this reaction with heterogeneous catalysts

244 were typically studied at the mole ratio of DMC to glycerol in the range of 2–5. [17, 50, 51] The

245 excess mole of DMC was applied which also functioned as solvent in the transesterification

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246 reaction. Therefore, it was not necessary to add another solvent for mixing DMC and glycerol.

247 In this work, when increasing the molar ratio of DMC: glycerol from 1 to 2.5 glycerol, the

248 conversion and GC yield increased as driven by an excess amount of DMC towards GC

249 formation and improved miscibility of glycerol with DMC. However, as observed in the

250 reaction system, there was a possibility for phase separation between DMC and glycerol when

251 their molar ratio was less than 2. Therefore, it was important to point out that adding a high

252 amount of DMC to glycerol would lead to a decrease in GC yield according to the drop of GC

253 selectivity at DMC:glycerol equal to 3.5 as illustrated in Fig.2. This was directly related to the

254 formation of glycerol dicarbonate by-product from a side reaction [14] as shown in scheme 1.

255 According to the results, the optimum mole ratio of DMC to glycerol of 2.5 was in agreement

256 with previous research works and insignificantly depended on catalysts, i.e., dolomite, Na-

257 based zeolite, K_2CO_3/MgO[32, 42, 52] and hydrotalcite.[53]

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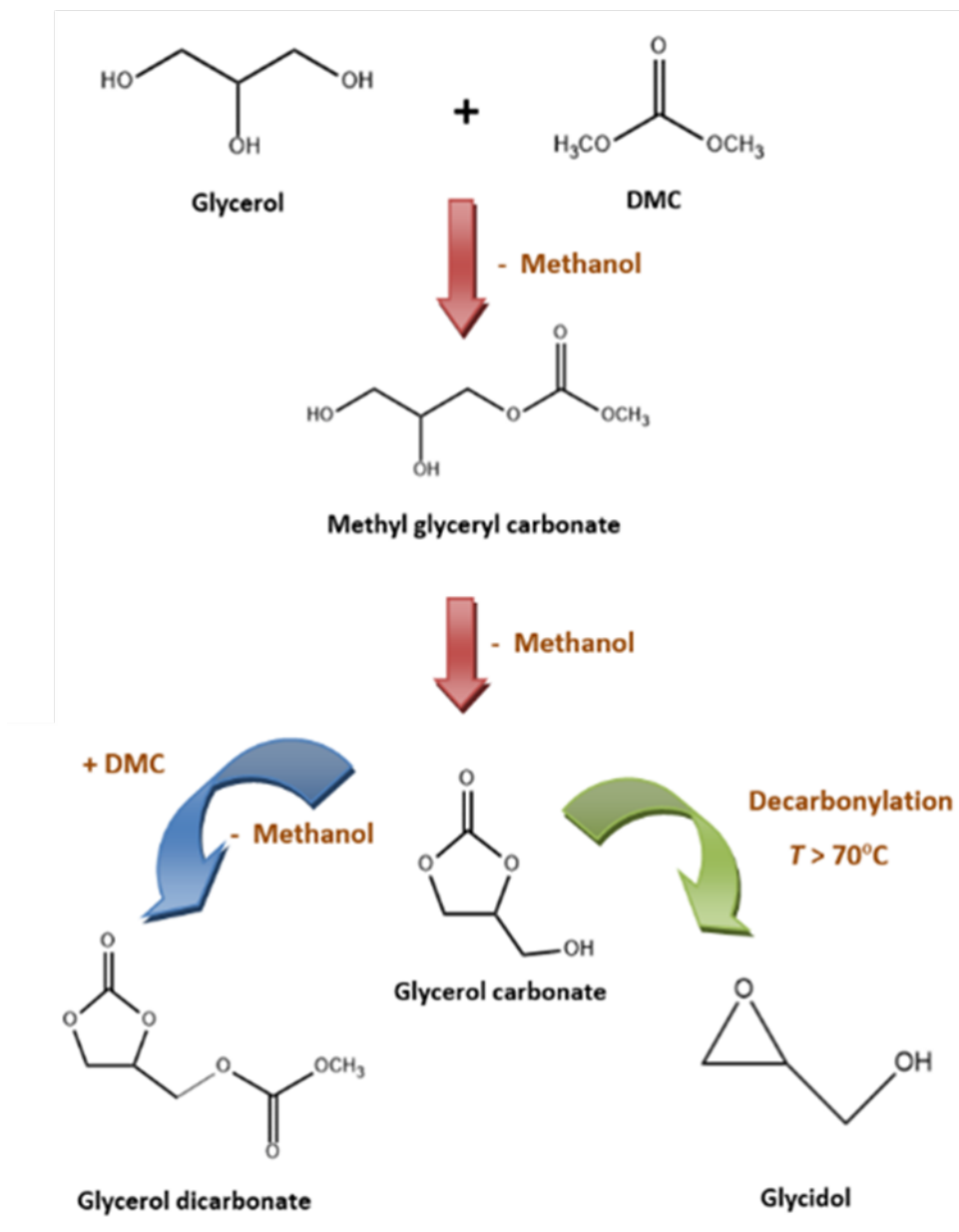
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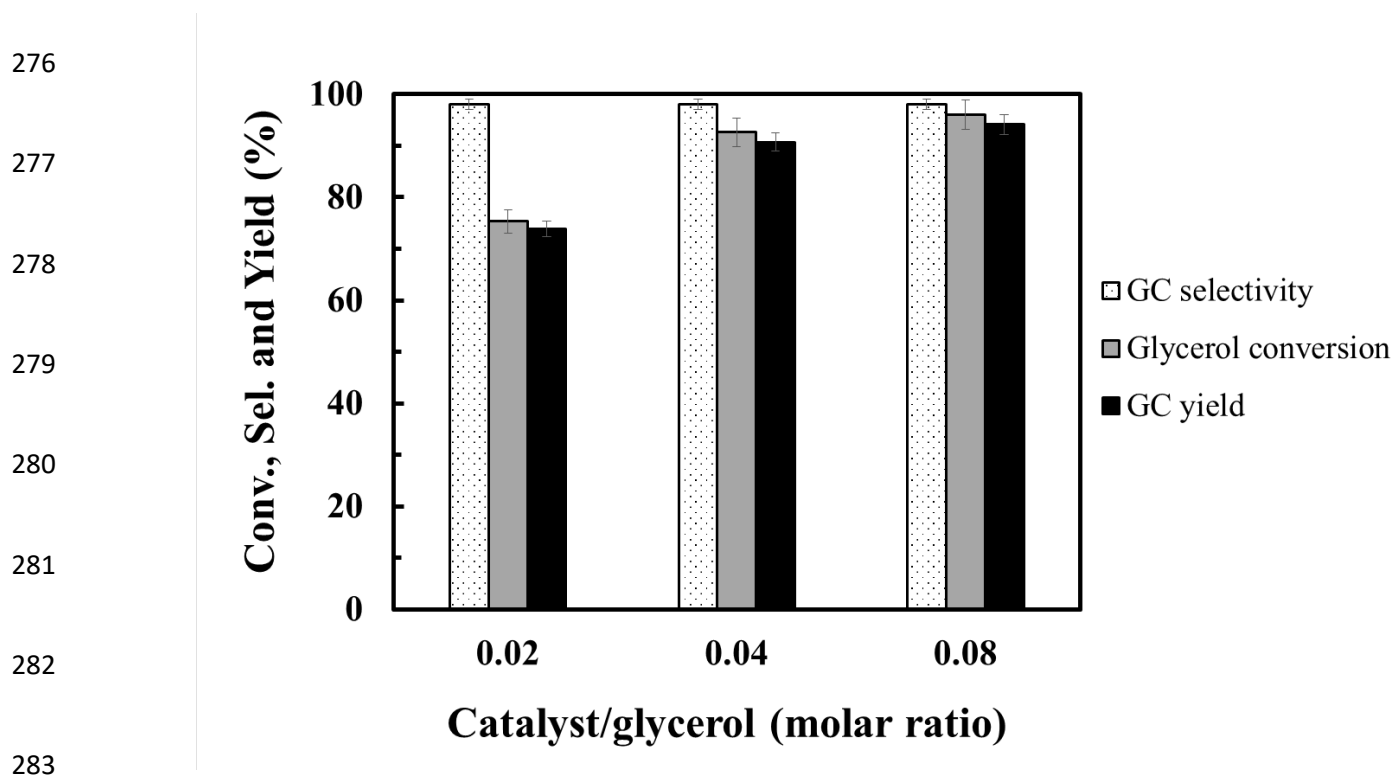261

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272   **Scheme 1.** Possible side reactions during GC production.

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3.2.3 Effect of catalyst loading

Fig.3. Effect of catalyst loading on catalytic activity (DMC: glycerol = 2.5:1, reaction temperature = 60 °C and reaction time = 180 min).

In the transesterification reaction, the amount of active basic sites has a significant influence on the catalytic activity. An increase of catalyst loading led to increased amount of active sites. The glycerol conversion and GC yield increased with increasing molar ratio of catalyst as shown in Fig.3. The conversion of glycerol and yield of GC obtained 96% and 94% within 180 min of reaction time with the mole ratio of CaO to glycerol equal to 0.08.
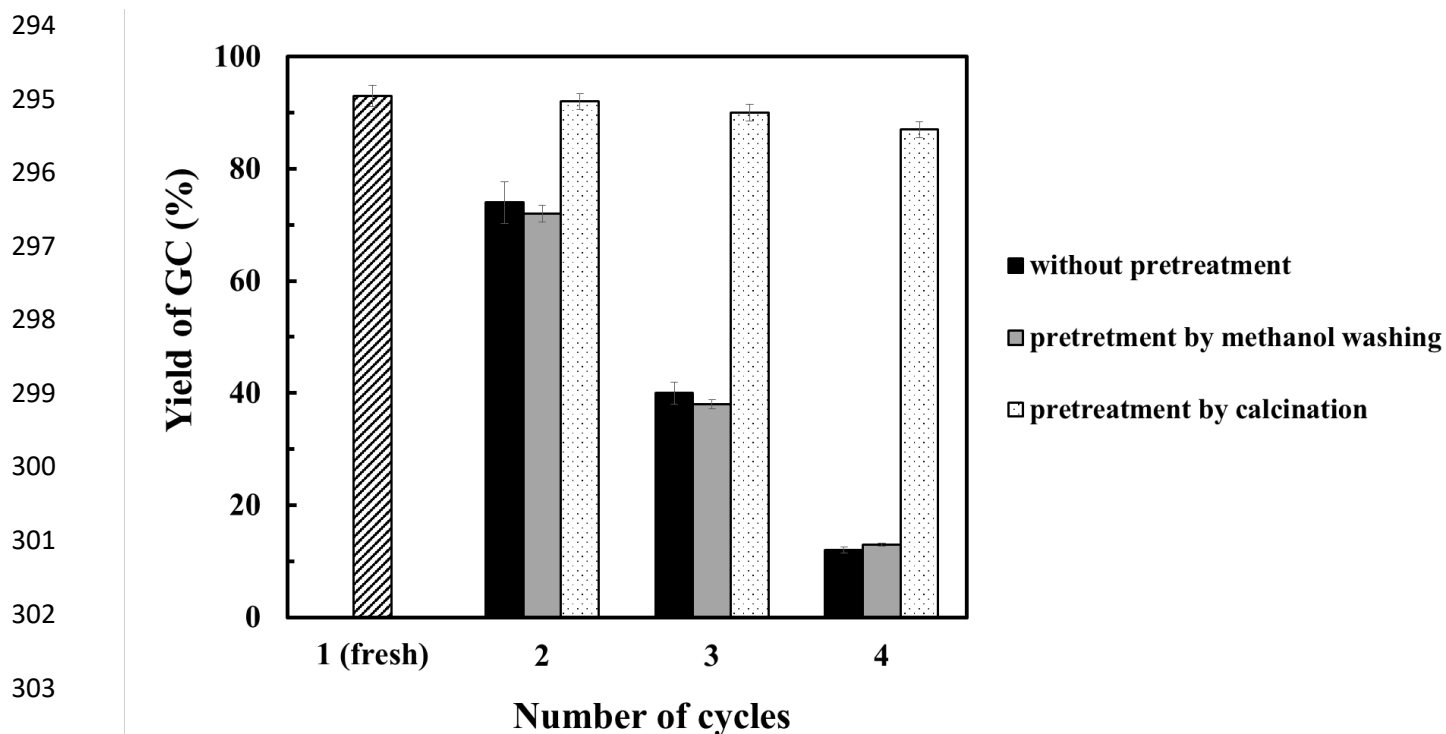
3.3 Reusability

Fig.4. Reusability of eggshell-derived CaO.

The reusability of the catalysts for transesterification was evaluated as shown in Fig.4. The used catalyst was separated by filtration and reused in the next cycle without pre-treatment or regeneration (Fig.4 black). The results showed that glycerol conversion rapidly decreased after each cycle from 94% (first cycle) to 12% (fourth cycle). In Fig.4, the grey bar represented the used catalyst after filtration and washing with methanol, indicating the similar trend as one as observed for no pretreatment with rapid decrease in catalytic activity. This implies the organic impurities on the active site of the catalyst did not establish dominant deactivation. Meanwhile, the white bar in Fig.4 denoted the used catalyst after each cycle which was filtered, dried at 110 $^{\circ}$C overnight, and calcined at 900 $^{\circ}$C for 2.5 h. The results indicated that the yield of GC obtained above 87% in 4 cycles, which means that the catalyst could be reused at least 4 times. Therefore, it can be concluded that the calcination stage at high temperature was necessary to

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318　enhance the catalyst reusability. However, there was some gradual loss of catalytic activity

319　which would be due to the structural change and sintering that occurred during the catalytic

320　and regeneration process by calcination at high temperature as the surface area, mean pore

321　diameter and total pore volume decreased to 1.43 m^2/g, 4.72 nm and 0.0053 cm^3/g, respectively

322　as shown in Table 1.

323　　The phase transformation can be ensured with XRD characterization of the used catalyst

324　as shown in Fig.5 to investigate and compare the structure of the remaining number of active

325　phases at each cycle with fresh CaO eggshell (Fig.5A). The first used catalyst possessed many

326　peaks as calcium diglyceroxide, calcium methoxide and calcium carbonate which indicated

327　that CaO phase was transformed to calcium diglyceroxide, methoxide and carbonate phase

328　under reaction conditions as displayed in Fig.5B. The appearance of the active phases promoted

329　conversion to methoxide, diglyceroxide and carbonate phases with a decrease of basic strength

330　(see Table 1.) and reduced the performance of the catalyst. In addition, the 4th used catalyst

331　contained essentially calcium carbonate phase (Fig.5C) and served negatively as an inactive

332　phase in the transesterification reaction. Moreover, the TGA results (Fig.6) demonstrated the

333　weight loss of the 1st used catalyst around 200 ^oC and 700 ^oC which was attributed to the

334　decomposition of glyceroxide and carbonate, respectively. This indicated availability of

335　glyceroxide and carbonate on surface of the catalyst. After the 4th used catalyst, comparing to

336　the 1st used catalyst, drastical changes in TGA profile could be observed. The main weight loss

337　around 650-750 ^oC, owing to decomposition of $CaCO_3$ to CaO, confirmed that most of phase

338　on catalyst surface was in carbonate form, an inactive phase in transesterification between

339　glycerol and DMC. In addition, the characterization of the catalysts without calcination

340　pretreatment indicated that the basic strength changed from strong basic ($15.0 < H\_ < 18.4$) of

341　virgin catalyst to $9.8 < H\_ < 15.0$ after the 1st cycle and turn to weak basic strength ($7.2 < H\_<$

342　9.8) after the 4th cycle. Meanwhile, the amount of basicity decreased from the virgin catalyst

343　　of 0.482 mmol/g to 0.360 and 0.023 mmol/g, respectively because CaO active phase transform

344　　to $CaCO_3$ as an inactive phase. The physical properties i.e. BET surface area, mean pore

345　　diameter and total pore volume determined by N_2 physisorption also exhibited the change

346　　during the cycles corresponding to the phase transformation as shown in Table 1. The SEM

347　　image (Fig. S2) showed the change from irregular crystal structure of CaO to spherical like

348　　$CaCO_3$ [54] of the 4th used catalyst which was in good agreement with the above characterization

349　　methods.

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351　　**Table 1.** N_2 physisorption results, basic strength and basicity of fresh catalysts and spent

352　　catalyst.

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| Catalysts	BET surface area (m²/g)	Mean pore diameter (nm)	Total pore volume (cm³/g)	Basic strength	Basicity (mmol/g)
CaO eggshell	4.92	12.12	0.0149	15.0 < H_ < 18.4	0.481
Calcium methoxide	11.85	11.10	0.0328	15.0 < H_ < 18.4	0.200
Calcium diglyceroxide	1.47	27.02	0.0098	9.8 < H_ < 15.0	0.080
$CaCO_3$	3.25	14.11	0.0318	7.2 < H_ < 9.8	0.023
The 1st used catalyst w/o pretreatment	4.41	17.47	0.0193	9.8 < H_ < 15.0	0.360
The 4th used catalyst w/o pretreatment	3.22	7.56	0.0080	7.2 < H_ < 9.8	0.023
The 4th used catalyst with pretreatment by calcination	1.43	4.72	0.0053	15.0 < H_ < 18.4	0.400

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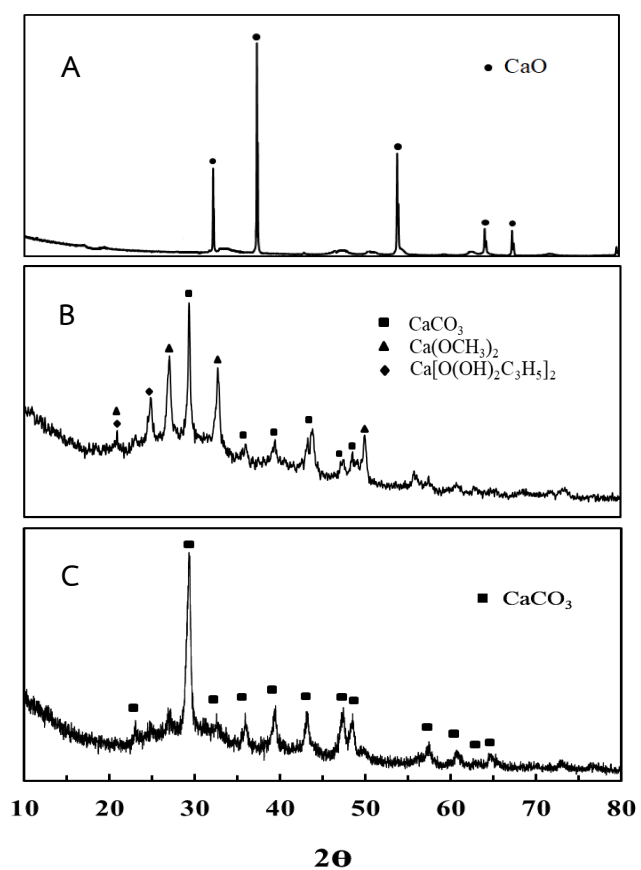
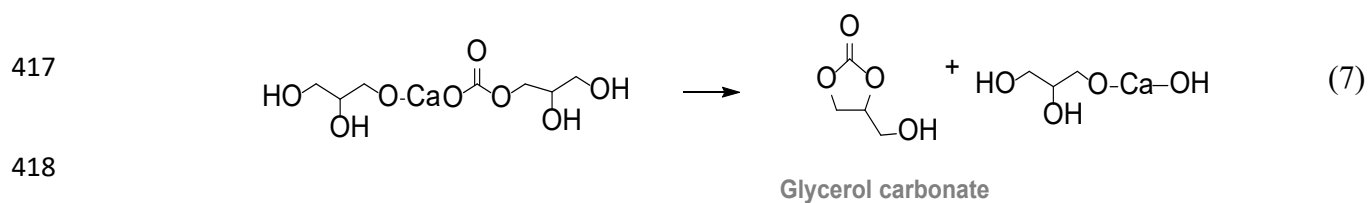**Fig.5.** XRD patterns of (A) the fresh CaO eggshell, (B) the 1st used catalyst and (C) the 4th used catalyst.
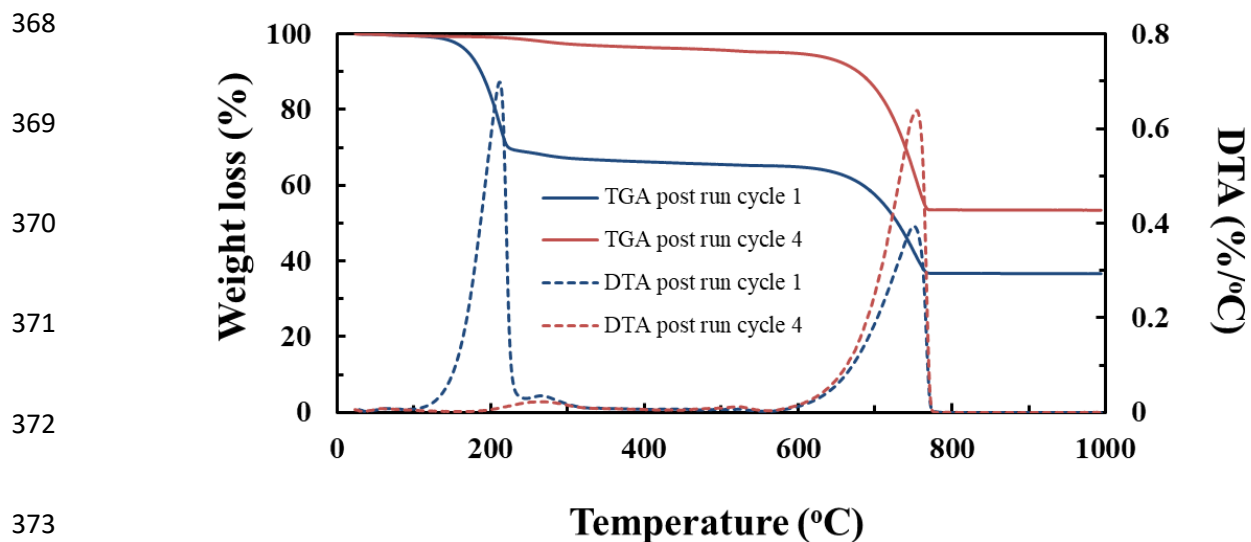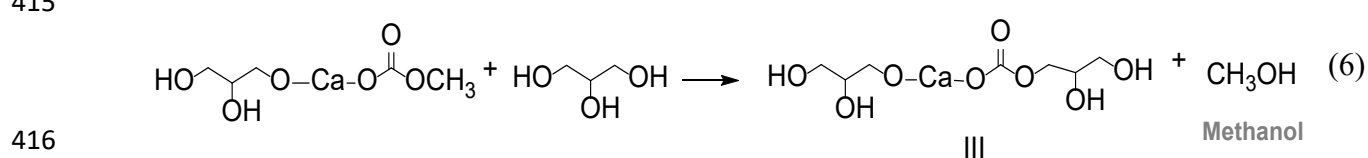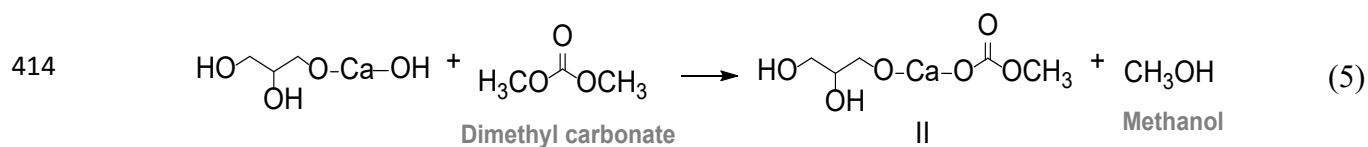
Fig.6. TGA (solid line) and DTA (dash line) of 1st used catalyst (blue) and 4th used catalyst (red).

3.4 Proposed mechanism of transesterification of glycerol and DMC catalyzed by CaO

The general mechanism of heterogeneous base catalysts in transesterification of glycerol and DMC had been illustrated in many researches.[31, 42, 55] In the first step herein, glycerol interacted with base catalyst to glycerol anion which further reacted with DMC to hydroxyl alkyl carbonate and methanol in the next step. Finally, the hydroxyl alkyl carbonate is converted to methanol and the target product as GC. Simanjuntak et al. (2011) [34] who investigated the mechanism of CaO-catalyzed in transesterification of glycerol and DMC, identified intermediate active species from the reaction as $Ca(C_3H_7O_3)(OCO_2CH_3)$. More explicitly, the later was presented in their proposed mechanism, the interaction between CaO and glycerol obtained calcium species I which then reacts with DMC to produce the calcium species II as a $Ca(C_3H_7O_3)(OCO_2CH_3)$ and loss of methanol. Then the calcium species II attacked the glycerol molecule to generate an active species III and methanol. Finally, the calcium species III transform to GC and regenerate to the calcium species I as shown in scheme

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390   2. They also proved in another experiment that $Ca(C_3H_7O_3)(OCO_2CH_3)$ can be converted to

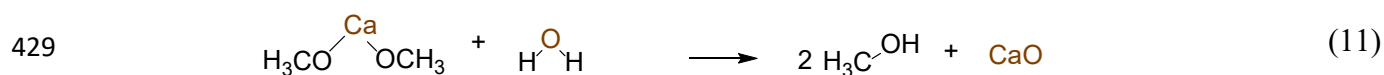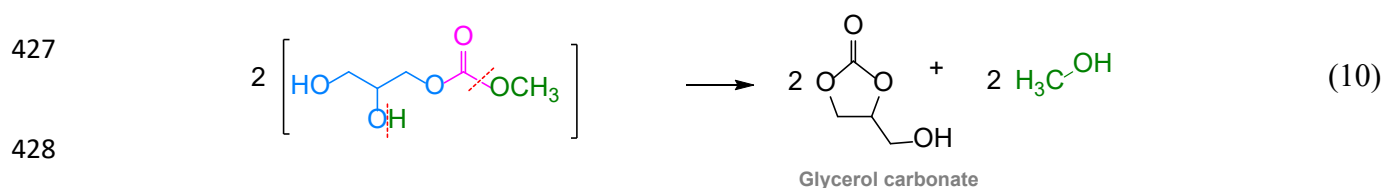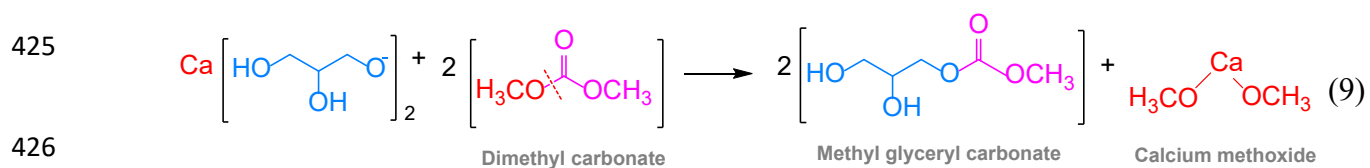391 $CaCO_3$ when exposing to the air for 1 h.

392   Consequently, this research investigates the difference of the mechanism of CaO catalysed

393   transesterification between glycerol and DMC based on the condensation reaction between

394   glycerol and CaO as illustrated in scheme 3, and previous work which described the mechanism

395   based on the insertion reaction of glycerol and CaO. The calcium cation is a relatively weak

396   acid attracting one of the primary hydroxyl groups of glycerol whereas the conjugated oxygen

397   anion from CaO catalyst displays a strong basic site attracting H^+ from glycerol forming

398   calcium diglyceroxide and water or somewhat water derivative species, respectively (Eq.8 in

399   Scheme 3). Then, calcium diglyceroxide would attract carbonyl carbon of DMC as a co-

400   reactant to generate calcium methoxide and methyl glyceryl carbonate as intermediates (Eq.9

401   in Scheme 3). Methyl glyceryl carbonate restructures would be transformed into glycerol

402   carbonate and methanol (Eq.10 in Scheme 3). Finally, calcium methoxide would react with

403   water to obtain methanol and regenerate CaO (Eq.11 in Scheme 3). According to scheme 3, the

404   calcium diglyceroxide can be generated by the interaction of CaO and glycerol, as confirmed

405   by Fuji et al. (1968) [56] Meanwhile, calcium methoxide appeared during the transesterification

406   reaction.[57] Moreover, the occurrence of water (Eq.8 in Scheme 3) might cause the catalyst

407   deactivation which relates to TOF-SIMS results, the presence of calcium species with water

408   including $Ca(C_3H_7O_3)-H_2O$, $Ca(C_3H_7O_3)(OCO_2CH_3)-2H_2O-H$, $Ca(C_3H_7O_3)(OCO_2CH_3)$

409   H_2O-H, etc. by Simanjuntak et al. (2011) [34] We hypothesize, that the formation of water could

410   cause the transformation of CaO to $CaCO_3$ and lead to catalyst deactivation. This point will be

411   further described in the deactivation mechanism section.

412

$$CaO + \underset{\substack{\text{Glycerol}}}{HO\overset{\displaystyle OH}{\wedge}OH} \longrightarrow \underset{\substack{\text{I}}}{HO\overset{\displaystyle OH}{\wedge}O\text{-}Ca\text{-}OH} \qquad (4)$$

413

414

$$\underset{\substack{OH}}{HO\wedge O\text{-}Ca\text{-}OH} + \underset{\substack{\text{Dimethyl carbonate}}}{H_3CO\overset{\displaystyle O}{\underset{\| }{C}}OCH_3} \longrightarrow \underset{\substack{\text{II}}}{HO\wedge O\text{-}Ca\text{-}O\overset{\displaystyle O}{\underset{\| }{C}}OCH_3} + \underset{\substack{\text{Methanol}}}{CH_3OH} \quad (5)$$

415

$$HO\wedge O\text{-}Ca\text{-}O\overset{\displaystyle O}{\underset{\| }{C}}OCH_3 + HO\wedge OH \longrightarrow HO\wedge O\text{-}Ca\text{-}O\overset{\displaystyle O}{\underset{\| }{C}}O\wedge OH + \underset{\substack{\text{Methanol}}}{CH_3OH} \quad (6)$$

$$\text{III}$$

416

417

$$HO\wedge O\text{-}CaO\overset{\displaystyle O}{\underset{\| }{C}}O\wedge OH \longrightarrow \underset{\substack{\text{Glycerol carbonate}}}{\overset{\displaystyle O}{\underset{\| }{C}}} + HO\wedge O\text{-}Ca\text{-}OH \qquad (7)$$

418
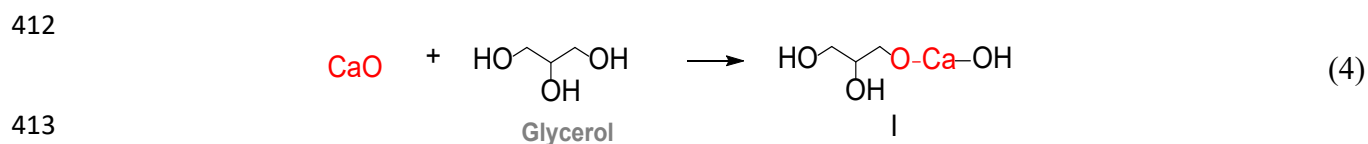
419

420 **Scheme 2**. Proposed mechanisms of CaO-catalyzed transesterification of DMC and glycerol

421 by Simanjuntak et al. (2011) [34] based on insertion reaction between glycerol and CaO.

422

423

$$2 \left[\text{Glycerol} \cdot \text{H}^+ \right] + CaO \longrightarrow Ca\left[\text{glyceroxide} \right]_2 + H_2O \quad (8)$$

424

Glycerol   Calcium diglyceroxide

425

$$Ca\left[\text{glyceroxide} \right]_2 + 2\left[\text{Dimethyl carbonate} \right] \longrightarrow 2\left[\text{Methyl glyceryl carbonate} \right] + Ca(OCH_3)_2 \quad (9)$$

426

Dimethyl carbonate   Methyl glyceryl carbonate   Calcium methoxide

427

$$2\left[\text{Methyl glyceryl carbonate} \right] \longrightarrow 2\left[\text{Glycerol carbonate} \right] + 2\ H_3C\text{-}OH \quad (10)$$

428

Glycerol carbonate

429

$$Ca(OCH_3)_2 + H_2O \longrightarrow 2\ H_3C\text{-}OH + CaO \quad (11)$$

430
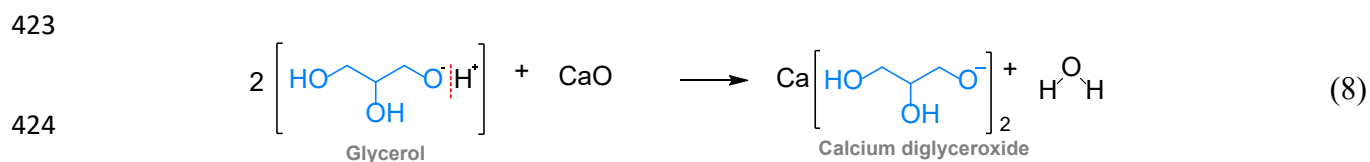
Scheme 3. Possible mechanisms of CaO-catalyzed transesterification of DMC and glycerol by

this research base on the condensation reaction between glycerol and CaO.

433

3.5 Deactivation mechanism of CaO in transesterification between glycerol and DMC

Many works described CaO deactivation, mostly based on the formation of $Ca(OH)_2$ or

$CaCO_3$. Ochoa-Gomez et al. (2009) [31] reported that the catalytic activity of CaO would

decrease dramatically after the first cycle by carbonation and hydration in the air. In addition,

the reusability of calcined dolomite was studied by Algoufi et al. (2017) [32]. The XRD pattern

of the 4th cycle of calcined dolomite indicated that CaO would be converted to $CaCO_3$ by

reaction with CO_2 during the reaction cycle. Whereas in the work of Li et al. (2011) [33], the

calcium species; CaO, $Ca(OH)_2$ and calcium methoxide ($Ca(OCH_3)_2$) were examined by

exposure to air for 4 weeks. The results from IR spectra confirmed the phase of catalyst as

similar to that of fresh catalyst, which revealed that the catalyst in air exposure was not the

444   cause of catalyst deactivation. In addition, they proposed that the interaction of catalyst with

445   reaction mixture would be responsible for conversion to the basic calcium carbonate

446       $Ca_x(OH)_y(CO_3)_z$, leading to a decrease in catalytic activity. Furthermore, Simanjuntak et al.

447   (2011) [34] observed calcium compound $Ca(C_3H_7O_3)(OCO_2CH_3)$ as an active phase that occurred

448   *in situ* during the transesterification between glycerol and DMC and the later presented a

449   similar activity to CaO. Once exposed to air, $Ca(C_3H_7O_3)(OCO_2CH_3)$ most likely reacted with

450   CO_2 and then was converted to $CaCO_3$. From the above mentioned observations, although most

451   researchers agreed that the deactivation of CaO catalyst is due to $CaCO_3$ formation [31, 32], in

452   consistent with XRD result of the 4th used catalyst (Fig.5C), the detailed mechanism of the

453   deactivation is still not fully revealed.

454   Another highlight in this study is the observation of difference between glycerol and DMC

455   consumption and additional amount of methanol by-product even with high selectivity of GC

456   (negligible glycerol dicarbonate and glycidol formation) when the reused catalyst was

457   employed. Theoretically, the ratio of methanol to GC of ca. 2.0 is expected according to their

458   stoichiometry. On the other hand, the mole of methanol to GC exhibited higher than the

459   stoichiometric ratio as indicated in Fig.7 (A).

460   Without catalyst pretreatment by calcination at 900 °C, methanol to GC ratio increased

461   with the number of cycles used as shown in Fig.7 (A) while it was only slightly larger than 2.0

462   and quite constant when the catalyst was calcined before reuse (Fig.7 (B)). In other words, the

463   extent of methanol to GC ratio over stoichiometric ratio (Fig. 7(A)) increased along with the

464   extent of $CaCO_3$ formation (Fig. 5).

465

466

(A)

468

469

470

471

472

473

(B)

474

475

476

477

478

479
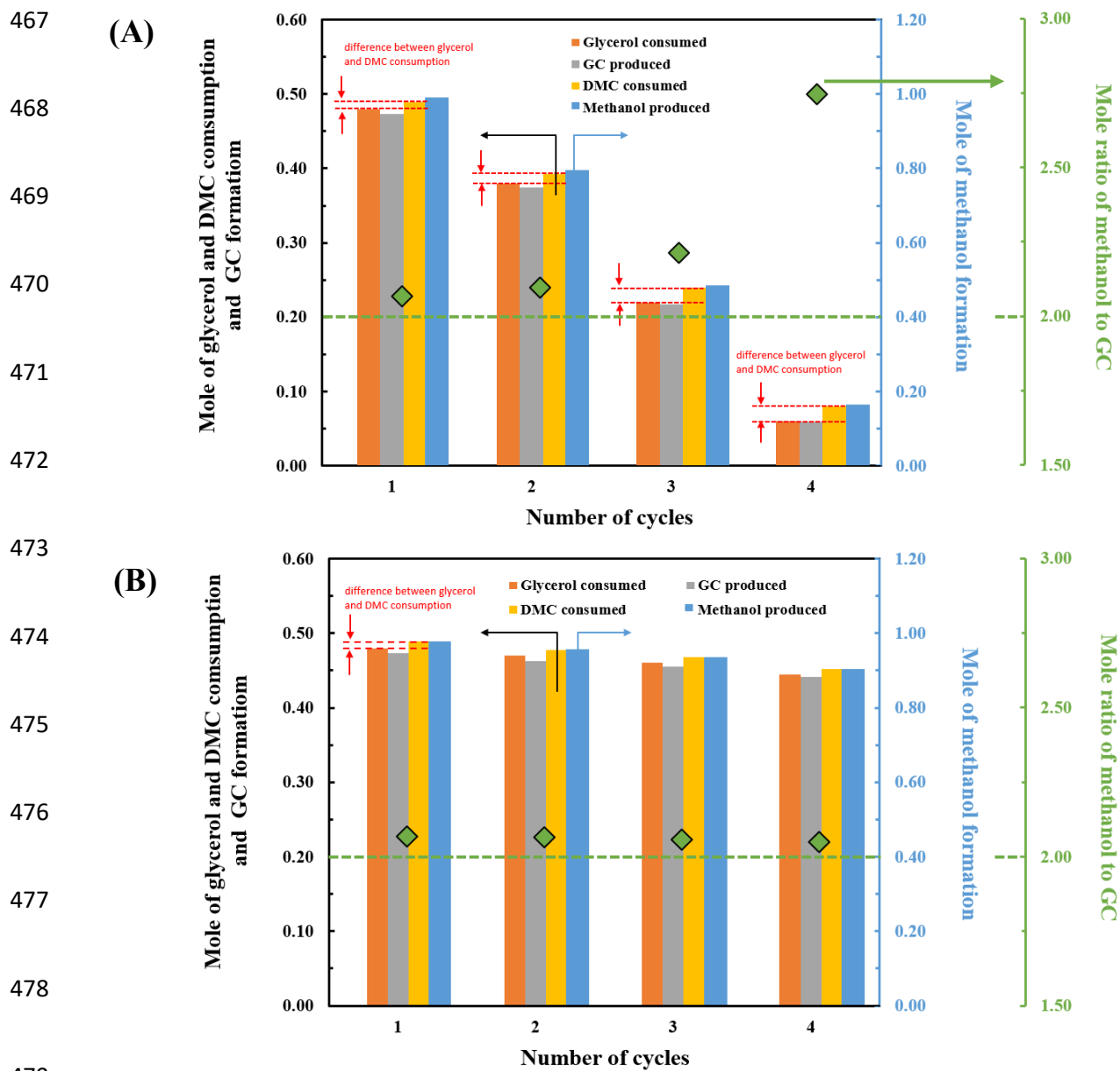
Fig.7. Mole of glycerol and DMC consumption and GC and methanol formation, and

corresponding methanol to GC ratio at different catalyst cycles. (A) without catalyst

pretreatment and (B) pretreatment by calcination. The dashed line denoted theoretical

stoichiometric of methanol to GC of 2.0.

In addition, the mole of DMC was found excessively used than the stoichiometric ratio

with glycerol to produce GC. This can be remarked in Fig. 7 (A) by the difference between

487   glycerol and DMC consumption which increased with the number of cycles. This result again

488   occurred with high GC selectivity which implies that further DMC consumption through a side

489   reaction.

490   The generation of water (as proposed Eq.8 in Scheme 3) with the observation of

491   products/reactants that are not following their stoichiometric ratio allows to hypothesize CaO

492   transformation in the reactions as follow.

493   Proposed *in situ* CaO deactivation reaction:

494           $CaO + H_2O \rightarrow Ca(OH)_2$ (12)

495           $Ca(OH)_2 + C_3H_6O_3 \rightarrow 2CH_3OH + CaCO_3$ (13)
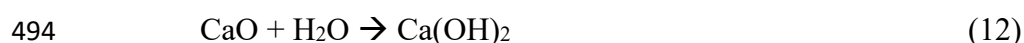
496   This hypothesis was further supported by performing the reaction of CaO, DMC and water

497   at an equivalent molar ratio of CaO, DMC and water at 60 °C reaction temperature for 3 h.

498   After the reaction, the collected catalyst was filtered and characterized by XRD to investigate

499   the phase transformation of the catalyst. It was evidenced that CaO was converted to the $CaCO_3$

500   phase in CaO and DMC system after adding water, as shown in supporting information Fig.S4.

501   Consequently, this XRD result corroborated with assumption that the generated water from

502   Eq.8 would react with CaO and DMC to produce carbonate phase, and extra methanol mole,

503   described in Eqs.12-13.

504

505   4. Conclusion

506   This research revealed a significant difference in the deactivation mechanism of CaO for

507   glycerol carbonate production via the transesterification of glycerol with dimethyl carbonate.

508   The appearance of the CaO as an active phase was converted to alkoxide phases such as

509   methoxide, diglyceroxide and carbonate phases with a decreasing basic strength and reducing

510   performance of the catalyst correlated with glycerol conversion from 96% to 12% after the 4th

511   cycle. The ratio of methanol to GC occurrence, which was higher than 2.0 towards the desired

512   reaction stoichiometric ratio, was a significant observation and correlated well with the extent

513   of $CaCO_3$ formation. The proposed mechanism of CaO catalyzed transesterification of glycerol

514   into GC based on the condensation reaction of glycerol with *in situ* formation of water or water-

515   derivative species is consistent with that characterized previously.[34] These findings allowed us

516   to hypothesize a deactivation mechanism which remains consistent with the outcome of

517   independent experimental result that demonstrated that CaO can react with DMC and water

518   into methanol and $CaCO_3$, corroborating with methanol to GC non-stoichiometric ratio of 2.0

519   and thus enabling alternative monitoring of catalyst deactivation.

520   However, it is of commendable to note that the calcination of post-run catalyst at 900 °C

521   exhibited nearly constant catalytic activity and the mole ratio of methanol to GC remained

522   constant at the desired reaction stoichiometry of ca. 2.0. Catalyst was therefore efficiently

523   recovered and reused for at least four times.

524

Authors contribution statement

526

527   **Wanichaya Praikaew:** Conceptualization; Methodology; Formal analysis; Data Curation;

528   Validation; Investigation; Visualization; Writing – original draft; Writing - Review & Editing.

529   **Worapon Kiatkittipong:** Conceptualization; Data Curation; Validation; Supervision; Writing

530   Review & Editing; Funding acquisition**.**

531   **Farid Aiouache:** Writing - Review & Editing.

Vesna Najdanovic-Visak: Writing - Review & Editing.

Mutsee Termtanun: Writing - Review & Editing.

Jun Wei Lim: Writing - Review & Editing.

Su Shiung Lam: Writing - Review & Editing.

Kunlanan Kiatkittipong: Writing - Review & Editing.

Navadol Laosiripojana: Writing - Review & Editing.

Sunya Boonyasuwat: Writing - Review & Editing.

Suttichai Assabumrungrat: Writing - Review & Editing; Funding acquisition.

Declaration of interests

None.

Acknowledgments

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